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MODIFICATION AND CHARACTERISATION OF CARBON FIBRE ION EXCHANGE MEDIA

by

Ibiba Dateinm Harry

Submitted in partial fulfillment of the requirements for the award of

Doctor of Philosophy

in

Chemical Engineering

Advanced Separation Technologies Group
Department of Chemical Engineering
Loughborough University
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ABSTRACT

This thesis examines the use of electrochemically treated viscose rayon based activated carbon cloth (ACC) for the removal of metal ions from aqueous effluent streams. Two types of treatment were performed: (i) electrochemical oxidation and (ii) electrochemical reduction to enhance cation and anion sorption capacities of the ACC, respectively. Electrochemical oxidation resulted in a loss of 61% BET surface area due to blockage of pores through formation of carboxylic acidic groups but its cation exchange capacity and oxygen content increased by 365% and 121%, respectively. The optimum constant current at which a combination of applied current and oxidation time at any extent of oxidation to produce ACC of maximum cation exchange capacity was found to be 1.1 A, with voltage of 4.2 V and current density of 0.8 mA/m². Batch sorption experiments showed that the maximum copper and lead sorption capacities for electrochemically oxidised ACC increased 17 and 4 times, respectively, for noncompetitive sorption and 8.8 and 8.6 times, respectively for competitive sorption. Therefore, electrochemically oxidised ACC is an effective adsorbent for treating aqueous solution contaminated with copper/lead in both single component and multi-component systems. Industrial wastewaters are multicomponent systems, therefore, electrochemical oxidation of ACC is an efficient way of enhancing lead and copper ions sorptive capacity for industrial wastewater treatment. Electrochemical reduction resulted in a loss of 28% BET surface area due to formation of ether groups but its anion exchange capacity increased by 292%. The optimum constant current at which a combination of applied current and reduction time at any extent of reduction to produce ACC of maximum anion exchange capacity was found to be 5.5 A, with voltage of 9.8 V and current density of 6.4 mA/m². Batch sorption experiments showed that the maximum chromium(VI) sorption capacity for electrochemically reduced ACC increased 2.12 times, with highest maximum chromium(VI) sorption capacity of 3.8 mmol/g at solution pH 4. Most industrial wastewaters contaminated with chromium(VI) are highly acidic, therefore, electrochemical reduction of ACC is an efficient way of enhancing chromium(VI) sorptive capacity for industrial wastewater treatment.

KEYWORDS: Viscose rayon based activated carbon cloth, sorption isotherms, electrochemical oxidation, electrochemical reduction, lead, copper, chromium(VI), competitive and noncompetitive sorption, characterisation.
# TABLE OF CONTENTS

1. INTRODUCTION..................................................................................................................1
   1.1. TARGET POLLUTANTS OF STUDY..................................................................................3
       1.1.1. Copper.......................................................................................................................3
       1.1.2. Lead..........................................................................................................................4
       1.1.3. Chromium(VI)...........................................................................................................4
   1.2. SEPARATION PROCESSES FOR WASTEWATER TREATMENT.....................................5
       1.2.1. Chemical Precipitation..............................................................................................6
       1.2.2. Electrochemical Processes..........................................................................................7
       1.2.3. Membrane Processes..................................................................................................7
           1.2.3.1. Isotropic microporous membranes.....................................................................7
           1.2.3.2. Nonporous dense membranes............................................................................7
       1.2.4. Ion Exchange.............................................................................................................8
       1.2.5. Adsorption................................................................................................................9
   1.3. RESEARCH OBJECTIVES...............................................................................................10

2. LITERATURE REVIEW.........................................................................................................12
   2.1. INTRODUCTION.............................................................................................................12
   2.2. ADSORPTION OF COPPER............................................................................................12
       2.2.1. Conclusions..............................................................................................................17
   2.3. ADSORPTION OF LEAD....................................................................................................19
       2.3.1. Conclusions..............................................................................................................25
   2.4. COMPETITIVE AND NONCOMPETITIVE ADSORPTION OF COPPER AND LEAD..........................26
       2.4.1. Conclusions..............................................................................................................31
   2.5. ADSORPTION OF CHROMIUM(VI)..................................................................................32
       2.5.1. Conclusions..............................................................................................................40
   2.6. ACTIVATED CARBON FIBRES.........................................................................................42
       2.6.1. Precursors of Carbon Fibre.......................................................................................42
       2.6.2. Production of Viscose Rayon Based Carbon Fibres....................................................44
           2.6.2.1. Alkalisation..........................................................................................................44
           2.6.2.2. Shredding............................................................................................................44
           2.6.2.3. Preripening.........................................................................................................45
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.3.</td>
<td>Sips Isotherm</td>
<td>109</td>
</tr>
<tr>
<td>3.3.4.</td>
<td>Multicomponent Isotherms</td>
<td>110</td>
</tr>
<tr>
<td>3.3.5.</td>
<td>Brunauer-Emmet-Teller (BET) Isotherm</td>
<td>112</td>
</tr>
<tr>
<td>3.4.</td>
<td>CONCLUSIONS</td>
<td>115</td>
</tr>
<tr>
<td>4.1.</td>
<td>INTRODUCTION</td>
<td>116</td>
</tr>
<tr>
<td>4.2.</td>
<td>MATERIALS</td>
<td>116</td>
</tr>
<tr>
<td>4.3.</td>
<td>EXPERIMENTAL</td>
<td>116</td>
</tr>
<tr>
<td>4.3.1.</td>
<td>Conversion of Activated Carbon Cloth (ACC) to Hydrogen Form</td>
<td>116</td>
</tr>
<tr>
<td>4.3.2.</td>
<td>Electrochemical Oxidation of ACC</td>
<td>117</td>
</tr>
<tr>
<td>4.3.3.</td>
<td>Electrochemical Reduction of ACC</td>
<td>119</td>
</tr>
<tr>
<td>4.3.4.</td>
<td>Characterisation of ACCs</td>
<td>120</td>
</tr>
<tr>
<td>4.3.4.1.</td>
<td>Sodium capacity determination</td>
<td>120</td>
</tr>
<tr>
<td>4.3.4.2.</td>
<td>Chloride capacity determination</td>
<td>121</td>
</tr>
<tr>
<td>4.3.4.3.</td>
<td>pH Titration</td>
<td>122</td>
</tr>
<tr>
<td>4.3.4.4.</td>
<td>Zeta potential measurement</td>
<td>123</td>
</tr>
<tr>
<td>4.3.4.5.</td>
<td>Elemental analysis</td>
<td>123</td>
</tr>
<tr>
<td>4.3.4.6.</td>
<td>Fourier transform infra red (FTIR) spectroscopy analysis</td>
<td>124</td>
</tr>
<tr>
<td>4.3.4.7.</td>
<td>Surface area and pore size distribution</td>
<td>124</td>
</tr>
<tr>
<td>4.3.4.8.</td>
<td>Scanning electron microscopy (SEM)</td>
<td>124</td>
</tr>
<tr>
<td>4.3.5.</td>
<td>Adsorption Studies</td>
<td>125</td>
</tr>
<tr>
<td>4.3.5.1.</td>
<td>Speciation of metal ions in aqueous solution</td>
<td>125</td>
</tr>
<tr>
<td>4.3.5.2.</td>
<td>Batch sorption experiments for copper(II) and lead(II)</td>
<td>125</td>
</tr>
<tr>
<td>4.3.5.3.</td>
<td>Batch sorption experiments for chromium(VI)</td>
<td>127</td>
</tr>
<tr>
<td>5.1.</td>
<td>INTRODUCTION</td>
<td>129</td>
</tr>
<tr>
<td>5.2.</td>
<td>CHARACTERISATION OF ACCS</td>
<td>129</td>
</tr>
<tr>
<td>5.2.1.</td>
<td>Sodium Capacity</td>
<td>129</td>
</tr>
<tr>
<td>5.2.2.</td>
<td>pH Titrations</td>
<td>136</td>
</tr>
<tr>
<td>5.2.3.</td>
<td>Zeta Potential Measurements</td>
<td>139</td>
</tr>
<tr>
<td>5.2.4.</td>
<td>Elemental Analysis</td>
<td>141</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>5.2.5. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>5.2.6. Reactions in Electrochemical Cell</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>5.2.7. Nitrogen Adsorption-Desorption Results</td>
<td>146</td>
<td></td>
</tr>
<tr>
<td>5.2.8. Surface Area Results</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td>5.2.9. Pore Size Distribution (PSD) Results</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td>5.2.10. Scanning Electron Microscopy (SEM)</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>5.3. BATCH SORPTION EXPERIMENTS</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>5.3.1. Speciation of Metal Ions in Aqueous Solution</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>5.3.2. Sorption Isotherm Models</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>5.3.3. Effect of Electrochemical Oxidation on Lead(II) and Copper(II) Sorption Equilibria</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>5.3.4. Competitive Lead(II) and Copper(II) Sorption Equilibria</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>5.3.5. Effect of pH on Lead(II) and Copper(II) Sorption</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>5.3.6. Mechanism of Lead(II) and Copper(II) Sorption onto EO and UO ACCs</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>5.4. CONCLUSIONS</td>
<td>173</td>
<td></td>
</tr>
<tr>
<td>6. RESULTS AND DISCUSSIONS OF CHARACTERISATION OF ELECTROCHEMICALLY REDUCED ACTIVATED CARBON CLOTH AND ADSORPTION STUDIES</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>6.1 INTRODUCTION</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>6.2. CHARACTERISATION OF ACCS</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>6.2.1 Chloride Capacity</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>6.2.2. pH Titrations</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>6.2.3. Zeta Potential Measurements</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>6.2.4. Elemental Analysis</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>6.2.5. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>6.2.6. Reactions in Electrochemical Cell</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>6.2.7. Nitrogen Adsorption-Desorption Results</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>6.2.8. Surface Area Results</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>6.2.9. Pore Size Distribution (PSD) Results</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td>6.2.10. Scanning Electron Microscopy (SEM)</td>
<td>204</td>
<td></td>
</tr>
<tr>
<td>6.3. BATCH SORPTION EXPERIMENTS</td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>6.3.1. Speciation of Chromium(VI) Ions in Aqueous Solution</td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>6.3.2. Sorption Isotherm Models</td>
<td>207</td>
<td></td>
</tr>
</tbody>
</table>
6.3.3. Effect of Electrochemical Reduction and Electrochemical Oxidation on Chromium(VI) Sorption Equilibrium ............................................................. 209
6.3.4. Effect of pH on Chromium(VI) Sorption .......................................................... 213
6.3.5. Mechanism of Chromium(VI) Sorption onto as-received ACC, ER ACC
and EO ACC ........................................................................................................ 216
6.4. CONCLUSIONS ............................................................................................ 221
7. CONCLUSIONS AND FUTURE WORK .................................................................. 223
7.1. GENERAL CONCLUSIONS ........................................................................ 223
7.1.1. Comparative Study .......................................................................................... 226
7.2. FUTURE WORK .............................................................................................. 228
8. REFERENCES .................................................................................................. 230
9. APPENDICES .................................................................................................. 255
9.1. RESEARCH PUBLICATIONS ....................................................................... 255
LIST OF FIGURES

Figure 2.1. Possible structures of surface oxygen groups (Boehm, 1994) ..................55
Figure 2.2. Proton addition to Y-Pyron like structures (Boehm, 1994) .....................56
Figure 2.3. Possible structures of basic surface sites on a graphene layer (Boehm, 1994) ........................................................................................ 57
Figure 2.4. Nitric acid oxidation of a hydrocarbon (Vinke et al., 1994) .....................65
Figure 4.1 Equipment used for electrochemical oxidation ................................... 117
Figure 4.2. Schematic of electrochemical cell used for electrochemical oxidation ...... .118
Figure 4.3. Schematic of electrochemical cell used for electrochemical reduction ...... 119
Figure 4.4. Varian AA 200 atomic absorption spectrophotometer (AAS) ............... 126
Figure 5.1. Sodium capacity result for unoxidised ACC (UO) and electrochemically oxidised ACC (EO) at different conditions .....................130
Figure 5.2. NaOH uptake versus extent of electrochemical oxidation for 4 h at different currents ................................................................. 131
Figure 5.3. NaOH uptake versus extent of electrochemical oxidation at 1.1 A for different oxidation times .......................................................... 132
Figure 5.4. NaOH uptake versus extent of electrochemical oxidation at 1.1 A and 2.2 A .............................................................................. 133
Figure 5.5. NaOH uptake versus oxidation time at 1.1 A and 2.2 A ........................ 134
Figure 5.6. NaOH uptake versus applied current for different extents of electrochemical oxidation ......................................................................... 135
Figure 5.7. Ion released versus equilibrium solution pH for unoxidised and electrochemically oxidised ACCs at 1.1 A for 6 h and 2.2 A for 3 h ............... 137
Figure 5.8. Zeta potential versus equilibrium solution pH for unoxidised ACC and electrochemically oxidised ACCs at 1.1 A for 6 h and 2.2 A for 3 h .......... 139
Figure 5.9. FTIR spectra for unoxidised ACC ................................................... 143
Figure 5.10. FTIR spectra for electrochemically oxidised ACC at 1.1 A for 6 h ...... 143
Figure 5.11. Nitrogen adsorption-desorption isotherm for unoxidised ACC (UO) ......146
Figure 5.12. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 1 h (i.e. 7,920 c/g extent of oxidation) .......... 147
Figure 5.13. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 2 h (i.e. 15,840 c/g extent of oxidation) ......... 147
Figure 5.14. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 3 h (i.e. 23,760 c/g extent of oxidation)........148
Figure 5.15. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 2 h (i.e. 7,920 c/g extent of oxidation)........148
Figure 5.16. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 4 h (i.e. 15,840 c/g extent of oxidation)........149
Figure 5.17. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 6 h (i.e. 23,760 c/g extent of oxidation)........149
Figure 5.18. BET surface area versus extent of oxidation for ACCs electrochemically oxidised at 1.1 A (EO 1.1 A) and at 2.2 A (EO 2.2 A)........151
Figure 5.19. Pore size distribution for unoxidised ACC (0 c/g) and electrochemically oxidised ACCs at 1.1 A at 7,920 c/g, 15,840 c/g and 23,760 c/g extents of oxidation...153
Figure 5.20. Pore size distribution for unoxidised ACC (0 c/g) and electrochemically oxidised ACCs at 2.2 A at 7,920 c/g, 15,840 c/g and 23,760 c/g extents of oxidation...153
Figure 5.21. Pore size distribution for electrochemically oxidised ACCs at 1.1 A and 2.2 A at 7,920 c/g extent of oxidation...........................................................154
Figure 5.22. Pore size distribution for electrochemically oxidised ACCs at 1.1 A and 2.2 A at 15,840 c/g extent of oxidation...........................................................154
Figure 5.23. Pore size distribution for electrochemically oxidised ACCs at 1.1 A and 2.2 A at 23,760 c/g extent of oxidation...........................................................155
Figure 5.24. SEM of unoxidised and selected electrochemically oxidised ACCs....158
Figure 5.25. Speciation curve for 0.0157 M copper in nitrate solution..............159
Figure 5.26. Speciation curve for 0.0193 M lead in nitrate solution....................160
Figure 5.27. Non-competitive and competitive (Cu + Pb) sorption isotherms of copper and lead onto UO and EO at solution pH 5...............................163
Figure 5.28. Non-competitive adsorption isotherms of copper and lead onto UO and EO at solution pH 5...........................................................164
Figure 5.29. Competitive adsorption isotherms of copper and lead onto UO (UO competitive) and EO (EO competitive) at solution pH 5...............165
Figure 5.30. Non-competitive (UO Cu) and Competitive (UO Cu Competitive) adsorption isotherms of copper onto UO at solution pH 5.................166
Figure 5.31. Non-competitive (EO Cu) and Competitive (EO Cu Competitive) adsorption isotherms of copper onto EO at solution pH 5.................166
Figure 5.32. Non-competitive (UO Pb) and Competitive (UO Pb Competitive) adsorption isotherms of lead onto UO at solution pH 5..........................167
Figure 5.33. Non-competitive (EO Pb) and Competitive (EO Pb Competitive) adsorption isotherms of lead onto EO at solution pH 5..........................167
Figure 5.34. Non-competitive adsorption isotherms of copper onto EO at solution pH 3, 4 and 5..........................................................169
Figure 5.35. Non-competitive adsorption isotherms of lead onto EO at solution pH 3, 4 and 5..........................................................170
Figure 6.1. Chloride capacity result for as-received ACC and electrochemically reduced (ER) ACC at different conditions........................................176
Figure 6.2. HCl uptake versus extent of electrochemical reduction for 4 h at different currents..........................................................177
Figure 6.3. HCl uptake versus extent of electrochemical reduction at 5.5 A for different reduction times..................................................178
Figure 6.4. HCl uptake versus extent of electrochemical reduction at 5.5 A and 6.6 A..........................................................179
Figure 6.5. HCl uptake versus reduction time at 5.5 A and 6.6 A..............180
Figure 6.6. HCl uptake versus applied current for different extents of electrochemical reduction..........................................................181
Figure 6.7. Ion released versus equilibrium solution pH for as-received ACC, ER ACC and EO ACC..........................................................183
Figure 6.8. Zeta potential versus equilibrium solution pH for as-received ACC, ER ACC and EO ACC..........................................................184
Figure 6.9. FTIR spectra for as-received ACC..................................................188
Figure 6.10. FTIR spectra for ER ACC..................................................188
Figure 6.11. Nitrogen adsorption-desorption isotherm for as-received ACC..........................................................190
Figure 6.12. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 0.8 h (i.e. 15,840 c/g extent of reduction)........191
Figure 6.13. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 1.2 h (i.e. 23,760 c/g extent of reduction)........191
Figure 6.14. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 1.6 h (i.e. 31,680 c/g extent of reduction)........192
Figure 6.15. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 2.4 h (i.e. 47,520 c/g extent of reduction)......192
Figure 6.16. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 3 h (i.e. 59,400 c/g extent of reduction).............193
Figure 6.17. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 4 h (i.e. 79,200 c/g extent of oxidation).............193
Figure 6.18. Comparison of the adsorption isotherms of nitrogen for as-received ACC, electrochemically reduced ACC at 5.5 A for 3 h (ER ACC) and electrochemically oxidised ACC at 1.1 A for 6 h (EO ACC)..............................195
Figure 6.19. BET surface area versus extent of reduction for ACCs electrochemically reduced at 5.5 A..........................................................196
Figure 6.20. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 15,840 c/g extent of reduction....................198
Figure 6.21. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 23,760 c/g extent of reduction......................199
Figure 6.22. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 31,680 c/g extent of reduction......................199
Figure 6.23. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 47,520 c/g extent of reduction......................200
Figure 6.24. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 59,400 c/g extent of reduction......................200
Figure 6.25. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 79,200 c/g extent of reduction......................201
Figure 6.26. Pore size distribution for as-received ACC, electrochemically reduced ACC at 5.5 A for 3 h (ER ACC) and electrochemically oxidised ACC at 1.1 A for 6 h (EO ACC).........................................................203
Figure 6.27. SEM of as-received ACC, selected electrochemically oxidised ACC and selected electrochemically reduced ACCs..............................205
Figure 6.28. Speciation curve for 0.01 M chromium in sodium dichromate solution.................................................................206
Figure 6.29. Sorption isotherms of chromium(VI) onto as-received ACC, ER ACC and EO ACC at solution pH 4............................209
Figure 6.30. Sorption isotherms of chromium(VI) onto as-received ACC, ER ACC and EO ACC at solution pH 6 ...........................................................210
Figure 6.31. Sorption isotherms of chromium(VI) onto as-received ACC, ER ACC and EO ACC at solution pH 8 ...........................................................211
Figure 6.32. Sorption isotherms of chromium(VI) onto as-received ACC, at solution pH 4, 6 and 8 ...........................................................213
Figure 6.33. Sorption isotherms of chromium(VI) onto ER ACC, at solution pH 4, 6 and 8 ...........................................................214
Figure 6.34. Sorption isotherms of chromium(VI) onto EO ACC, at solution pH 4, 6 and 8 ...........................................................215
LIST OF TABLES

Table 2.1. Comparison of experimental conditions, adsorption capacities of adsorbents for copper(II) and surface properties of adsorbents ................................................................. 18
Table 2.2. Comparison of experimental conditions, adsorption capacities of adsorbents for lead(II) and surface properties of adsorbents ........................................................................ 25
Table 2.3. Comparison of experimental conditions, adsorption capacities of adsorbents for competitive and noncompetitive lead(II) and copper(II) and surface properties of adsorbents ........................................................................ 31
Table 2.4. Comparison of experimental conditions, adsorption capacities of adsorbents for chromium(VI) and surface properties of adsorbents ......................................................... 41
Table 2.5. Comparison of ozone modification conditions, surface properties of different ozone modified adsorbents and the different applied processes for the ozone modified adsorbents ........................................................................ 63
Table 2.6. Comparison of nitric acid modification conditions, surface properties of different nitric acid modified adsorbents and the different maximum adsorption capacities for the nitric acid modified adsorbents ................................................................. 74
Table 2.7. Comparison of modification conditions in different chemicals, surface properties of adsorbents modified in different chemicals and the different maximum adsorption capacities for the chemically modified adsorbents ................................................................. 83
Table 2.8. Comparison of modification conditions in different gases, surface properties of adsorbents modified in different gases and the different maximum adsorption capacities for the adsorbents modified in gases ................................................................. 86
Table 2.9. Comparison of electrochemical oxidation conditions in different electrolytes, surface properties of different electrochemically oxidised adsorbents and the different applied processes for the electrochemically oxidised adsorbents ........................................................................ 98
Table 2.10. Comparison of maximum cation exchange capacities obtained by ozone modification of adsorbents, modification of adsorbents in different chemicals, modification of adsorbents in gases and electrochemical oxidation of adsorbents ........................................................................ 100
Table 3.1. Comparison of physisorption and chemisorption ........................................................................ 102
Table 5.1. Electrochemical properties of unoxidised and electrochemically oxidised ACCs .......................... 141
Table 5.2. Elemental analysis of unoxidised and electrochemically oxidised ACCs...........142
Table 5.3. Band assignments for FTIR spectra of unoxidised (UO) and
electrochemically oxidised (EO) ACC...............................................................144
Table 5.4. Surface area specifications of unoxidised ACC (UO) and
electrochemically oxidised ACCs (EO) at different conditions.........................151
Table 5.5. Langmuir and Freundlich isotherm constants for non-competitive (N Cu)
and competitive (C Cu ) copper and non-competitive (N Pb)
and competitive(C Pb) lead sorption..............................................................161
Table 5.6. Experimental and Langmuir model maximum metal ion sorbed
onto EO and UO...........................................................................................162
Table 5.7. Experimentally determined maximum non-competitive (N Cu and N Pb)
and competitive (C Cu and C Pb) metal ions sorbed onto EO and H+ ion released
from EO........................................................................................................172
Table 6.1. Electrochemical properties of as-received ACC, electrochemically reduced
ACC and electrochemically oxidised ACC......................................................185
Table 6.2. Elemental analysis of as-received ACC, electrochemically reduced
ACC and electrochemically oxidised ACC......................................................186
Table 6.3. Band assignments for FTIR spectra of as-received ACC and ER ACC.....189
Table 6.4. Surface area specifications of as-received ACC, electrochemically
oxidised ACC (EO) and electrochemically reduced ACCs (ER)
at different conditions....................................................................................197
Table 6.5. Langmuir and Freundlich isotherm constants and experimental
values for maximum chromium(VI) ions sorbed (qe) for ACCs
at solution pH 4, 6 and 8 .............................................................................208
Table 6.6. Experimental values for maximum Cr(VI) ions sorbed onto ACCs
and H+ or OH- ion released from ACCs......................................................217
Table 7.1. Comparison of maximum sorption capacities of adsorbents for target
pollutants of study at different solution pH values (CCPb and CCu are.
competitive lead and copper from multicomponent solution of copper and lead)....226
1. INTRODUCTION

Activated carbons are a group of carbon materials that have been processed to produce highly developed internal surface area and porosity and so have a large capacity for adsorbing chemicals from liquids or gases. (Suffet et al., 1978; Jankowska et al., 1991; Patrick, 1995; Biniak et al., 1999; Streat and Horner, 2000; Saha et al., 2001a). The use of activated carbons as adsorbents started in 1500 BC by the Egyptians for medical purposes and as purifying agents (Bansal et al., 1988). Since then, industry has developed a wider range of utilisation of activated carbons for both liquid and gas applications. Granular carbons were used during the First World War in the purification of gases and extraction of vapours from gas streams. They were also used in industry, for the recovery of liquid petroleum from natural gas, extraction of benzene from manufactured coal-gas, recovery of volatile solvent vapours from various industrial processes and the removal of chemical species from aqueous solutions in order to purify water and recover metals.

Due to its wide ranges of applications and low cost compared with possible competitive adsorbents, several new forms and shapes of activated carbons with special characteristics have been produced. Activated carbon now exists in granular (GAC), powder (PAC) and fibre forms. The carbon fibres are produced in the form of cloth (ACC) and felt (ACF). The porous structure of ACC is composed mainly of micropores, while GAC and PAC contain a complex porous network of macropores, mesopores and micropores. In the ACC the access to the micropores is directly from the external surface, however, in the GAC and PAC, the macropores are opened to the particle external surface and then branch into mesopores and finally into the micropores. Most of the adsorption in all the activated carbon forms take place in the micropores, thus adsorption area in ACC can be accessed more easily than in other forms (Suziki, 1994). The application of granular activated carbons in water treatment can result in slow intraparticle diffusion and complicated handling and regeneration procedures (Suziki, 1991). Carbon fibres can be prepared from synthetic and natural precursors. They possess surface area between 1000 and 2100 m²/g, which is more than the surface area of granular activated carbon. They are robust and compact and easier to handle and therefore, offer opportunities for the design of intensified water treatment (Brasquet and Le Cloirec, 1997; Rangel-Mendez and Streat, 2002b; Park
and Kim, 2004c; Park and Kim, 2005). The ACCs are highly microporous, approximately 90% of the total pore volume is attributed to the micropores. These micropores are directly accessible, thereby increasing intraparticle diffusion so that the overall sorption rate is faster than granular activated carbons that possess a combination of micropores, mesopores and macropores (Baudu et al., 1991; Brasquet and Le Cloirec, 1997; Rangel-Mendez and Streat, 2002b). Therefore, they show some significant potential advantages over granular activated carbons. For the PAC processes, the overall rate of adsorption is very fast, but it presents the disadvantage of complicated handling. The overall rate of adsorption in ACC is as fast as PAC but it does not have the handling problems existing in PAC.

Adsorption has been widely used for the removal of trace contaminants from potable water and industrial effluents. Several adsorbents such as zeolites, clays, metal silicates, biosorbents and activated carbons have been used. However, the uses of activated carbons have been predominant since they are versatile adsorbents that can be used in both gas and liquid phase applications due to their good physical and chemical properties. They are extensively used in wastewater treatment for the removal of several contaminants. Their large surface area makes the sorption of metal ions from aqueous solutions possible, which is a very important environmental issue. Due to their high toxicity to human and aquatic life, researchers working on wastewater treatment are primarily concerned with the presence of heavy metals, radionuclides and synthetic chemicals in aqueous solutions. Wastewaters that contain high concentrations of metal ions originate mainly from industrial establishments which have increased due to the increase in industrialisation in the last few decades. The European Community Council Directive 98/78/EC (Council Directive, 1998) has highlighted some of the most toxic heavy metals in residual waters and their limits of concentrations in drinking water are as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Limit (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>10</td>
</tr>
<tr>
<td>Boron</td>
<td>1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>50</td>
</tr>
<tr>
<td>Copper</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>10</td>
</tr>
<tr>
<td>Mercury</td>
<td>1</td>
</tr>
</tbody>
</table>
Nickel  
20 µg/L  
Selenium  
10 µg/L

1.1. TARGET POLLUTANTS OF STUDY

Since wastewater pollutants come from a variety of sources, it is impossible to make a comprehensive study of all pollutants in a single research study. However, study of a few targeted model pollutants is feasible and the results can be extended further in interpreting the behaviour of similar pollutants. In this study the selected model pollutants are copper, lead and chromium(VI).

1.1.1. Copper

Copper is a widely used industrial metal whose applications include electrical wiring, plumbing, production of alloys (e.g. brass and bronze), air conditioning, tubing and roofing. The properties of copper that make it suitable for these applications are high electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation, attractive appearance, ready availability and high recyclability. Copper exists mainly as Cu²⁺ in aqueous solution. Copper is broadly classified as a transition metal. Many transition metals are required by humans and many living organisms in minute but definite quantities. Elements required in such small amounts are called trace elements. These trace elements include copper, manganese, iron, cobalt, nickel and chromium (Hill and Holman, 2000). They are essential for effective catalytic activity of various biological enzymes. Copper is a very important trace metal that is predominantly found in the nuclei and mitochondria of the living cell. One of the most important enzymes containing copper is cytochrome oxidase. It is involved when energy is obtained from oxidation of food. In the absence of copper, cytochrome oxidase is completely inhibited and the living organism is unable to metabolise food effectively. However, chronic copper poisoning causes gastrointestinal bleeding, hypotension, convulsions, significant DNA damage and death (Hill and Holman, 2000; Mohan et al., 2006). The major source of copper pollution involves the discharge of industrial wastewaters, primarily from the plating industry. Other sources include petroleum refining, fertiliser manufacturing, coal-fired power stations, incinerators and sewage treatment plants. The general population may be exposed to increased levels of copper in drinking water largely as a result of the corrosion of
plumbing materials. Contact with copper may also result from the use of copper fungicides and algaecides.

1.1.2. Lead
Lead has important uses as a relatively inert material. It has been used as an inert material for gas and water pipes, for cable sheathing and for chemical vessels. Lead is also used for the plates of lead-acid accumulators (batteries), roof and cable covering, production of alloys (e.g. solder and printing metals) and as a screen for radioactivity. Lead exists mainly as Pb$^{2+}$ in aqueous solution. Lead is classified as a heavy metal. Heavy metal is the classification that is generally applied to those metals of particular concern in the treatment of industrial wastewaters. Heavy metals include copper, silver, zinc, cadmium, mercury, lead, chromium, iron and nickel. Other metals that may be considered as heavy metals are tin, arsenic, selenium, molybdenum, cobalt, manganese and aluminium. Most of the heavy metals appear in inorganic form in industrial wastewater, except in textiles and dyeing where they are found in organic form. Unlike most organic pollutants, heavy metals are non-degradable and can accumulate in living tissues. Lead is a very toxic metal. The organs adversely affected by lead are the central nervous system and the blood system. Acute lead poisoning can seriously affect the gastrointestinal track and the nervous system. The relatively immediate effects of acute lead poisoning are nausea, abdominal pains, anorexia, insomnia, irritability, and coordination loss. In severe situations neurological effects such as restlessness, hyperactivity, confusion and impairment of memory, coma and death can occur (Fergusson, 1990). The four major routes for entry of lead into the human body are food, drink, air and dust. The major source of lead pollution involves the discharge of industrial wastewaters, primarily from plating, printing, battery manufacturing and dyeing industries. Other sources include lead in petrol, lead in paint, lead glazed vessels and lead solder.

1.1.3. Chromium(VI)
Chromium compounds are widely used in anodising operations in the surface finishing industry, electroplating and leather industry (Hu et al., 2003). Chromium can be used as a protective and non-corroding metal owing to the presence of an unreactive layer of chromate. It can also be used in the production of iron-free alloys and metal containing ceramics. Chromium is mainly classified as a transition metal. Chromium
exists in two oxidation states, chromium(III) and chromium(VI). However, chromium never forms simple ions in the higher oxidation state since this will result in ions of extremely high charge density. Hence chromium compounds in the higher oxidation state are either covalently bonded (CrO₃) or contain complex ions (CrO₄²⁻).

Chromium(III) is required for normal carbohydrate and lipid metabolism in mammals. It reduces decline in glucose tolerance when added to chromium deficient diet. Chromium(III) deficiency in humans and other mammals results in symptoms like diabetes and cardiovascular disease: decreased glucose tolerance, increased concentration of circulating insulin, decreased insulin receptor number, elevated cholesterol and triglyceride levels (King, 1994; Hill and Holman, 2000). There is no evidence of any toxic effects of chromium(III).

In contrast chromium(VI) is highly toxic, carcinogenic, mutagenic and teratogenic (Han et al., 2000; Han et al., 2007; Garg et al., 2007). Some chromium(VI) compounds (e.g. dichromates and chromic acids) have long been known as skin irritants. They have been shown to be some of the most important causes of occupational contact dermatitis (King, 1994).

The major source of water contamination with chromium ions is industrial wastewaters from surface metal treatment plants and from tanneries. Chromium(VI) concentration in industrial wastewaters ranges from 5-50 mg/L. Other sources include, metal cleaning, plating, metal processing, automobile parts manufacturing and ink formulating industries.

1.2. SEPARATION PROCESSES FOR WASTEWATER TREATMENT
It is obvious that the presence of metals in aqueous solution even in very low concentrations can be extremely toxic to many life forms. As a consequence, equipment and processes are continuously being developed to remove and/or recover metals from wastewater streams. Different processes have been applied, such as adsorption, ion exchange, chemical precipitation, electrochemical processes, membrane processes, biological processes and liquid-liquid extraction. The selection of any of these processes will depend on the characteristics of the wastewater and the
concentrations of the pollutants. The application of some of the processes mentioned above will be discussed in this section.

1.2.1. Chemical Precipitation

This process is one of the most commonly used methods to remove metals from wastewater streams. The process involves the alteration of the physical and chemical states of the pollutants so as to facilitate their removal through the process of sedimentation (Tchobanoglous, 1991). The optimum solution pH values at which metals precipitate are different. So wastewater containing different metals needs to be treated in stages at different solution pH values.

Hydroxides, sulphides, phosphates and carbonates are the most commonly used precipitants (Brooks, 1991). Sodium sulphide has been very effective for the precipitation of metals from aqueous solutions. The high reactivity of sulphur with metal ions and low solubility of sulphur complexes formed with metals over a wide range of solution pH makes sulphide a more attractive reagent than hydroxide (Bhattacharyya et al., 1979). Carbonate precipitates normally at lower concentrations than hydroxide and the product of carbonate precipitation separates from solution better than that of hydroxide precipitation. Sulphide precipitation occurs at lower solution pH than carbonate precipitation. The reaction time for sulphide precipitation is also less, but fine solids are formed, therefore, coagulation is needed at the separation stage. The main obstacles to sulphide precipitation are production of hydrogen sulphide and the toxic effect of sulphides although the sludge produced is subject to less leaching.

However, chemical precipitation produces sludge that requires secondary treatment steps such as filtration and dewatering. The achievable concentration through this process is above the permissible levels in drinking water. Kroschwitz (1999) reported effluent levels achievable in heavy metal removal by precipitation as 50 μg/L for arsenic, 50 μg/L for selenium, 120 μg/L for nickel and 20 μg/L for mercury. These concentrations are higher than the permissible levels in drinking water. In addition, the process is likely to pollute drinking water with the chemicals used for precipitation. Therefore, there is the need to explore other methods for heavy metal removal from wastewater.
1.2.2. Electrochemical Processes
These methods are based on the reduction and oxidation reactions occurring at electrodes and the movement of ions across the electrolytic cell due to applied voltage. The reactions generate electrons to convert metal ions to their elemental state. Therefore, electrochemical processes do not need additional reagents. These processes have been extensively utilised in the removal and recovery of metals from wastewater mainly in hydrometallurgy and semi-conductor industries (Brooks, 1991). Wastewater containing more than 1% w/w trace metals can be successfully treated by electrochemical process. However, it is necessary to modify the process in order to obtain high efficiency without excessive consumption of energy for dilute solutions. The consumption of energy makes it an expensive process.

1.2.3. Membrane Processes
A membrane is a discrete thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is completely uniform in composition and structure. It may also be chemically or physically heterogeneous, e.g. containing holes or pores of finite dimensions. Technology has advanced in this field and different kinds of membranes have been developed.

1.2.3.1. Isotropic microporous membranes
Isotropic microporous membranes consist of pores of diameter 0.01-10 μm. All particles larger than the largest pores are completely rejected by the membrane. Particles smaller than the largest pores, but larger than the smallest pores are partially rejected according to the pore size distribution of the membrane. Particles much smaller than the smallest pores pass through the membrane. Thus separation of solutes by microporous membranes is mainly a function of the molecular or particle size of the solutes and pore size distribution of the membrane. In general, only molecules that differ considerably in sizes can be effectively separated by microporous membranes, e.g. in ultrafiltration and microfiltration.

1.2.3.2. Nonporous dense membranes
Nonporous dense membranes consist of dense films through which permeants are transported by diffusion under the driving force of pressure, concentration or electric
potential gradient. The separation of various components of a solution is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. An important property of nonporous dense membranes is that even permeants of similar size may be separated when their concentration in the membrane (i.e. their solubility) differs significantly. Most gas separation and reverse osmosis processes use dense membranes to perform separation. Using an electrical driving force, electrodialysis, an electric current is applied across the membrane to separate target ions from wastewater. This enhances the process as the transport of ions across the porous or permeable membrane becomes faster. Either cations or anions are allowed to pass through the membrane whilst the ions of opposite charge are restricted. This process has been widely applied in desalination plants.

Membrane processes can be used at the end of series of separation processes to reduce the concentration of metal ions below statutory discharge limits (Broom et al., 1994). They are also very efficient but have high operational and capital costs.

1.2.4. Ion Exchange

Ion exchange involves the exchange of ions of similar charge between a solid phase and an aqueous solution. Ion exchangers are insoluble solid materials that carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same charge when the ion exchanger is in contact with an aqueous solution. Carriers of exchangeable cations are cation exchangers and carriers of exchangeable anions are anion exchangers. Certain materials are capable of exchanging both cations and anions, therefore, they are amphoteric ion exchangers. The most important application of ion exchange is purification and demineralisation of water. This process works in two stages. The first stage involves passing the wastewater through a cation exchanger which results in the exchange of the hydrogen ions from the exchanger with the cations from the wastewater. The second stage involves passing the wastewater from the first stage into an anion exchanger which results in the exchange of hydroxyl ions from the exchanger with the anions from the wastewater. Ion exchange is a reversible process, so the ion exchangers can be regenerated.
The most important ion exchange materials are; ion exchange resins, ion exchange coals and mineral ion exchangers (Helfferich, 1995). Mineral ion exchangers are mainly zeolites and glauconites. Many coals are natural ion exchangers. They contain carboxylic and/or other weak acidic functional groups and therefore can be used as cation exchangers. Helfferich (1995) reported that, as far as practical applications are concerned, organic resins are the most important ion exchangers. Their main advantages are high chemical and mechanical stability, high ion exchange capacities and high exchange rates. The removal of metal ions by ion exchangers is recommended for concentrations less than $1000 \text{ mg/L}$ and in solutions with small quantities of competitive ions.

1.2.5. Adsorption

Ion exchange resembles adsorption because in both cases, dissolved species are taken up by solids. The characteristic difference between the two processes is that ion exchange, in contrast to adsorption, is a stoichiometric process. Ions removed from the solution are replaced by an equivalent amount of other ionic species of the same charge from the ion exchanger. In adsorption, solutes are taken up without being replaced by other species from the adsorbent. Adsorption differs from ion exchange, since it involves physical interaction of molecular species in solution with the surface of a porous adsorbent. The mechanism of interaction is by weak electrostatic forces, e.g. Van der Waals forces, London forces, hydrophobic interactions and hydrogen bonding.

However, nearly every ion exchange process is accompanied by electrolyte sorption or desorption. Also, the most common adsorbents such as alumina and activated carbon can act as ion exchangers. For ionic species, e.g. trace metals, it is possible to obtain interaction with specific functional groups at the surface of the adsorbent. In the case of activated carbon, adsorption involves an ion exchange mechanism and/or a specific chemical interaction between the ions and the surface functional groups. Activated carbon is the most widely studied and used adsorbent in the adsorption of organic and inorganic micropollutants from water. The physical and chemical properties, uses and applications of carbonaceous adsorbents and adsorption theory will be discussed in details in chapters 2 and 3.
1.3. RESEARCH OBJECTIVES

From the above discussion of some separation processes, activated carbon remains the most attractive adsorbent for the removal of organic and inorganic micropollutants from water due to its wide ranges of application and low costs compared to other adsorbents. As discussed in Section 1, carbon fibres have potential advantages over granular and powder activated carbons. The selectivity and sorption capacity of conventional activated carbons towards heavy metals is rather low. However, metal sorption onto activated carbon can be considerably enhanced by the introduction of weakly acidic functional groups such as carboxylic, carbonyl, phenolic and lactonic through electrochemical oxidation of activated carbons in different electrolytes and also by chemical oxidation using reagents such as nitric acid, air, phosphoric acid, hydrogen peroxide and ozone (Wu et al., 1995; Park and Kim, 2001; Rangel-Mendez and Streat, 2002b). Hence the objectives of this research are to evaluate the sorption performances of as-received and modified viscose rayon based ACCs for the removal of metal ions from water. Different techniques of modification of ACC such as electrochemical oxidation and electrochemical reduction will be studied. Then the modified and as-received ACCs will be characterised by using sodium capacity, chloride capacity, pH titration, zeta potential measurements, elemental analysis, Fourier Transform Infra Red (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD), nitrogen adsorption-desorption isotherms and scanning electron microscopy (SEM).

Activated carbon fibres have been employed for the removal of metal ions from single component solutions. However, it is necessary to evaluate their performance in multicomponent solutions since the presence of only one metal ion is a rare situation either in nature or in wastewaters. Therefore, in this research the feasibility of using as-received and modified ACCs for the removal of toxic metal ions, copper, lead and chromium(VI) from water will be evaluated.

In the first instance, single component sorption isotherms will be determined for the as-received and modified ACCs. The effect of adsorbate concentration and solution pH on the sorption process will be analysed. Then competitive sorption between the metal ions will be analysed.
The objectives of this research are summarised as:

- Electrochemical oxidation of a viscose rayon based activated carbon cloth (ACC) to alter the surface functional groups on the ACC to improve its cation sorption ability.
- Determination of optimum conditions for electrochemical oxidation of the viscose rayon based ACC.
- Electrochemical reduction of a viscose rayon based ACC to alter the surface functional groups on the ACC to improve its anion sorption ability.
- Determination of optimum conditions for electrochemical reduction of the viscose rayon based ACC.
- Physical and chemical characterisation of as-received and modified ACCs will be used to analyse the relationship between the physical and chemical properties of the ACCs and their sorption behaviour.
- Evaluation of as-received and electrochemically oxidised ACCs for noncompetitive and competitive removal of copper(II) and lead(II) ions from aqueous solutions.
- Evaluation of as-received, electrochemically reduced and electrochemically oxidised ACCs for the removal of chromium(VI) ions from aqueous solution.
- Correlation of equilibrium data by conventional theoretical models.
- Postulation of possible sorption mechanism of copper(II) and lead(II) ions onto as-received and electrochemically oxidised ACCs.
- Postulation of possible sorption mechanism of chromium(VI) ions onto the as-received, electrochemically oxidised and electrochemically reduced ACCs.
2. LITERATURE REVIEW

2.1. INTRODUCTION
This chapter is a literature review of the adsorption of the target pollutants onto different adsorbents, production of viscose rayon based activated carbon cloth, some methods of modification of different adsorbents and some theoretical aspects of adsorption.

2.2. ADSORPTION OF COPPER
Ferro-Garcia et al. (1988) studied the adsorption of $\text{Zn}^{2+}$, $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$ onto almond shell-based, olive stone-based and peach stone-based granular activated carbons at different solution pH values. They also investigated the effect of the presence of $\text{Cl}^-$, $\text{CN}^-$, $\text{SCN}^-$ or EDTA on the adsorption of all the metal ions. They observed that adsorption of all the metal ions onto the three granular activated carbons increased with increase in solution pH. This was attributed to the changes on the carbon surface charge at different solution pH values. It was also observed that the adsorption of the metal ions onto the three granular carbons increased in the order, $\text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$. This was attributed to the hydrated ionic radii and polarizabilities of the metal ions. Maximum adsorption capacities of 0.102, 0.053 and 0.145 mmol/g of $\text{Zn}^{2+}$, $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$, respectively were observed at solution pH 5 and 313 K. The maximum adsorption capacity of $\text{Zn}^{2+}$ was observed on the almond shell-based granular activated carbon while the maximum adsorption capacities of $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$ were observed on olive stone-based granular activated carbon. Finally, it was observed that the presence of $\text{Cl}^-$, $\text{CN}^-$ or $\text{SCN}^-$ increased the adsorption capacities of all metal ions while the presence of EDTA decreased the adsorption capacities of all metal ions. This was attributed to the formation of some complex ions between the metal ions and the $\text{Cl}^-$, $\text{CN}^-$ or $\text{SCN}^-$ and greater size of EDTA that made the corresponding complex ions inaccessible to a number of pores in the granular activated carbons.

Sag et al. (1998) studied the biosorption of Cu(II) and Zn(II) onto a filamentous fungus (Rhizopus arrhizus) at different solution pH values. They observed maximum Cu(II) and Zn(II) adsorption capacities of 0.53 and 0.2 mmol/g, respectively, at solution pH 4.
and 298 K for the filamentous fungus. The higher adsorption capacity of Cu(II) was attributed to greater electronegativity and smaller hydrated ionic radius of Cu(II) than Zn(II).

Karabulut et al. (2000) studied the sorption of Cu(II) and Zn(II) ions onto low-rank Turkish coals at different solution pH values. They observed maximum sorption capacities of 0.26 and 0.18 mmol/g of Cu(II) and Zn(II), respectively, for the coals at solution pH 4 and 293 K. They also observed an increase in sorption capacities of Cu(II) and Zn(II) with an increase in solution pH. This was attributed to increase in dissociation of carboxylic acid sites on the coal surface with an increase in solution pH.

Saha et al. (2000) studied the sorption of copper, cadmium, nickel and zinc ions on thiol-based chelating polymeric resins (thiomethyl resin and Duolite GT-73). They observed that copper sorption on both resins were identical. The maximum copper sorption capacity was found to be 0.39 mmol/g at solution pH 4 and 293 K. They also observed that the metal sorption capacities for all the resins follow the order Cu$^{2+}$ > Cd$^{2+}$ > Zn$^{2+}$ > Ni$^{2+}$. An increase in copper sorption with increase in solution pH was also observed. This was attributed to slight dissociation of thiol groups on the resins and formation of disulphide bonds (-S-S-) at low solution pH, thereby reducing the availability of thiol (-SH) groups for interaction with metal ions.

Lee et al. (2001) studied the sorption of Cu(II) ions onto chitosan-tripolyphosphate chelating resin at different solution pH values. They observed a drastic decrease in Cu(II) affinity for the resin at low solution pH and attributed it to competition of Cu(II) ions with hydronium ions. Maximum Cu(II) sorption capacity of 3.15 mmol/g was observed at solution pH 5 and 303 K. They concluded that sorption of Cu(II) ions onto the resin was by chelation rather than ion-exchange mechanism.

Shawabkeh et al. (2002) studied the adsorption of copper and strontium onto pecan shell-based granular activated carbon at different solution pH values. Maximum adsorption capacities of 1.5 mmol/g of Cu$^{3+}$ at solution pH 3.7 and 298 K and 2.1 mmol/g of Sr$^{2+}$ at solution pH 8.5 were observed for the pecan shell-based granular activated carbon. They also observed an increase in adsorption capacities of Cu$^{2+}$ and
Sr$^{2+}$ for the pecan shell-based granular activated carbon with an increase in solution pH. This was attributed to a decrease in the degree of competition between H$^+$ ion and Cu$^{2+}$ or Sr$^{2+}$ for the ion exchange sites at higher solution pH.

Yavuz et al. (2003) studied the sorption of Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ onto raw kaolinite at 313 K. Maximum sorption capacities of 0.0081, 0.0156, 0.028 and 0.173 mmol/g of Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$, respectively, were observed for the raw kaolinite. This was attributed to complex formation between the metal ions and silanol and aluminol functional groups on the kaolinite.

Agbenin and Olojo (2004) studied competitive sorption of copper and zinc ions onto savanna soil at different solution pH values. They observed maximum sorption capacities of 0.0062 and 0.0048 mmol/g of copper and zinc ions, respectively, for the savanna soil at solution pH 5.5 and 313 K. The preferential retention of copper to zinc was attributed to higher electronegativity for copper (2) than zinc (1.6) that made more complex formation between copper and the savanna soil. They also observed that sorption of copper and zinc increased with increase in solution pH. This was attributed to competition of Zn$^{2+}$ or Cu$^{2+}$ ions with H$^+$ ions at low solution pH, therefore, reducing complex formation between Zn$^{2+}$ or Cu$^{2+}$ with the savanna soil.

Acar and Eren (2006) compared copper(II) ions removal abilities of sawdust (SD) and activated sawdust (ASD) from aqueous solutions at different solution pH values. They observed maximum adsorption capacities of 0.086 and 0.212 mmol/g of copper for SD and ASD, respectively, at solution pH 5.5 and 293 K. The higher maximum adsorption capacity for ASD was attributed to the activation of the sawdust with sulphuric acid that made it more acidic than SD. They also observed an increase in adsorption of copper with an increase in solution pH. This was attributed to increase in the number of negatively charged sites and decrease in the number of positively charged sites as the solution pH increases, therefore, the adsorption of copper increased due to electrostatic attraction.

King et al. (2006) studied the removal of copper(II) from aqueous solutions by teak leaves powder at different solution pH values. They observed maximum adsorption capacity of 1.38 mmol/g of copper(II) for the teak leaves powder at solution pH 5.5
and 298 K. This was attributed to a high content of ionisable carboxyl groups from mannuronic and guluronic acids on the surface of the teak leaves powder. They also observed an increase in adsorption of copper with increase in solution pH for the teak leaves powder. This was attributed to inhibition of copper(II) removal as a result of competition between $H^+$ and $Cu^{2+}$ ions on the sorption sites at low solution pH and exposure of carboxylate groups at high solution pH which increased the negative charge density on the teak leaves powder surface, therefore, increasing the attraction of metallic ions with positive charge and allowing the adsorption onto the teak leaves powder surface.

Kumar et al. (2006) studied the removal of copper(II) from aqueous solution by marine green algae powder at different solution pH values. They observed a maximum adsorption capacity of 0.42 mmol/g of copper for the marine green algae powder at solution pH 5 and 298 K. They also observed an increase in adsorption of copper with an increase in solution pH for the marine green algae powder. This was attributed to the overall surface of the marine green algae powder becoming negatively charged as solution pH increased, therefore, attracting more of the positively charged copper ions.

Mohan et al. (2006) studied the removal of copper and cadmium from aqueous solutions by Kraft Lignin (a biosorbent) at different solution temperatures and pH values. They observed maximum adsorption capacities of 1.23 and 0.93 mmol/g of copper and cadmium, respectively, for the biosorbent at solution pH 7 and 313 K. Higher adsorption capacity of copper was attributed to the fact that copper ions have smaller hydrated radii (8.38 Å) than cadmium ions (8.52 Å), therefore, copper ions can enter into smaller pores and have greater access to the surface of the Lignin and copper having higher electronegativity (1.9) than cadmium (1.69), therefore, copper ions have stronger attraction to the Lignin than cadmium ions. An increase in sorption capacities of both metal ions with increase in solution pH and temperature was also observed. The increase in sorption capacities with increase in solution pH was attributed to competition between $H^+$ ions and $Cu^{2+}$ or $Cd^{2+}$ ions and protonation of negative functional groups on the Lignin that reduced the Lignin ability to coordinate with $Cu^{2+}$ or $Cd^{2+}$ at low solution pH. The increase in sorption capacities with increase in solution temperature was attributed to the sorption process being endothermic.
Pehlivan et al. (2006) compared the abilities of sugar beet pulp (SBP) and fly ash (FA) to remove copper and zinc ions from aqueous solutions at different solution pH values. They observed maximum sorption capacities of 0.49 and 0.54 mmol/g of copper and zinc, respectively, for SBP and maximum sorption capacities of 0.11 and 0.12 mmol/g of copper and zinc, respectively, for FA at solution pH 5.5 and 298 K. The higher maximum sorption capacities for SBP was attributed to the presence of carboxylic groups on the SBP surface, which makes it more acidic than FA that contains hydroxyl groups. The PZC for SBP was observed at pH 3.5 while the PZC for FA was observed at pH 7. They also observed an increase in adsorption of copper and lead with increase in solution pH for SBP and FA. For SBP, this was attributed to the carboxylic groups being negatively charged at high solution pH, therefore enhancing the attraction of metal ions. For FA it was attributed to the FA surface being positively charged at solution pH lower than the PZC (i.e., pH 7) and negatively charged at solution pH higher than the PZC.

Rao et al. (2006) studied the removal of copper and cadmium from aqueous solutions by ceiba pentandra hull-based granular activated carbon. They observed maximum adsorption capacities of 0.13 and 0.069 mmol/g of copper and cadmium, respectively, for the ceiba pentandra hull-based granular activated carbon at solution pH 6 and 303 K. This was attributed to the presence of C=O and S=O functional groups on the carbon surface. They also observed an increase in the sorption capacities of copper and cadmium with increase in solution pH. This was attributed to the carbon surface being positively charged below pH 5.7, which is the PZC of the carbon and the uptake of metal ions will be quite low due to electrostatic repulsion. With increase in solution pH above the PZC the negative charge on the carbon surface increases thereby enhancing the metal adsorption.

Chen et al. (2007b) prepared series of activated palygorskite clay by activating the palygorskite clay with different concentrations of HCl and used them as adsorbents for the removal of Cu(II) from aqueous solutions at different solution pH values. They observed an increase in adsorption capacity of Cu(II) for the activated palygorskite clay with increase in HCl concentration used for the palygorskite clay activation. A maximum adsorption capacity of 0.51 mmol/g of Cu(II) at solution pH 7 and 303 K was obtained on palygorskite clay activated with 12 mol/L HCl. This was attributed to
the increase in the originated silanol groups (Si-OH) by acid activation on the palygorskite clay. They also observed an increase in adsorption of Cu(II) with increase in solution pH for the activated palygorskite clay. This was attributed to the formation of negatively charged sites at solution pH above the PZC (i.e., pH 4.1) for the activated palygorskite clay that increased with further increase in solution pH.

Weng et al. (2007) investigated the adsorption characteristics of Cu(II) onto spent activated clay (SAC) at different solution temperatures and pH values. The maximum adsorption capacity for SAC towards Cu(II) was observed to be 0.208 mmol/g at solution pH 6 and 300 K. This was attributed to the low PZC of pH 3.4 for SAC due to acidic activation of the clay. They also observed an increase in adsorption of Cu(II) with an increase in solution pH. This was attributed to cation exchange interaction with SiO₂ and Al₂O₃ functional groups in the interlayer of the clay particle bearing permanent negative charges at solution pH above the PZC, which increased with further increase in solution pH. They also observed an increase in adsorption of Cu(II) with increase in solution temperature. This was attributed to the increased rate of diffusion of Cu(II) ions into the SAC pores with increase in solution temperature and the Cu(II) adsorption onto the SAC being endothermic.

Zhang et al. (2007) used a synthetic graft copolymer of cross-linked starch/acrylonitril as an adsorbent for the removal of Cu(II) ions from aqueous solution at solution pH 5 and different solution temperatures. They observed a maximum adsorption capacity of 1.53 mmol/g of copper for the graft copolymer at solution pH 5 and 293 K. This was attributed to a reversible reaction between the Cu(II) ions and the surface phase of the graft copolymer. However, a decrease in adsorption of Cu(II) ions with increase in solution temperature was observed. This was attributed to the adsorption of Cu(II) ions from aqueous solution onto the graft copolymer being an exothermic process.

2.2.1. Conclusions
Table 2.1 shows the comparison of experimental conditions, adsorption capacities of adsorbents for copper(II) and surface properties of the different adsorbents shown in the literature review in this section. It is obvious that very few adsorbents were characterised in details to explain the mechanism of adsorption. It is also obvious that the highest maximum copper(II) adsorption capacity of 3.15 mmol/g was observed for
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>PZC</th>
<th>IEP</th>
<th>Functional Group</th>
<th>Sodium capacity (mmol/g)</th>
<th>pH</th>
<th>Temp. (K)</th>
<th>Maximum adsorption capacity (mmol/g)</th>
<th>Reference</th>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>313</td>
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<td>Filamentous fungus</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>298</td>
<td>0.53</td>
<td>Sag et al. (1998)</td>
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<tr>
<td>Low rank coals</td>
<td>-</td>
<td>-</td>
<td>Carboxyl</td>
<td>-</td>
<td>4</td>
<td>293</td>
<td>0.26</td>
<td>Karabulut et al. (2000)</td>
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<td>Thiol-based polymeric resins</td>
<td>-</td>
<td>pH 1</td>
<td>Thiol</td>
<td>-</td>
<td>4</td>
<td>293</td>
<td>0.39</td>
<td>Saha et al. (2000)</td>
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<td>Chitosini-tripolyphosphate</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>303</td>
<td>3.15</td>
<td>Lee et al. (2001)</td>
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<tr>
<td>chelating resin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.7</td>
<td>298</td>
<td>1.5</td>
<td>Shawabkehe et al. (2002)</td>
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<tr>
<td>Pecan shell-based GAC</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>5.5</td>
<td>313</td>
<td>0.173</td>
<td>Yavuz et al. (2003)</td>
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<td>Raw kaolinite</td>
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<td>Silanol, Aluminol</td>
<td>-</td>
<td>5.5</td>
<td>313</td>
<td>0.0062</td>
<td>Agbenin and Olojo (2006)</td>
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<tr>
<td>Savana soil</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>5.5</td>
<td>313</td>
<td>0.212</td>
<td>Acar and Eren (2006)</td>
</tr>
<tr>
<td>Activated sawdust</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.5</td>
<td>293</td>
<td>1.38</td>
<td>King et al. (2006)</td>
</tr>
<tr>
<td>Teak leaves powder</td>
<td>-</td>
<td>-</td>
<td>Carboxyl</td>
<td>-</td>
<td>5.5</td>
<td>298</td>
<td>1.38</td>
<td>King et al. (2006)</td>
</tr>
<tr>
<td>Marine green algae powder</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>298</td>
<td>0.42</td>
<td>Kumar et al. (2006)</td>
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<tr>
<td>Kraft lignin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>313</td>
<td>1.23</td>
<td>Mohan et al. (2006)</td>
</tr>
<tr>
<td>Sugar beet pulp</td>
<td>pH 3.5</td>
<td>-</td>
<td>Carboxyl</td>
<td>-</td>
<td>5.5</td>
<td>298</td>
<td>0.49</td>
<td>Pehlivan et al. (2006)</td>
</tr>
<tr>
<td>Hull-based GAC</td>
<td>pH 5.7</td>
<td>-</td>
<td>C=O, S=O</td>
<td>-</td>
<td>6</td>
<td>303</td>
<td>0.13</td>
<td>Rao et al. (2006)</td>
</tr>
<tr>
<td>Activated polygorskite clay</td>
<td>pH 4.1</td>
<td>-</td>
<td>Silanol</td>
<td>-</td>
<td>7</td>
<td>303</td>
<td>0.51</td>
<td>Chen et al. (2007b)</td>
</tr>
<tr>
<td>Spent activated clay</td>
<td>pH 3.4</td>
<td>-</td>
<td>SiO₂, Al₂O₃</td>
<td>-</td>
<td>6</td>
<td>300</td>
<td>0.208</td>
<td>Weng et al. (2007)</td>
</tr>
<tr>
<td>Cross-linked starch/acrylonitril</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>293</td>
<td>1.53</td>
<td>Zhang et al. (2007)</td>
</tr>
</tbody>
</table>

Table 2.1. Comparison of experimental conditions, adsorption capacities of adsorbents for copper(II) and surface properties of adsorbents.
chitosan-tripolyphosphate chelating resin (Lee et al. 2001). However, this adsorbent is very expensive and so not economically favourable. The maximum copper(II) adsorption capacity for granular activated carbon that is economically favourable, but with technically difficult process when compared to activated carbon fibre was observed for pecan shell-based granular activated carbon (Shawabkeh et al., 2002) as 1.5 mmol/g. Therefore, it is necessary to modify activated carbon fibre to enhance the Cu(II) sorption capacity of the activated carbon fibre. As explained in chapter 1 the choice of activated carbon fibre is based on the fact that it is economically favourable with technically easy process. It is also necessary to do detailed characterisation of the modified activated carbon fibre so as to determine the physical and chemical composition of the modified activated carbon fibre, since these properties define the most efficient working conditions of adsorbents and also provide the factors for the proposal of the adsorption mechanisms. These are some of the objectives of this research.

2.3. ADSORPTION OF LEAD

Tan and Teo (1987) compared the adsorption of lead(II) from aqueous solution by four powder activated carbons, namely Carbon A (BDH decolourising carbon), Carbon B (Nurit D general purpose carbon), Carbon C (Merck general purpose carbon) and Carbon D (Singapore activated carbon company water treatment carbon) at different solution pH values. They observed adsorption capacities of 0.097, 0.054, 0.061 and 0.05 mmol/g of lead for Carbon A, Carbon B, Carbon C and Carbon D, respectively, at solution pH 7.8. They also observed an increase in adsorption of lead with increase in solution pH for Carbon A, Carbon B, Carbon C and Carbon D. Maximum adsorption capacities of 1.023, 0.89, 1.004 and 0.985 mmol/g of lead for Carbon A, Carbon B, Carbon C and Carbon D, respectively were observed at solution pH 12 and 301 K.

Li et al. (2004) studied biosorption of cadmium(II) and lead(II) ions by Phanerochaete chrysosporium, a filamentous fungus at different solution pH values and temperatures. They observed maximum adsorption capacities of 0.06 and 0.14 mmol/g of lead and cadmium, respectively, for the filamentous fungus at 300 K and solution pH 4.5. The higher adsorption of cadmium was attributed to the ionic radius of Pb(II) ion (121 pm) being larger than that of cadmium(II) ion (97 pm). They also observed an increase in adsorption of both metals with increase in solution pH. However, a decrease in
adsorption of both metals with increase in solution temperature was observed, indicating that the adsorption process is exothermic.

Sekar et al. (2004) investigated the removal of lead from aqueous solution by coconut shell-based activated carbon at different solution pH values. The cation exchange capacity of the activated carbon was 0.322 mmol/g. They observed maximum adsorption capacity of 0.187 mmol/g of lead for the activated carbon at solution pH 4.5 and 318 K. They also observed an increase in adsorption of lead with increase in solution pH. This was attributed to the ion exchange mechanism between H⁺ ions and Pb²⁺ ions on the activated carbon surface:

\[ 2(S-COH) + Pb^{2+} \leftrightarrow (S-CO)_{2}Pb + 2H^{+} \]  

(2.1)

where S is the surface of the activated carbon. In acidic solution, the activated carbon surface being positively charged, adsorption of Pb²⁺ ions are not favoured because electrostatic attraction between positively charged adsorbent and positively charged metal ions is not possible.

Shawabkeh et al. (2004) converted fly ash from oil shale into zeolite by sodium hydroxide hydrothermal activation. Cation exchange capacity of 1.66 mmol/g and PZC of pH 4.7 were observed for the produced zeolite. They used the produced zeolite as an ion exchanger for treatment of wastewater for lead and cadmium ions. They observed maximum adsorption capacities of 0.85 and 0.34 mmol/g of cadmium and lead, respectively, for the zeolite at solution pH 7 and 293 K. This was attributed to dissociation of hydroxyl functional groups on the fly ash. The greater removal efficiency of the zeolite towards cadmium was attributed to cadmium having lower ionic radius than lead, even though lead has higher electronegativity (2.33) than cadmium (1.69).

Agrawal et al. (2005) used sea nodule residue (SNR), a waste material containing oxides and hydroxides of manganese, iron and silicon as an adsorbent for removal of lead from aqueous solutions at different solution pH values and temperatures. They observed a maximum adsorption capacity of 0.478 mmol/g of lead for SNR at 333 K and solution pH 5.6. This was attributed to surface complex formation of Pb²⁺ or PbOH⁺ species on negatively charged species, such as oxides of manganese, iron and silicon on the surface of SNR. They also observed an increase in lead adsorption with
increase in solution pH. This was attributed to the fact that at lower solution pH than PZC, which is at pH 4.8 for SNR, the surface of SNR would have a high positive charge density, therefore, the uptake of Pb\(^{2+}\) ions would be quite low due to electrostatic repulsion. With increase in solution pH beyond the PZC, the negative charge density on the surface of SNR would increase, thereby raising the interaction of positively charged lead species with SNR and enhancing the adsorption. They also observed an increase in lead adsorption with increase in solution temperature, indicating that the adsorption process is endothermic with a probability of activated diffusion with increase in solution temperature.

Ho and Ofomaja (2005) studied the adsorption of lead ions from aqueous solution by palm kernel fibre at different solution temperatures but at constant solution pH 5. They observed maximum adsorption capacity of 0.241 mmol/g of lead for the palm kernel fibre at 338 K. They also observed an increase in adsorption of lead with increase in solution temperature. This was attributed to the adsorption of lead onto the palm kernel fibre being an endothermic process.

Mouflih et al. (2005) investigated the use of granular natural phosphate rock (NP) and activated granular phosphate rock (AP) for the removal of lead from aqueous solutions at different solution pH values and temperatures. They observed maximum adsorption capacities of 0.45 and 0.97 mmol/g of lead for NP and AP, respectively, at 318 K and solution pH 3. The higher adsorption capacity for AP was attributed to the change of its surface area due to activation. They also observed an increase in lead adsorption with increase in solution temperature for NP and AP. This was attributed to the adsorption of lead onto NP and AP being endothermic. However, they observed a decrease in lead adsorption with increase in solution pH for NP and AP. This was attributed to dissolution of NP and AP at low solution pH that exposed more active sites of phosphate and carbonate functional groups that was detected by FTIR analysis on NP and AP, thereby enhancing the adsorption of lead onto NP and AP.

Issabayeva et al. (2006) evaluated the performance of a palm shell-based granular activated carbon (PSAC) to remove lead ions from aqueous solutions at solution pH 3 and 5 but at constant temperature 300 K. They determined the total acidity of PSAC by Boehm’s method of titration (Boehm, 1994) and detected carboxyl and lactone
functional groups on the PSAC. They observed maximum lead adsorption capacities of 0.4 and 0.46 mmol/g at solution pH 3 and 5, respectively, for PSAC, which are above the PZC (pH 1.43) of PSAC. The higher adsorption capacity at solution pH 5 was attributed to competition between Pb$^{2+}$ ions and H$^+$ ions for the adsorption sites on PSAC surface at low solution pH that decreases with increase in solution pH.

Lodeiro et al. (2006) studied cadmium(II) and lead(II) adsorption by brown seaweed, Cystoseira baccata (a biosorbent) from aqueous solutions at different solution pH values. FTIR analysis detected carboxyl and hydroxyl functional groups on the seaweed. Cation exchange capacity of 2.2 mmol/g was also observed for the seaweed. They observed maximum metal uptake values of 0.899 and 0.897 mmol/g of cadmium(II) and lead(II), respectively, at solution pH 4.5 and 298 K for the seaweed. The metal uptake by the seaweed was attributed to the presence of carboxylic groups on the surface of the seaweed, which participated in the metal uptake. They also observed an increase in metal uptake with increase in solution pH. This was attributed to a change in the ionic state of the acidic functional groups involved in the metal binding with increase in solution pH.

Chen and Wang (2007a) investigated the use of natural palygorskite clay for the removal of Pb(II) from aqueous solutions at different solution pH values but at constant temperature 303 K. They observed maximum adsorption capacity of Pb(II) onto the natural palygorskite clay as 0.476 mmol/g at solution pH 6. This was attributed to cation exchange between Pb(II) and silanol functional groups on the surface of the palygorskite clay. They also observed an increase in Pb(II) adsorption with an increase in solution pH. This was attributed to the palygorskite clay becoming more negatively charged as the solution pH increased, thereby enhancing the adsorption of positively charged Pb(II) ions.

Deng et al. (2007) investigated the adsorption of lead(II) ions onto green algae from wastewater at different solution pH values and temperatures. FTIR analysis detected hydroxyl and carbonyl functional groups on the green algae. They observed maximum adsorption of lead(II) ions onto the green algae as 0.96 mmol/g at solution pH 5 and 298 K. They also observed an increase in lead(II) ions adsorption with increase in solution pH. This was attributed to deprotonation of the functional groups on the
surface of the green algae with an increase in solution pH. Finally, they observed increase in lead(II) ions adsorption with increase in solution temperature. This was attributed to the adsorption of lead(II) ions onto the green algae being endothermic.

Farinella et al. (2007) evaluated the efficiency of grape bagasse for Cd(II) and Pb(II) adsorption. FTIR analysis detected the presence of carboxyl and hydroxyl functional groups on the surface of the grape bagasse. They also found maximum adsorption capacities of Cd(II) and Pb(II) to be 0.52 and 0.18 mmol/g, respectively for the grape bagasse at solution pH 3 and 298 K. This was attributed to the presence of hydroxyl and carboxylic functional groups on the surface of the grape bagasse.

Gercel and Gercel (2007) investigated the adsorption of lead(II) ions onto granular activated carbon prepared from biomass plant at different solution pH values and temperatures. They observed maximum adsorption capacity of 1.16 mmol/g of lead for the granular activated carbon at solution pH 5 and 313 K. They also observed an increase in lead(II) ions adsorption with increase in solution pH. This was attributed to the competition between Pb$^{2+}$ ions and H$^+$ ions for available sites at low solution pH and an increase in negative charge density on the granular activated carbon surface due to deprotonation as solution pH increases. Finally, they observed an increase in lead(II) ions adsorption with increase in solution temperature, indicating that adsorption of lead(II) ions onto the granular activated carbon prepared from biomass plant is endothermic. This was attributed to the enlargement of pore size and/or further activation of the activated carbon surface at high solution temperature.

Girgis et al. (2007) studied the removal of lead ions from aqueous, non-buffered, solutions by H$_3$PO$_4$ activated peach stone-based carbon. They activated finely ground peach stones by soaking the ground stones in 50% H$_3$PO$_4$ for 24 h. The soaked finely ground peach stones were then activated at 773 K for 4 h, in the absence of any gas flow (PS55), under the flow of nitrogen gas (PS55N), under the flow of carbon dioxide (PS55C), under the flow of air (PS55A) and under the flow of steam (PS55S). They observed maximum adsorption capacities of 0.41, 0.34, 0.31, 0.985 and 0.56 mmol/g of Pb$^{2+}$ ions for PS55, PS55N, PS55C, PS55A and PS55S, respectively at solution pH 5.5 and 298 K. The highest uptake of Pb$^{2+}$ ions observed for PS55A was attributed to flowing air during activation at 773 K that generated acidic oxygen functional groups,
which was detected by FTIR analysis as carboxyl and hydroxyl, which took part in the cation exchange process with the Pb$^{2+}$ ions. The lowest uptake of Pb$^{2+}$ ions observed for PS55C was attributed to flowing carbon dioxide during activation at 773 K that reduced oxygen functional groups on the PS55C.

King et al. (2007) studied biosorption of lead ions from aqueous solutions by Syzygium cumini L. leaves at different solution pH values but at constant solution temperature 303 K. They observed maximum adsorption capacity of 0.157 mmol/g of lead for the Syzygium cumini L. leaves at solution pH 6. They also observed increase in lead uptake with increase in solution pH. This was attributed to the presence of carboxylic groups on the Syzygium cumini L. leaves that dissociate more with increase in solution pH, therefore, increasing the negative charge density on the Syzygium cumini L. leaves surface which increased the attraction of metallic ions with positive charges, therefore, increasing biosorption of lead ions onto the Syzygium cumini L. leaves surface.

Pimentel et al. (2007) investigated Pb$^{2+}$ ions adsorption by granular retorted shale at different solution pH values and temperatures. They observed maximum adsorption capacity of 0.178 mmol/g of Pb$^{2+}$ for the granular retorted shale at solution pH 5.5 and 303 K. This was attributed to complex formation of Pb$^{2+}$ with hydroxyl groups on the surface of the granular retorted shale to form mono and binuclear inner sphere complexes as follows:

$$S-OH + Pb^{2+} + H_2O \Leftrightarrow S-O-PbOH_2^+ + H^+ \quad (2.2)$$

$$S-OH + HO-Pb^+ \Leftrightarrow S-O-Pb^+ + H_2O \quad (2.3)$$

where S is the surface of the granular retorted shale.

They also observed an increase in Pb$^{2+}$ adsorption with increase in solution pH. This was attributed to increase in solution pH favouring the incorporation of the ions to the adsorbent surface. They also observed an increase in Pb$^{2+}$ adsorption with increase in solution temperature, which showed that the adsorption of Pb$^{2+}$ onto the granular retorted shale is endothermic.
## 2.3.1. Conclusions

Table 2.2 shows the comparison of experimental conditions, adsorption capacities of adsorbents for lead(II) and surface properties of adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>PZC</th>
<th>IEP</th>
<th>Functional group</th>
<th>Sodium capacity (mmol/g)</th>
<th>pH</th>
<th>Temp. (K)</th>
<th>Maximum adsorption capacity (mmol/g)</th>
<th>Reference</th>
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<td>BDH decolourising PAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12</td>
<td>301</td>
<td>1.023</td>
<td>Tan and Teo (1987)</td>
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<td>Filamentous fungus</td>
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<td>300</td>
<td>0.06</td>
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<td>0.187</td>
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<td>Fly ash-based zeolite</td>
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<td>Hydroxyl</td>
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<td>0.34</td>
<td>Shawabkeh et al. (2004)</td>
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<td>Sea nodule residue</td>
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<td>Oxides and of Fe, Mn, Si</td>
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<td>3</td>
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<td>0.97</td>
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<td>0.46</td>
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<td></td>
<td>Silanol</td>
<td></td>
<td>6</td>
<td>303</td>
<td>0.476</td>
<td>Chen and Wang (2007a)</td>
</tr>
<tr>
<td>Green algae</td>
<td></td>
<td></td>
<td>Hydroxyl, Carboxyl</td>
<td></td>
<td>5</td>
<td>298</td>
<td>0.96</td>
<td>Deng et al. (2007)</td>
</tr>
<tr>
<td>Grape bagasse</td>
<td></td>
<td></td>
<td>Hydroxyl, Carboxyl</td>
<td></td>
<td>3</td>
<td>298</td>
<td>0.18</td>
<td>Farinella et al. (2007)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>313</td>
<td>1.16</td>
<td>Gercel and Gercel (2007)</td>
</tr>
<tr>
<td>Peach stone-based GAC</td>
<td></td>
<td></td>
<td>Carboxyl, Hydroxyl</td>
<td></td>
<td>5.5</td>
<td>298</td>
<td>0.985</td>
<td>Girgis et al. (2007)</td>
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<tr>
<td>Syzygium cumini L. leaves</td>
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<td></td>
<td>Carboxyl</td>
<td></td>
<td>6</td>
<td>303</td>
<td>0.157</td>
<td>King et al. (2007)</td>
</tr>
<tr>
<td>Granular retorted shale</td>
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<td></td>
<td>Hydroxyl</td>
<td></td>
<td>5.5</td>
<td>303</td>
<td>0.178</td>
<td>Pimentel et al. (2007)</td>
</tr>
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</table>

Table 2.2. Comparison of experimental conditions, adsorption capacities of adsorbents for lead(II) and surface properties of adsorbents.
adsorbents for lead(II) and surface properties of the different adsorbents shown in the literature review in this section. It is obvious that very few adsorbents were characterised to explain the mechanism of adsorption. It is also obvious that the highest maximum lead(II) adsorption capacity of 1.16 mmol/g was observed for biomass plant-based granular activated carbon (Gercel and Gercel, 2007). However, this adsorbent is technically difficult when compared to activated carbon fibre although, it is not expensive and so economically favourable. The maximum lead(II) adsorption capacity for palm kernel fibre that is not expensive and so economically favourable, with technically easy process as it is in fibre form instead of powder or granular form, as discussed in chapter 1, was 0.241 mmol/g (Ho and Ofomaja, 2005), which is low. Therefore, it is necessary to modify activated carbon fibre to enhance its lead(II) adsorption capacity. It is also necessary to do detailed characterisation of the modified activated carbon fibre so as to determine the physical and chemical composition of the modified activated carbon fibre, since these properties define the most efficient working conditions of adsorbents and also provides the factors for the proposal of the adsorption mechanisms. These are some of the objectives of this research.

2.4. COMPETITIVE AND NONCOMPETITIVE ADSORPTION OF COPPER AND LEAD

Demirbas et al. (2005) studied noncompetitive adsorption of copper(II) ions and lead(II) ions onto Amberlite IR-120 synthetic resin from aqueous solutions. They observed cation exchange capacity for the synthetic resin as 1.9 mmol/g. They also observed maximum adsorption capacities of copper(II) ions and lead(II) ions for the synthetic resin as 0.218 and 0.291 mmol/g, respectively, at solution pH 9 and 293 K. This was attributed to dissociation of $-\text{SO}_3\text{H}$ functional groups on the synthetic resin. The higher adsorption of lead(II) ions was attributed to lower radii for the hydrated lead(II) ions than the hydrated copper(II) ions and higher charge density for the lead(II) ions than the copper(II) ions, therefore, binding lead(II) ions more strongly than copper(II) ions by electrostatic attraction.

Fiol et al. (2006) investigated crushed olive stone waste as biosorbent for competitive and noncompetitive Pb(II) and Cu(II) ions adsorption from aqueous solutions. They observed maximum adsorption capacities of 0.0447 and 0.0319 mmol/g of Pb(II) and
Cu(II) ions, respectively, for the crushed olive stone waste for noncompetitive batch experiments. However, the maximum adsorption capacities of Pb(II) and Cu(II) ions for the crushed olive stone waste increased to 0.0526 and 0.0506 mmol/g, respectively, for competitive batch experiments. This was attributed to the binding sites not being specific and are not limited to a maximum binding capacity.

Han et al. (2006) investigated competitive and noncompetitive Pb(II) and Cu(II) ions removal by manganese oxide coated sand (MOCS) from aqueous solutions at solution pH 4 and 293 K. They observed maximum adsorption capacities of 0.00762 and 0.0057 mmol/g of Pb(II) and Cu(II) ions, respectively, for MOCS for noncompetitive batch experiments. However, the maximum adsorption capacities of Pb(II) and Cu(II) ions for MOCS reduced to 0.00714 and 0.00294 mmol/g, respectively, for competitive batch experiments of initial equimolar lead(II) and Cu(II) ion concentrations. The slight reduction in Pb(II) maximum adsorption capacity for competitive batch experiments was attributed to Pb(II) ions having a better affinity to MOCS than Cu(II) ions. The reduction in the maximum adsorption capacities of Pb(II) and Cu(II) ions for competitive batch experiments was attributed to competition between Pb(II) and Cu(II) ions for adsorption sites on the MOCS.

Hawari and Mulligan (2006) investigated the feasibility of anaerobic granules prepared from anaerobic granular sludge, as a biosorbent for noncompetitive lead and copper removal from aqueous solutions at solution pH 5.5 and 293 K. They observed maximum biosorption capacities of 1.23 and 0.87 mmol/g of lead and copper, respectively, for the anaerobic granules. This was attributed to the presence of carboxylate, carbonyl and hydroxyl functional groups on the surface of the anaerobic granules.

Liu et al. (2006) studied noncompetitive adsorption of Cu^{2+} and Pb^{2+} ions onto organobentonite modified by 4'-methylbenzo-15-crown-5 (MB15C5) from aqueous solutions. They observed cation exchange capacity of 1.08 mmol/g for MB15C5. They also observed maximum adsorption capacities of 0.403 and 0.488 mmol/g of Cu^{2+} and Pb^{2+} ions, respectively, for MB15C5 at solution pH 5 and 298 K. The preferential adsorption order of Pb^{2+} > Cu^{2+} was attributed to partial dehydration of the hydrated Cu^{2+} and Pb^{2+} ions, for adsorption onto the surface of MB15C5 to take place, since the
diameters of hydrated Pb$^{2+}$ ions (8.02 Å) and Cu$^{2+}$ ions (8.38 Å) are greater than the interlayer spacing of the MB15C5. So Pb species with lower hydration energy were more easily dehydrated than Cu species, making Pb$^{2+}$ ions adsorption higher.

Sprynskyy et al. (2006) studied competitive and noncompetitive adsorption of Cu$^{2+}$ and Pb$^{2+}$ ions by ground clinoptilolite rock at different solution pH values but at constant temperature 298 K. They observed cation exchange capacity of 0.54 mmol/g for the ground clinoptilolite. They also observed maximum adsorption capacities of 0.134 and 0.41 mmol/g of Pb$^{2+}$ and Cu$^{2+}$ ions, respectively, for the ground clinoptilolite rock for noncompetitive batch experiments at solution pH 6.2. However, the maximum adsorption capacities of Pb$^{2+}$ and Cu$^{2+}$ ions for the ground clinoptilolite rock reduced to 0.0067 and 0.021 mmol/g, respectively, for competitive batch experiments at solution pH 6.2. This was attributed to competition between Pb$^{2+}$ ions and Cu$^{2+}$ ions for active sites on the surface of the ground clinoptilolite. They also observed an increase in Pb$^{2+}$ and Cu$^{2+}$ ions adsorption with increase in solution pH for noncompetitive batch experiments. This was attributed to competition between Pb$^{2+}$ or Cu$^{2+}$ ions with H$^+$ ions at low solution pH. As the solution pH increases, the concentration of H$^+$ ions decreases and this leads to an increase in the adsorption of Pb$^{2+}$ and Cu$^{2+}$ ions.

Tunali et al. (2006) studied competitive and noncompetitive biosorption of Pb(II) and Cu(II) ions from aqueous solutions onto bacterial strain isolated from metal polluted soil at solution pH 5 and 298 K. The maximum biosorption capacities for the bacterial strain were determined as 0.21 and 0.19 mmol/g of Pb(II) and Cu(II), respectively, for noncompetitive batch experiments. This was attributed to the presence of −SO$_3$ and −C−N functional groups, detected by FTIR analysis, on the bacterial strain. However, the maximum biosorption capacities for the bacterial strain were determined as 0.18 and 0.12 mmol/g of Pb(II) and Cu(II), respectively, for competitive batch experiments. The lower biosorption capacities of Pb(II) and Cu(II) for the bacterial strain in competitive batch experiments, was attributed to the competition between Pb$^{2+}$ ions and Cu$^{2+}$ ions for the biosorption sites on the surface of the bacterial strain.

Unlu and Ersoz (2006) studied the noncompetitive adsorption of Pb(II) and Cu(II) ions onto biopolymeric resin from aqueous solutions. They observed maximum adsorption
capacities of 0.0411 and 0.0195 mmol/g of Pb(II) and Cu(II) ions, respectively, for the biopolymeric resin at solution pH 6 and 293 K. This was attributed to metal uptake process by complexation with hydroxyl and carbonyl functional groups on the surface of the biopolymeric resin.

Uslu and Tanyol (2006) investigated the competitive and noncompetitive biosorption of lead(II) and copper(II) ions by dried biomass (P. putida) from aqueous solutions at different solution temperatures but at constant pH 5.5. They observed maximum biosorption capacities of lead(II) and copper(II) ions as 0.896 and 0.807 mmol/g, respectively, for P. putida, for noncompetitive batch experiments of initial lead(II) ion concentration of 1.31 mmol/L and initial copper(II) ion concentration of 3.83 mmol/L at solution temperature 303 K. This was attributed to metal uptake process by complexation with phosphate and amino functional groups on the surface of the P. putida. However, the maximum biosorption capacities of lead(II) and copper(II) ions for P. putida reduced to 0.147 and 0.329 mmol/g of lead(II) and copper(II) ions, respectively, for competitive batch experiments of initial lead(II) ion concentration of 0.27 mmol/L and initial copper(II) ion concentration of 0.97 mmol/L. The higher reduction in competitive biosorption capacity of lead(II) ions is due to the lower initial molar concentration of lead(II) ions in the competitive batch experiments. They also observed that competitive and noncompetitive lead(II) biosorption processes by P. putida are exothermic while competitive and noncompetitive copper(II) biosorption processes by P. putida are endothermic.

Wilson et al. (2006) used peanut shell-based granular activated carbon for noncompetitive adsorption of copper and lead ions at solution pH 4.8 and 298 K. They observed cation exchange capacity of 3.05 mmol/g for the peanut shell-based granular activated carbon. They also observed maximum adsorption capacities of 0.793 and 0.943 mmol/g of copper and lead ions, respectively, for the peanut shell-based granular activated carbon. This was attributed to the presence of negative charges on the surface of the peanut shell-based granular activated carbon.

Alinnor (2007) investigated noncompetitive adsorption of lead and copper ions from aqueous solutions by ground fly ash at solution pH 6 and 313 K. Maximum copper and lead ions adsorption capacities of 0.32 and 0.106 mmol/g, respectively, were obtained.
for the ground fly ash. The adsorption of lead and copper ions onto the ground fly ash was attributed to complex formation between Pb$^{2+}$ and Cu$^{2+}$ ions and the oxides like SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and CaO on the surface of the ground fly ash.

Amarasinghe and Williams (2007) studied competitive and noncompetitive adsorption of copper and lead ions onto tea waste from aqueous solutions at solution pH 5.5 and 295 K. Maximum copper and lead ion adsorption capacities of 0.755 and 0.314 mmol/g, respectively, for the tea waste were observed for noncompetitive batch experiments. However, a decrease in maximum copper and lead ion adsorption capacities to 0.25 and 0.097 mmol/g, respectively, was observed for the tea waste for competitive batch experiments. The lower decrease in maximum lead ion adsorption capacity of 0.217 mmol/g, as compared to decrease in maximum copper ion adsorption capacity of 0.51 mmol/g was attributed to copper ions being more hydrated than lead ions and a more hydrated cation will interact less with the adsorbent. The dehydration occurred more on the hydrated lead species because the hydration enthalpies for the lead and copper ions are -1481 and -2100 KJ/Kg, respectively.

Dahiya et al. (2007) explored the sorption potential of ground crab shell and ground arca shell biomass for noncompetitive adsorption of copper and lead ions from aqueous solutions at solution pH 5.5 and 298 K. Maximum copper and lead ion adsorption capacities of 0.608 and 0.096 mmol/g, respectively, were obtained for the crab shell biomass at equilibrium, while maximum copper and lead ion adsorption capacities of 0.28 and 0.089 mmol/g, respectively, were obtained for the arca shell biomass at equilibrium.

Wang et al. (2008) studied noncompetitive adsorption of copper and lead from aqueous solutions by fly ash, an industrial waste at solution pH 5 and 303 K. They investigated individual adsorption and co-adsorption with humic acid, for copper and lead. They observed maximum adsorption capacities of 0.087 and 0.11 mmol/g of lead and copper ions, respectively, for the fly ash in noncompetitive adsorption. This was attributed to complex formation between Pb$^{2+}$ and Cu$^{2+}$ ions and hydroxyl functional groups on the surface of the fly ash. For the co-adsorption with humic acid system, an increase in adsorption of lead and copper ions was observed. For Pb-HA, adsorption of lead ions increased to 0.179 mmol/g and for Cu-HA, adsorption of copper ions
increased to 0.44 mmol/g. The increase in adsorption in the presence of humic acid was attributed to formation of metal-ligand complexes on the fly ash surface which was enhanced by humic acid, since humic acid is a good complexing agent for many metal ions and its binding with metal ions improved the adsorption of lead and copper ions.

### 2.4.1. Conclusions

Table 2.3 shows the comparison of experimental conditions, maximum competitive

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Functional group</th>
<th>pH</th>
<th>Temp. (K)</th>
<th>Pb(^{2+})</th>
<th>Cu(^{2+})</th>
<th>Pb(^{2+})</th>
<th>Cu(^{2+})</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Amberlite IR-120 synthetic resin</td>
<td>-SO(_3)H</td>
<td>9</td>
<td>293</td>
<td>0.291</td>
<td>0.218</td>
<td>-</td>
<td>-</td>
<td>Demirbas et al. (2005)</td>
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<tr>
<td>Manganese oxide coated sand</td>
<td>-</td>
<td>4</td>
<td>293</td>
<td>0.0076</td>
<td>0.0057</td>
<td>0.0071</td>
<td>0.003</td>
<td>Han et al. (2006)</td>
</tr>
<tr>
<td>Anaerobic granules</td>
<td>Carboxyl, Hydroxyl</td>
<td>5.5</td>
<td>293</td>
<td>1.23</td>
<td>0.87</td>
<td>-</td>
<td>-</td>
<td>Hawari and Mulligan (2006)</td>
</tr>
<tr>
<td>Organobentonite</td>
<td>-</td>
<td>5</td>
<td>298</td>
<td>0.488</td>
<td>0.403</td>
<td>-</td>
<td>-</td>
<td>Liu et al. (2006)</td>
</tr>
<tr>
<td>Ground cliptilolite rock</td>
<td>-</td>
<td>6.2</td>
<td>298</td>
<td>0.134</td>
<td>0.41</td>
<td>0.0067</td>
<td>0.021</td>
<td>Spinksy et al. (2006)</td>
</tr>
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<td>Bacterial strain</td>
<td>-SO(_3), -C-N</td>
<td>5</td>
<td>298</td>
<td>0.21</td>
<td>0.19</td>
<td>0.18</td>
<td>0.12</td>
<td>Tunali et al. (2006)</td>
</tr>
<tr>
<td>Biopolymeric resin</td>
<td>Hydroxyl, Carbonyl</td>
<td>6</td>
<td>293</td>
<td>0.0411</td>
<td>0.0195</td>
<td>-</td>
<td>-</td>
<td>Unlu and Ersoz (2006)</td>
</tr>
<tr>
<td>Dried biomass (P. putida)</td>
<td>Phosphate, Amino</td>
<td>5.5</td>
<td>303</td>
<td>0.896</td>
<td>0.807</td>
<td>0.147</td>
<td>0.329</td>
<td>Uslu and Tanyol (2006)</td>
</tr>
<tr>
<td>Peanut shell-based GAC</td>
<td>-</td>
<td>4.8</td>
<td>298</td>
<td>0.943</td>
<td>0.793</td>
<td>-</td>
<td>-</td>
<td>Wilson et al. (2006)</td>
</tr>
<tr>
<td>Ground fly ash</td>
<td>Oxides of Si, Al, Ca, Fe</td>
<td>6</td>
<td>313</td>
<td>0.106</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>Alinnor (2007)</td>
</tr>
<tr>
<td>Tea waste</td>
<td>-</td>
<td>5.5</td>
<td>295</td>
<td>0.314</td>
<td>0.755</td>
<td>0.097</td>
<td>0.25</td>
<td>Amarasinghe and Williams (2007)</td>
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<td>Ground crab shell</td>
<td>-</td>
<td>5.5</td>
<td>298</td>
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<td>0.608</td>
<td>-</td>
<td>-</td>
<td>Dahiya et al. (2007)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Hydroxyl</td>
<td>5</td>
<td>303</td>
<td>0.087</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>Wang et al. (2008)</td>
</tr>
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</table>

Table 2.3. Comparison of experimental conditions, adsorption capacities of adsorbents for competitive and noncompetitive lead(II) and copper(II) and surface properties of adsorbents.
and noncompetitive lead(II) and copper(II) adsorption capacities of adsorbents and surface properties of the different adsorbents shown in the literature review in this section. It is obvious that no adsorbent was characterised to explain the mechanism of adsorption since there was no determination of point of zero charge (PZC) and isoelectric point (IEP) for all the adsorbents. It is also obvious that the highest maximum noncompetitive lead(II) and copper(II) adsorption capacities of 1.23 and 0.87 mmol/g, respectively, were observed for anaerobic granules (Hawari and Mulligan, 2006). However, this adsorbent is technically difficult. It is also obvious that very few studies for competitive adsorption of lead(II) and copper(II) onto adsorbents were performed. The highest maximum competitive lead(II) and copper(II) adsorption capacities of 0.18 and 0.329 mmol/g, respectively, were observed for bacterial strain, (Tunali et al., 2006) and dried biomass, P. putida (Uslu and Tanyol, 2006), respectively. However, the adsorption capacities are very low even though the bacterial strain and biomass are economically favourable. Therefore, it is necessary to evaluate adsorbent performance in multicomponent solution with modified carbon fibre since the presence of only one metal ion is a rare situation either in nature or in wastewaters. It is also necessary to do detailed characterisation of the modified activated carbon fibre so as to determine the physical and chemical composition of the modified activated carbon fibre, since these properties define the most efficient working conditions of adsorbents and also provides the factors for the proposal of the adsorption mechanisms. These are some of the objectives of this research.

2.5. ADSORPTION OF CHROMIUM(VI)

Bautista-Toledo et al. (1994) studied the adsorption of Cr(III) and Cr(VI) on three activated carbons from aqueous solutions. The three activated carbons used were, commercial activated carbon (M), HNO₃ oxidised commercial activated carbon (MO) and some of the HNO₃ oxidised commercial activated carbon (MO) heated at 837 K in N₂ flow for 2 h to eliminate some of the oxygen groups on the surface of the MO (MO-873). They observed an oxygen content of 16%, 38.9% and 19.4% on M, MO and MO-873, respectively. FTIR analysis detected the presence of carboxylic and hydroxyl functional groups on MO, while the presence of hydroxyl and quinone functional groups were detected on M and MO-873, respectively. They observed maximum Cr(III) adsorption capacities of 0.052, 0.49 and 0.0039 mmol/g for M, MO and MO-873, respectively. The highest Cr(III) adsorption capacity for MO was
attributed to the formation of carboxylic acid groups on the surface of MO during HNO\textsubscript{3} oxidation, while the lowest Cr(III) adsorption capacity for MO-873 was attributed to the elimination of most of the carboxylic acid groups on the surface of MO-873 by thermal treatment. They also observed maximum Cr(VI) adsorption capacities of 0.133, 0.298 and 0.035 mmol/g for M, MO and MO-873, respectively. The higher Cr(VI) adsorption capacity for M when compared to Cr(III) adsorption capacity for M was attributed to the adsorption of Cr(VI) anions by protonation of the hydroxyl groups on the surface of M. However, the adsorption of Cr(VI) onto MO was attributed to reduction of Cr(VI) to Cr(III) by the hydroxyl functional groups on the surface of MO. The lowest Cr(VI) adsorption capacity for MO-873 was attributed to the elimination of most of the carboxylic and hydroxyl groups on the surface of the MO-873 by thermal treatment, therefore, reducing the adsorption of Cr(VI) anions by protonation of the surface functional groups on MO-873.

Aggarwal et al. (1999) studied the adsorption isotherms of Cr(III) and Cr(VI) ions on activated carbon fibre (ACF-307) and nitric acid oxidised ACF-307. They also studied the adsorption isotherms of Cr(III) and Cr(VI) ions on activated carbon fibre obtained by degassing the nitric acid oxidised ACF-307 at 1223 K. They observed maximum Cr(III) adsorption capacities of 0.07, 0.372 and 0.018 mmol/g for ACF-307, nitric acid oxidised ACF-307 and degassed ACF-307, respectively. The highest Cr(III) adsorption capacity for nitric acid oxidised ACF-307 was attributed to the formation of carboxylic acid groups on the surface of ACF-307 by nitric acid oxidation, while the lowest Cr(III) adsorption capacity for degassed ACF-307 was attributed to the elimination of the acidic functional groups on the surface of ACF-307 by thermal treatment, making it more basic. However, they observed maximum Cr(VI) adsorption capacities of 0.49, 0.28 and 1.26 mmol/g for ACF-307, nitric acid oxidised ACF-307 and degassed ACF-307, respectively. The lowest Cr(VI) adsorption capacity for oxidised ACF-307, was attributed to the negative charges on its surface due to dissociation of carboxylic acid groups. They concluded that adsorption of Cr(VI) onto oxidised ACF-307 was by reduction of Cr(VI) to Cr(III) by quinone groups and then adsorption of Cr(III) onto oxidised ACF-307. The highest Cr(VI) adsorption capacity for degassed ACF-307 was attributed to the elimination of almost all the acidic groups by degassing at very high temperature of 1223 K. Therefore, the dominating groups on the degassed ACF-307 were quinone groups that became positively charged due to
protonation of the functional groups on ACF-307 and so increased the adsorption of Cr(VI) ions that are in anionic forms.

Park et al. (1999b) used 35 wt% sodium hydroxide as electrolyte for electrochemical oxidation of phenol-based activated carbon fibre (ACF) at 298 K and current density of 450 mA/m². They studied the adsorption of Cr(VI) onto the electrochemically oxidised ACF and unoxidised ACF at solution pH 3 and 298 K. They observed sodium capacities of 0.325 and 0.812 mmol/g for unoxidised ACF and electrochemically oxidised ACF, respectively. From FTIR analysis, they observed an increase in hydroxyl and ether groups on the electrochemically oxidised ACF. This is likely to be due to the sodium hydroxide used as the electrolyte for oxidation. They observed an increase in maximum adsorption capacity of Cr(VI) from 0.293 mmol/g for unoxidised ACF to 0.372 mmol/g for electrochemically oxidised ACF. This was attributed to the increase in hydroxyl and ether functional groups on the ACF by electrochemical oxidation in basic sodium hydroxide. Also, at solution pH 3, at which the batch sorption experiments were performed, the hydroxyl and ether functional groups are highly protonated and Cr(VI) exists as HCrO₄⁻, so an increase in hydroxyl and ether functional groups enhanced Cr(VI) adsorption. They, therefore, concluded that the reactions between HCrO₄⁻ and oxygen functional groups on the ACF are as follows:

\[ C_{x}O + H_{2}O + HCrO_{4}^{-} \leftrightarrow C_{x}OH_{2}Cr^{+} + 2OH^{-} \] (2.4)

\[ C_{x}O_{2} + H_{2}O + HCrO_{4}^{-} \leftrightarrow C_{x}O_{2}HO_{2}Cr^{+} + 2OH^{-} \] (2.5)

Selomulya et al. (1999) investigated the removal of Cr(VI) from aqueous solutions onto coconut shell-based, wood-based and dust coal-based activated carbons at different solution pH values. The point of zero charge (PZC) values were observed at pH values of 1.7, 7.6 and 9.1 for wood-based activated carbon, dust coal-based activated carbon and coconut shell-based activated carbon, respectively, indicating that dust coal-based activated carbon and coconut shell-based activated carbon are basic and wood-based activated carbon is acidic. They observed Cr(VI) maximum adsorption capacities of 1.69, 1.96 and 2.06 mmol/g for the wood-based activated carbon, the dust coal-based activated carbon and the coconut shell-based activated carbon, respectively at solution pH 2. The adsorption of Cr(VI) onto wood-based activated carbon with the lowest PZC was attributed to reduction of Cr(VI) to Cr(III).
by hydroxyl groups on the wood-based activated carbon and then adsorption of Cr(III) onto the negatively charged surface of the wood-based activated carbon. However, the adsorption of Cr(VI) onto coconut shell-based activated carbon and dust coal-based activated carbon were attributed to the surfaces of the activated carbons being positively charged at solution pH 2, which is below the PZC values of the activated carbons and so were able to adsorb Cr(VI) ions in anionic forms. They also observed a decrease in Cr(VI) adsorption with increase in solution pH. For the wood-based activated carbon, this was attributed to a decrease in the reduction of Cr(VI) to Cr(III) with an increase in solution pH. For the coconut shell-based activated carbon and dust shell-based activated carbon it was attributed to a decrease in the surface positive charges with increase in solution pH.

Gupta et al. (2001) conducted batch experiments to determine Cr(VI) adsorption properties of green algae spirogyria species from aqueous solutions at different solution pH values but at constant temperature 291 K. Maximum Cr(VI) adsorption capacity of 0.283 mmol/g was observed for the green algae at solution pH 2. They also observed that Cr(VI) adsorption decreased with an increase in solution pH. This was attributed to negatively charged chromium species (chromate/dichromate) being electrostatically attracted to the positively charged functional groups produced by protonation of the functional groups, which is likely to be hydroxyl, on the surface of the algae at low solution pH values. As the solution pH increases deprotonation made the positive charges decrease and dissociation of the functional groups made the surface the green algae to be negatively charged and repulsed the anions, thereby reducing Cr(VI) adsorption.

Guo et al. (2002) studied the adsorption of hexavalent chromium from aqueous solutions by rice husk-based activated carbon (RHC) at different solution pH values and solution temperatures. They observed maximum Cr(VI) adsorption capacity of 0.885 mmol/g for the RHC at solution pH 5 and 333 K. They also observed an increase in Cr(VI) adsorption with increase in solution temperature. This was attributed to an increase in intraparticle diffusion rate of Cr(VI) ions into the pores of RHC at higher temperature as diffusion is an endothermic process. They also observed a decrease in Cr(VI) adsorption with an increase in solution pH. This was attributed to an increase in negative charges on the RHC surface with an increase in solution pH,
thus the electrostatic force of attraction between RHC surface and Cr(VI) decreased, thereby reducing Cr(VI) adsorption.

Selvaraj et al. (2003) studied the removal of Cr(VI) from aqueous solutions by distillery sludge at different solution pH values but at constant temperature 298 K. The PZC was found to be at pH 5.9 for the distillery sludge. Maximum Cr(VI) adsorption capacity of 0.12 mmol/g was observed for the distillery sludge at solution pH 3. They also observed a decrease in Cr(VI) adsorption with an increase in solution pH for the distillery sludge. This was attributed to the surface of the distillery sludge being protonated at low solution pH (that is at solution pH below the PZC) and attracted the anionic species of Cr(VI). As the solution pH increased there was deprotonation on the surface of the distillery sludge that reduced the electrostatic attraction between the Cr(VI) species and the distillery sludge surface, with a consequent decrease in adsorption.

Saha et al. (2004) investigated the removal of Cr(VI) from aqueous solutions by Amberlite XAD-7 resin impregnated with Aliquat 336 (SIR) at different impregnated ratios, solution pH 6 and 298 K. They observed maximum Cr(VI) sorption capacity of 0.97 mmol/g for SIR prepared at 2 g Aliquat 336/g polymer. They also observed that the maximum Cr(VI) sorption capacity increased with increase in impregnation ratio of the SIR. The Cr(VI) sorption onto SIR was attributed to the presence of chloride ion on the structure of SIR that could potentially be exchanged for a bichromate ion (HCrO₄⁻), while the chromate ion (CrO₄²⁻) could potentially be exchanged for two chloride ions.

Karthikeyan et al. (2005) investigated the adsorption of Cr(VI) onto Hevea Brasilinesis (Rubber wood) sawdust activated carbon from aqueous solutions at different solution pH values and temperatures. They observed maximum Cr(VI) sorption capacity of 1.23 mmol/g for the sawdust activated carbon at solution pH 2 and 323 K. They also observed a decrease in Cr(VI) adsorption with increase in solution pH. This was attributed to protonation of the surface of the sawdust activated carbon that increased the H⁺ ions on the sawdust activated carbon surface at acidic solution pH that resulted in strong electrostatic attraction between the positively charged sawdust activated carbon surface and the negatively charged chromate ions,
therefore, enhancing the adsorption of Cr(VI). Finally, they observed an increase in Cr(VI) adsorption with increase in solution temperature. This was attributed to increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the sawdust activated carbon at higher temperatures and the adsorption reaction being endothermic.

Shawabkeh (2006) studied the removal of chromium(VI) ions from aqueous solutions by activated granular rocks (carbo-aluminosilicate) at different solution pH values but at constant temperature 295 K. The PZC for activated carbo-aluminosilicate was found to be at pH 7.9. FTIR analysis detected the presence of hydroxyl and ether functional groups on the surface of the activated carbo-aluminosilicate. Maximum chromium(VI) adsorption capacity of 1.58 mmol/g was observed for activated carbo-aluminosilicate at solution pH 4. Decrease in chromium(VI) adsorption with increase in solution pH was also observed. This was attributed to protonation of the hydroxyl and ether functional groups on the surface of activated carbo-aluminosilicate at solution pH below the PZC, making the surface electropositive and attracted most of the chromium species in the form of $\text{HCrO}_4^-$ while at higher solution pH values, deprotonation occurred and dissociation of hydroxyl functional groups made the surface of the activated carbo-aluminosilicate to become electronegative and repulsed the $\text{CrO}_4^{2-}$ species.

Basha et al. (2007) studied the sorption of hexavalent chromium from aqueous solutions by unmodified brown algae (RB), chemically modified brown algae by cross-linking with epichlorohydrin (CB1) and brown algae oxidised by potassium permanganate (CB2) at solution pH 3 and 298 K. BET surface areas of 0.43, 0.51 and 0.37 m$^2$/g were obtained for RB, CB1 and CB2, respectively. FTIR analysis detected the presence of hydroxyl functional groups on RB, CB1 and CB2. However, the presence of carboxylic functional groups and ether functional groups were also detected on CB2 and CB1, respectively. The presence of carboxylic functional groups that was observed on CB2 was attributed to oxidation of some of the hydroxyl functional groups by potassium permanganate while the presence of ether functional groups that was observed on CB1 was attributed to cross-linking of hydroxyl functional groups with epichlorohydrin. They observed maximum chromium(VI) adsorption capacities of 0.342, 0.387 and 0.465 mmol/g for RB, CB2 and CB1, respectively. The highest chromium(VI) adsorption capacity for CB1 was attributed to
the presence of ether functional groups on CB1 that are more basic than carboxylic and hydroxyl functional groups on CB2 and RB, respectively.

El-Sikaily et al. (2007) investigated the removal of hexavalent chromium from aqueous solutions by dried green alga (Ulva Lactuca) and green alga-based activated carbon at different solution pH values but at constant temperature 298 K. They observed maximum Cr(VI) adsorption capacities of 0.204 and 2.16 mmol/g for dried green alga and green alga-based activated carbon, respectively, at solution pH 1. The higher maximum Cr(VI) adsorption capacity for green alga-based activated carbon was attributed to the net work pore structure generated during activation process that increased the specific surface area of the green alga-based activated carbon. However, a decrease in adsorption of Cr(VI) with increase in solution pH was observed for the dried green alga and green alga-based activated carbon. This was attributed to binding of the negatively charged chromium species through electrostatic attraction to positively charged functional groups on the surface of the sorbent cell wall at low solution pH. As the solution pH increased the functional groups became negatively charged and repulsed the negatively charged chromium species, thereby, reducing Cr(VI) adsorption.

Garg et al. (2007) studied the adsorption of Cr(VI) from aqueous solutions onto different agricultural wastes: sugarcane bagasse (SCB), maize corncob (MCC) and Jatropha oil cake (JOC) at different solution pH values. FTIR analysis detected the presence of hydroxyl and carbonyl functional groups on SCB, MCC and JOC. They observed maximum Cr(VI) adsorption capacities of 0.11, 0.058 and 0.226 mmol/g for SCB, MCC and JOC, respectively, at solution pH 2 and 298 K. They also observed a decrease in Cr(VI) adsorption with increase in solution pH for SCB, MCC and JOC. This was attributed to protonation of the hydroxyl and carbonyl functional groups on the surfaces of SCB, MCC and JOC at low solution pH values that resulted in electrostatic attraction between the positively charged SCB, MCC and JOC surfaces and chromate ions. At high solution pH values, deprotonation of the hydroxyl and carbonyl functional groups on SCB, MCC and JOC occurred and there was dual competition of CrO$_4^{2-}$ and OH$^-$ anions to be adsorbed on the SCB, MCC and JOC surfaces, therefore, reducing the Cr(VI) adsorption.
Han et al. (2007) investigated the ability of a microalgal isolate, Chlorella miniata to remove Cr(VI) from aqueous solutions at different solution pH values but at constant temperature 298 K. FTIR analysis detected the presence of amino and hydroxyl functional groups on the Chlorella miniata. They observed maximum Cr(VI) adsorption capacity of 0.673 mmol/g for the Chlorella miniata at solution pH 3. They also observed a decrease in Cr(VI) adsorption with an increase in solution pH for Chlorella miniata. This was attributed to easier biosorption of Cr(VI) onto protonated Chlorella miniata at low solution pH values. Reduction of Cr(VI) to Cr(III) was also observed during the adsorption experiments. They concluded that adsorption onto Chlorella miniata was due to protonation of amino functional groups on the Chlorella miniata while reduction of Cr(VI) to Cr(III) was due to the presence of hydroxyl functional groups on the Chlorella miniata.

Misaelides et al. (2008) investigated Cr(VI) adsorption from aqueous solutions by polyhexamethylene-guanidine-modified natural zeolitic materials obtained from Metaxades (PHMG-MTX) and Tedzami (PHMG-TZ) at different solution pH values but at constant temperature 298 K. They observed maximum Cr(VI) adsorption capacities of 0.055 and 0.04 mmol/g for PHMG-MTX and PHMG-TZ, respectively at solution pH 3. They also observed a decrease in Cr(VI) adsorption with increase in solution pH for PHMG-MTX and PHMG-TZ.

Mor et al. (2007) investigated the removal of Cr(VI) ions from aqueous solutions by activated alumina and activated charcoal at different solution pH values but at constant temperature 313 K. The PZC for activated charcoal was found to be at pH 5.3. They observed maximum Cr(VI) adsorption capacities of 0.143 and 0.248 mmol/g for activated alumina and activated charcoal, respectively, at solution pH 2. They also observed a decrease in Cr(VI) adsorption with an increase in solution pH for activated alumina and activated charcoal. This was attributed to the surface of activated alumina and C₃O and C₅O₂ functional groups on activated charcoal being highly protonated at low solution pH and favoured the adsorption of Cr(VI) in anionic form. With increase in solution pH, the degree of protonation of the surfaces of activated alumina and the functional groups on activated charcoal reduced and hence adsorption of Cr(VI) decreased.
Natale et al. (2007) studied the adsorption of chromium(VI) onto coal-based granular activated carbon (GAC) and char of South African coal (CSAC) from aqueous solutions at different solution pH values but at constant temperature 293 K. The PZC for CSAC and GAC were at pH values of 8.85 and 8, respectively, showing that both carbons are basic. The anion exchange capacity (chloride capacity) for GAC was 2.44 mmol/g. They observed reduction of Cr(VI) to Cr(III). This was attributed to the presence of hydroxyl functional groups on CSAC and GAC that reduced some Cr(VI) ions to Cr(III). They also observed maximum Cr(VI) adsorption capacities of 0.0058 and 0.135 mmol/g for CSAC and GAC, respectively, at solution pH 7.5 from Cr(VI) solution of 50 mg/L initial concentration. They also observed a decrease in Cr(VI) adsorption with an increase in solution pH for CSAC and GAC. This was attributed to protonation of active sites of CSAC and GAC, which are lactone and phenol functional groups, at low solution pH values that enhanced the adsorption of anions and competition of Cr(VI) ions with OH⁻ ions at high solution pH values that reduced the adsorption of Cr(VI) ions.

Uysal and Ar (2007) studied Cr(VI) removal efficiency of pine sawdust from aqueous solutions at different solution pH values and temperatures. They observed maximum Cr(VI) adsorption capacity of 0.25 mmol/g for the pine sawdust at solution pH 2 and 313 K. They also observed a decrease in Cr(VI) adsorption with increase in solution pH for the pine sawdust. This was attributed to active sites on the pine sawdust being positively charged at low solution pH values, therefore, negatively charged Cr(VI) ions adsorption increased. Finally, they observed an increase in Cr(VI) adsorption with an increase in solution temperature for the pine sawdust. This was attributed to adsorption of Cr(VI) onto the pine sawdust being endothermic.

2.5.1. Conclusions

Table 2.4 shows the comparison of experimental conditions, maximum chromium(VI) adsorption capacities of adsorbents and surface properties of the different adsorbents shown in the literature review in this section. It is obvious that very few adsorbents were characterised to explain the mechanism of adsorption. There was no determination of isoelectric point (IEP) for any adsorbent in this section and anion exchange capacity (chloride capacity) was determined for only one adsorbent. It is also obvious that the highest maximum chromium(VI) adsorption capacity of 2.16 mmol/g...
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>PZC</th>
<th>Functional group</th>
<th>Chloride capacity (mmol/g)</th>
<th>pH</th>
<th>Temp. (K)</th>
<th>Maximum adsorption capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green algae</td>
<td>-</td>
<td>Hydroxyl</td>
<td>-</td>
<td>2</td>
<td>291</td>
<td>0.283</td>
<td>Gupta et al. (2001)</td>
</tr>
<tr>
<td>Rice husk-based GAC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>333</td>
<td>0.885</td>
<td>Guo et al. (2002)</td>
</tr>
<tr>
<td>Distillery sludge</td>
<td>pH 5.9</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>298</td>
<td>0.12</td>
<td>Selvaraj et al. (2003)</td>
</tr>
<tr>
<td>Amberlite XAD-7 resin</td>
<td>-</td>
<td>Chloride</td>
<td>-</td>
<td>6</td>
<td>298</td>
<td>0.97</td>
<td>Saha et al. (2004)</td>
</tr>
<tr>
<td>Sawdust-based GAC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>323</td>
<td>1.23</td>
<td>Karthikeyan et al. (2005)</td>
</tr>
<tr>
<td>Activated carbo-aluminosilicate</td>
<td>pH 7.9</td>
<td>Hydroxyl, Ether</td>
<td>-</td>
<td>4</td>
<td>295</td>
<td>1.58</td>
<td>Shawabkeh et al. (2006)</td>
</tr>
<tr>
<td>Brown algae</td>
<td>-</td>
<td>Hydroxyl, Ether</td>
<td>-</td>
<td>3</td>
<td>298</td>
<td>0.465</td>
<td>Basha et al. (2007)</td>
</tr>
<tr>
<td>Green alga-based GAC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>298</td>
<td>2.16</td>
<td>El-Sikaily et al. (2007)</td>
</tr>
<tr>
<td>Jatropha oil cake</td>
<td>-</td>
<td>Carbonyl, Hydroxyl</td>
<td>-</td>
<td>2</td>
<td>298</td>
<td>0.226</td>
<td>Garg et al. (2007)</td>
</tr>
<tr>
<td>Microalgal isolate</td>
<td>-</td>
<td>Amino, Hydroxyl</td>
<td>-</td>
<td>3</td>
<td>298</td>
<td>0.673</td>
<td>Han et al. (2007)</td>
</tr>
<tr>
<td>Natural zeolitic materials</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>298</td>
<td>0.055</td>
<td>Misaelides et al. (2008)</td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>pH 5.3</td>
<td>C₅O, C₄O₂</td>
<td>-</td>
<td>2</td>
<td>313</td>
<td>0.248</td>
<td>Mor et al. (2007)</td>
</tr>
<tr>
<td>Coal-based GAC</td>
<td>pH 8</td>
<td>Lactone, Phenol</td>
<td>2.44</td>
<td>7.5</td>
<td>293</td>
<td>0.135</td>
<td>Natale et al. (2007)</td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>313</td>
<td>0.25</td>
<td>Uysal and Ar (2007)</td>
</tr>
</tbody>
</table>

Table 2.4. Comparison of experimental conditions, adsorption capacities of adsorbents for chromium(VI) and surface properties of adsorbents.

was observed for green alga-based GAC (El-Sikaily et al., 2007). However, though this adsorbent is economically favourable, its adsorption process is technically difficult. The maximum chromium(VI) adsorption capacity for the unmodified activated carbon fibre that is economically favourable, with a technically easy process was 0.49 mmol/g (Aggarwal et al., 1999), which is low. Therefore, it is necessary to modify activated carbon fibre to enhance its chromium(VI) adsorption capacity. It is also necessary to do detailed characterisation of the modified activated carbon fibre so as to determine the physical and chemical composition of the modified activated
carbon fibre, since these properties define the most efficient working conditions of adsorbents and also provides the factors for the proposal of the adsorption mechanisms. These are some of the objectives of this research.

2.6. ACTIVATED CARBON FIBRES
Activated carbon is defined as a processed carbon material with a highly developed porous structure and a large internal surface area (Jankowska et al., 1991). It consists principally of carbon (87-97%), but also contains such elements as hydrogen, oxygen, sulphur and nitrogen, as well as various compounds either originating from the precursor used in its production or generated during its manufacture.

Activated carbons are versatile adsorbents mainly due to their large surface area and surface reactivity. Activated carbons also possess favourable pore sizes which make the internal surface accessible and enhance the adsorption rate and mechanical strength (Bansal et al., 1988). The strong market position of activated carbons is related to their unique properties and lower cost compared to those of other competitive adsorbents. Through the choice of precursor, the method of activation and control of processing conditions, the adsorptive properties of activated carbons can be designed for diverse applications. Due to wide ranges of applications and low costs of activated carbons compared with possible competitive adsorbents, several new forms and shapes of activated carbons with special characteristics have been produced. Activated carbon now exists in granular (GAC), powder (PAC) and fibre forms. The carbon fibres are produced in the form of cloth (ACC) and felt (ACF).

2.6.1. Precursors of Carbon Fibre
Activated carbon can be produced from any material that has a high carbon content and low inorganic content. The precursors for activated carbons are mainly animal bones, fruit stones, nutshells, wood, coconut shell, coal, peat, lignin, pitch and wastes from petroleum and lubricant processing. Only six of all these precursors have been used on an industrial scale and in order of importance. The precursors used for production of activated carbon on an industrial scale are wood, bones, coal, lignin, coconut shell and peat. This is because they are currently the only economically viable precursors (Bansal et al., 1988; Noll et al., 1992). While considering the type of
precursor for the production of high quality activated carbon, the following factors must be considered:-

- Presence of low quantity of inorganics in the precursor.
- Volume and cost of precursor.
- Workability of the precursor.
- Storage of precursor.

Commercial activated carbon fibres are prepared from precursors, such as pitches, polyacrylonitrile (PAN), rayon, and resins (Sauder et al., 2004; Chiang et al., 2007). Though the choice of precursor depends on its availability, cost and purity, the manufacturing process and intended application of the product are very important. Petroleum pitch is one of the current precursors being used to produce carbon fibres even though the production started with polyvinyl chloride (PVC) pitch in Japan (Otani, 1965). The production of carbon fibres from petroleum pitch was faster than the production from PAN and rayon. However, the fibres are not as easy to handle as the PAN and rayon ones, since they are harder and more brittle. Moreover, they have poor compatibility with some matrix materials, high specific gravity and are produced in relatively lower volumes than PAN fibres.

Non-heterocyclic aromatic precursors are phenolic polymers, phenol formaldehyde resin, polyacenaphthalene, polyacrylether, certain polyamides and polyphenylene. They produce good yield of fibres and have easy cyclisation into graphite structure and easy elimination of non carbon atoms. Carbon fibres produced from coal have circular cross section and uniform diameter with smooth external surface and so are isotropic and are very poor in strength (Jorro et al. 1976). PAN is recognised as the most important precursor due to its high degree of molecular orientation, high melting point and large carbon fibre production (Taylor and Roy, 1994). PAN based carbon fibres dominate world consumption and represents nearly 90% of world wide sales (Bhattacharyya and Cheng, 1987). PAN’s advantage over other precursors lies in its unique properties. It does not melt prior to pyrolytic decomposition so the fibres produced have higher strength than those from other precursors. Viscose rayon based carbon fibres are very similar in terms of structure and properties to PAN based carbon fibres, although they have irregular cross-sectional shapes (Langley, 1973). However,
due to their lower cost compared to the PAN based ones, the viscose rayon based activated carbon fibres are preferred.

2.6.2. Production of Viscose Rayon Based Carbon Fibres (Wilks, 2001)
The starting material for the production of viscose rayon filaments is pulp, mainly produced from wood, linters and plants. For textile filaments the preferred precursor is bleached wood pulp with an α-cellulose content of 89-93%, it is normally in the form of sheets, rolls or crumbs. Since pulp fibres in their natural state are too short to be spun into yarns, they are dissolved and regenerated in filament forms. The spinnable solution is prepared by various steps: alkalisation, shredding, preripening, xanthation, viscose production and viscose maturing. The spinnable solution is then spun into filaments at the viscose spinning step, after the cellulose is regenerated from the viscose.

2.6.2.1. Alkalisation
The production of spinnable solution of pulp starts with the addition of 18-22% sodium hydroxide to the pulp at 290-318 K. The pulp absorbs water and sodium hydroxide, releases heat and loosens the cellulose lattice by swelling. This results in the formation of alkaline cellulose. Alkaline treatment is, apart from opening the molecular structure of the cellulose, aimed at converting as much cellulose as possible to alkaline cellulose:

\[
(C_6H_{10}O_5)_n + n\text{NaOH} \rightarrow (C_6H_9O_4\text{ONa})_n + n\text{H}_2\text{O}
\]  

(2.6)

The swollen alkaline cellulose mass is pressed to a weight equivalent of 2.5-3 times the original pulp weight to obtain an accurate ratio of alkali to cellulose. Alkaline cellulose of about 30% is obtained by pressing. The composition and condition of the alkaline cellulose depends on the temperature and composition of the sodium hydroxide.

2.6.2.2. Shredding
If the alkalisation started with pulp sheets or rolls, shredding into tiny pieces becomes necessary. The pressed alkaline cellulose is shredded mechanically to yield finely divided, fluffy particles called crumbs. This step provides increased surface area of the alkaline cellulose, thereby increasing its ability to react in subsequent steps.
2.6.2.3. Preripening

The degree of polymerisation (DP) of the alkaline cellulose crumbs is much higher than the DP desired for fibre formation. Therefore, the DP must be reduced to about 300 and 450 for regular and high-tenacity fibres, respectively. The alkaline cellulose is depolymerised by preripening (i.e. ageing) to the desired DP. The method for depolymerisation is to age the alkaline cellulose under controlled time and temperature (293-318 K). It is very important to avoid drying of the crumbs which will result in carbonate formation, particularly at high temperatures. To avoid drying, the ageing is performed in closed containers and the crumbs are constantly agitated. Depolymerisation is an exothermic process and depends on: time, temperature, the nature of the pulp and the composition of the alkaline cellulose (i.e. sodium hydroxide, water, hemicellulose and heavy metals). In this step the average molecular weight of the original pulp is reduced by a factor of 2-3. Reduction of the alkaline cellulose is done to get a viscose solution of desired viscosity and cellulose concentration.

2.6.2.4. Xanthation

Xanthation is the reaction of the depolymerised alkaline cellulose crumbs with carbon disulphide under controlled temperature (293-303 K) to form cellulose xanthate.

\[(C_6H_7O_4ONa)_n + nCS_2 \rightarrow (C_6H_7O_4S-SC-SCNa)_n\]  

Depending on the type of fibre and alkaline process used, between 150 kg and 400 kg of carbon disulphide is needed to produce 1000 kg of fibre. The carbon disulphide used is normally distilled at 320 K up to 98.5%, it should contain less than 5 ppm of hydrogen sulphide and be free from carbonyl sulphide and acid. The non-volatile residue content of the carbon disulphide should be less than 0.01% and the density should be 1.27 g/cm³. The depolymerised alkaline cellulose crumbs are put in a kneader. The required amount of carbon disulphide (15-55%) is added to the kneader. The temperature in the kneader is maintained at a constant temperature (293-303 K). The reaction of alkaline cellulose crumbs with carbon disulphide is very rapid and begins on the outer surface of the crumbs and proceeds into the crystalline structure. Xanthation speed depends on: temperature, the condition and composition of the alkaline cellulose, the amount of carbon disulphide added and the pressure of the carbon disulphide vapours formed during the process.
The alkaline cellulose crumbs that have been adjusted to the desired DP show more favourable behaviour during xanthation than the untreated alkaline cellulose crumbs. A much lesser amount of carbon disulphide is required for reaction and the reaction time is reduced for the alkaline cellulose crumbs with adjusted DP. In addition the spinning properties of the viscose obtained from them are better. Xanthation of alkaline cellulose is accompanied by several side reactions. These side reactions are responsible for the characteristic orange colour of the cellulose xanthate and the viscose made from it.

2.6.2.5. Viscose production
The cellulose xanthate crumbs produced are dissolved in sodium hydroxide either in batches or continuously. The process of dissolving is accelerated by stirring and tituration. The large xanthate substituents on the cellulose force the chains apart, reducing the interchain hydrogen bonds and allowing water molecules to solvate and separate the chains, leading to solution of the otherwise insoluble cellulose. However, due to the blocks of un-xanthated cellulose in the crystalline regions, the cellulose xanthate is not completely soluble at this stage. Due to the high viscosity the cellulose xanthate solution is called viscose. The viscosity varies from 3.5 Pa·s to over 10 Pa·s and depends on: the concentration of the cellulose xanthate, the degree of polymerisation of the cellulose and the degree of dissolution. The degree of dissolution depends on: dispersion, degree of substitution of xanthate substituents and their distribution and on the purity and concentration of the dissolving sodium hydroxide. The viscose contains 7-12% cellulose and 5-8% caustic compounds as well as various sulphur compounds and carbonates.

2.6.2.6. Viscose maturing
Maturing is another delay period, during which the viscose is allowed to mature for a period of time (50-80 h) at 291 K. The two important processes that occur during maturing are redistribution and loss of xanthate groups. The reversible xanthation reaction allows some of the xanthate groups to revert to hydroxyl groups with the release of carbon disulphide. The released carbon disulphide can escape or react with other hydroxyl groups on other portions of the cellulose chain. This makes the ordered or crystalline regions to gradually break down and more solution of the cellulose
xanthate is achieved. The carbon disulphide that is lost reduces the solubility of the cellulose xanthate and facilitates regeneration of the cellulose.

\[ (C_6H_9O_2O-SC-SNa)_n + nH_2O \rightarrow (C_6H_{10}O_3)_n + nCS_2 + nNaOH \]  \hspace{1cm} (2.8)

The decomposition speed of the cellulose xanthate depends on temperature and the concentration of the sodium hydroxide, cellulose and carbon disulphide from which it was produced.

Maturing is accompanied by filtration and degassing. The viscose is filtered to remove undissolved materials that might disrupt the spinning process or cause defects in the rayon filament. The viscose is degassed prior to extrusion to remove bubbles of air entrapped in it which will otherwise cause voids or weak spots, in the fine rayon filaments.

2.6.2.7. Viscose spinning

Production of viscose rayon filament, i.e., regeneration of the cellulose from viscose with the help of spin bath and treatment outside the spin bath, includes coagulation of the viscose, deswelling of the filaments, regeneration of the cellulose, neutralisation and stretching of the yarn.

The matured viscose is injected by precision pumps through fabric filters inside the spinneret support and then through the holes of the spinneret. The viscose emerges from the spinneret and enters the spin bath. The composition of the spin bath is adjusted to the desired conditions, depending on the composition of the viscose and the type of fibre to be spun. In general, a spin bath will contain 7-12% sulphuric acid, 12-24% sodium sulphate and 0.5-3% zinc sulphate. Sulphuric acid acidifies the cellulose xanthate, sodium sulphate imparts a high salt content to the bath which is useful in rapid coagulation of viscose and zinc sulphate reacts with the cellulose xanthate to cross link the cellulose molecules. Once the cellulose xanthate is neutralised and acidified, rapid coagulation of the rayon filaments occurs which is followed by simultaneous stretching and decomposition of cellulose xanthate to regenerated cellulose. Stretching and decomposition are vital for getting the desired tenacity and other properties of rayon. Slow regeneration and stretching will lead to
greater areas of crystallinity within the fibre as it is done with high-tenacity rayon. The dilute sulphuric acid decomposes the cellulose xanthate and generates cellulose by the process of wet spinning. Sodium and zinc sulphates control the rate of decomposition of the cellulose xanthate to cellulose and fibre formation.

\[(\text{C}_6\text{H}_5\text{O}_4\text{O} - \text{SC} - \text{SNa})_n + \left(n/2\right)\text{H}_2\text{SO}_4 \rightarrow \left(\text{C}_6\text{H}_{11}\text{O}_5\right)_n + n\text{CS}_2 + \left(n/2\right)\text{Na}_2\text{SO}_4 \quad (2.9)\]

The rayon filaments are stretched while the cellulose chains are still relatively mobile. This causes the chains to stretch out and orient along the fibre axis. As the chains become more parallel, interchain hydrogen bonds form, giving the filaments the properties necessary for use as textile fibres. The freshly regenerated rayon contains many salts and other water soluble impurities that are removed by washing. Finally, the group of filaments i.e. tow is passed through a rotary cutter to provide fibre which can be processed into cloth or felt.

2.6.3. Carbonisation

Activated carbon is obtained by the process of carbonisation followed by activation of the initial carbonaceous material which is viscose rayon based cloth in this study. Carbonisation is very important since it is during carbonisation that the initial pore structure is formed.

Oxidation with oxygen or air at low temperatures is an accepted process before carbonisation of carbon fibres from PAN or pitch, for fibre stabilisation. In the case of viscose rayon based cloth oxygen induces a dehydrogenation reaction of the precursor by oxidative dehydration, which leads to carbonaceous structures with enhanced thermal stability and an increase of 6% in carbonisation yield (Pastor et al., 1999). The stabilisation is conducted by oxidising the cloth in the air at a temperature range of 473-573 K using a heating rate of 278 K min\(^{-1}\). Once the required temperature is achieved, the cloth is further heated for 90 min at the required temperature. Oxidation of cellulose, i.e. the viscose rayon based cloth, converts primary hydroxyl groups to carbonyl groups, thus avoiding formation of levoglucosan and so enhances carbonisation yield. Carboxylic groups are also produced during the oxidation process. These carboxylic groups lead to intermediate reticulation by formation of hydrogen bonds therefore, making the cloth more stable for further heat treatment.
After stabilisation the viscose rayon based cloth is carbonised. The carbonisation of organic precursor is the thermal decomposition in an inert atmosphere when mainly oxygen and hydrogen are eliminated (Pastor et al., 1999). Carbonisations are complex reaction systems involving elimination of volatile products and structural reorganisation within the remaining solid phase. Generally, carbonisation is conducted at 873-1073 K under a flow of nitrogen (Jankowska et al., 1991). The cloth is heated up to 1070 K using specific heating rate in the range of 273-278 K min\(^{-1}\) and a flow of nitrogen at a flow rate of 100 ml min\(^{-1}\). Once the required temperature is achieved, the cloth is further heated for 60-120 min at the required temperature.

Pastor et al. (1999) carbonised viscose rayon based carbon cloth and observed initial elimination of 12 wt% of physically held water at temperature less than 973 K, with some rearrangements of structure within the cellulose. Later, structural water was eliminated by the combination of hydrogen and hydroxyl ions in the cellulose lattice. Between 513 K and 673 K, splitting of C-O and C-C bonds occurred with the production of tars, water, carbon monoxide and carbon dioxide resulting to a carbonisation yield of 18% and 24% of the mass of the original carbon cloth, for carbon cloths without stabilisation and with stabilisation, respectively.

The elimination of volatile products and structural rearrangements during carbonisation forms the initial pore structure which depends principally on the physical properties of the precursor and the rate of heating. Slower heating rates increase the micropore volume and produce micropores with narrower entrances. This is due to more cellulose decomposition that occurs in the slower and more controlled heating rate. If the final temperature for carbonisation is low, impurities such as tar may be left in the pores without decomposing. The presence of impurities will block the pores and result in a low surface area and limited surface activity.

However, the product obtained after carbonisation is a material that is virtually inactive as regards adsorption due to a relatively low internal surface area and porosity, hence the need for activation. The activation method increases the pore volume by widening the diameters of the pores generated during carbonisation and also creates new pores.
2.6.4. Activation

In the activation process the carbonaceous material is subjected to selective thermal treatment under suitable conditions which results in the formation of innumerable pores, fissures and cracks. However, the quality of the activated carbon depends on the type of oven used. A decrease in porosity has been observed in the following order: fluidised bed, multiple hearth furnace and rotary kiln (Brasquet and Le Cloirec, 1997). Technological processes involve activation with chemicals, steam or gas. Generally, there are two main activation processes used by industry to produce activated carbons: physical (or thermal) and chemical activation. The main difference between the two is that physical activation is performed at a higher temperature, resulting in a lower yield of activated carbon whereas chemical activation is performed at a lower temperature, resulting in a much higher yield of activated carbon.

2.6.4.1. Physical activation

Physical (or thermal) activation involves activation with air, oxygen, steam or carbon dioxide. Activation with air and oxygen are selective but involve the risk of external excessive burning of the carbon due to the highly exothermic reaction between them and carbon, therefore, causing excessive weight loss (Pimenov et al., 1995). Consequently steam and carbon dioxide are preferred for commercial applications. To achieve a sufficiently high reaction rate when using steam and carbon dioxide, the activation must be conducted at 1073-1273 K (Jankowska et al., 1991).

Porosity in activated carbon cloths is determined by the method of activation and the type of precursor. Partial gasification of the carbon with oxidant gases constitutes the physical activation method. The carbonised carbon cloth is activated in carbon dioxide or steam at 1098 K. In activation with carbon dioxide, the heating and cooling processes in the furnace are normally done with the carbon dioxide at a flow rate of 100 ml min$^{-1}$. In activation with steam, the furnace is heated initially with nitrogen at 100 ml min$^{-1}$ flow rate. A peristaltic pump is then connected at 873 K to the system to introduce a flow of water which vaporises in the furnace to produce steam at a flow rate of 100 ml min$^{-1}$. At the final activation temperature of 1098 K the nitrogen is disconnected and the activation proceeds with undiluted steam. In both cases, once the required temperatures are achieved, the cloths are further heated for 60-120 min at the required temperature.
Rodriguez-Reinoso et al. (2000) produced viscose rayon based activated carbon cloth by physical activation and reported that the initial mechanism during physical activation is the opening of previously inaccessible pores by the burning off of the amorphous carbon blocking the pores. With further activation, the carbon atoms of the elementary crystals react at different rates in different parts of the surface. Carbon atoms with unsaturated valences leave the surface as gaseous oxides. These processes lead to new pore formation in the first stage. In the second stage which is at medium or high activation level they lead to widening of the existing pores and the formation of larger pores by burning off the walls between adjacent pores.

The main factors affecting the gasification rate are: active site concentration in the carbon surface, presence of inorganic impurities and diffusion of reactive gases to active sites. The final activation temperature affects the activation rate and influences porosity development. Also, a lower activation rate produces a more uniform activation process. However, the activating gas used significantly influences the porosity of the product. Activation with carbon dioxide develops higher microporosity producing mainly micropores whilst activation with steam develops more widening of pores producing mainly mesopores.

2.6.4.2. Chemical activation

Compared to physical activation, chemical activation has the advantages of: relatively shorter time of activation, higher yield of activated carbon and better adsorption properties of the final product. However, it has the disadvantages of: difficulties in complete removal of activating agents from the activated carbon and increase in manufacturing cost due to difficulties involved in recovering chemical reagents.

Industrially, phosphoric acid, zinc chloride and potassium sulphide are mainly used as activating agents. Besides, other reagents exhibiting dehydrating activities may be used such as potassium thiocyanate and sulphuric acid (Jankowska et al., 1991). The carbonised viscose rayon based cloth is placed in an aqueous solution of 1-12 wt% phosphoric acid or 0.9-3.6 wt% zinc chloride. The mixture of the cloth and aqueous solution is put in a furnace with a gradual increase in temperature to 1098 K. The activation process then continues for 30-60 min. The activated carbon cloth is then
washed either in distilled water for cloth activated in phosphoric acid or in 1.5 M hydrochloric acid followed by distilled water for cloth activated in zinc chloride.

Huidobro et al. (2001) produced viscose rayon based activated carbon cloths by chemical activation using different chemicals and reported that impregnation of viscose rayon fabric with different chemicals modified the activation process. Dehydration became more predominant than depolymerisation and thus increased the activated carbon cloth yield. They also reported an increase in the fabric strength with the impregnation of the fabric with chemicals. They observed that activation in phosphoric acid produced a higher activated carbon cloth yield with wider microporosity whilst activation in zinc chloride produced lower activation carbon yield with narrower microporosity.

However chemical activation produces a carbon matrix that contains a considerable amount of heteroatoms (including residual of phosphates, sulphates and zinc) due to incomplete removal of activating agents (Jankowska et al., 1991).

2.6.5. Physical Properties of Activated Carbon Fibres
Activated carbons are physically characterised by their high surface area, well defined pore size, high mechanical and thermal strength and good electronic properties (Knocke and Hemphill 1981). The electrophysical properties of carbons such as electroconductivity and paramagnetism are attributed to their electronic structure. The electroconductivity is due to π-electrons moving along hexagonal aromatic planes in the system of conjugated bonds. It has been concluded that the precursor, conditions of thermal treatment and the factors influencing the structural transformation of carbonaceous material define the electrophysical characteristics of the final product obtained after activation (Namasivayam and Kadirevelu 1999). Activated carbons have large surface areas in the range of 800-2500 m²/g and large pore volume. According to the International Union of Pure and Applied Chemistry (IUPAC) system (Sing et al., 1985), the pore structures are divided into three categories as follows:
(i) Micropores (width less than 2 nm)
(ii) Mesopores (width between 2 nm and 50 nm)
(iii) Macropores (width more than 50 nm).
(iv) Micropores are also divided into two categories as follows:
(v) Ultra micropores (width less than 0.5 nm)
(vi) Super micropores (width between 1 nm and 2 nm).

Activated carbon fibres have more uniform microporous structure than granular activated carbons, therefore, having faster adsorption kinetics and a lower pressure drop than granular activated carbons (Park et al. 1999b; Boudow et al. 1999). They are also easier to use than granular or powder activated carbons since they are in cloth and felt forms. Normally, the porous structure of activated carbon fibres is composed mainly of micropores, with some mesopores but without macropores. Micropores exhibit a large surface area (greater than 95% of the total surface area) and high adsorption energy and thus play the most important role in adsorption (Suziki, 1994). Micropores and mesopores are considered to be more important than macropores in adsorption depending on the application, i.e. the nature of the molecules to be adsorbed. Macropores are considered to be transport arteries, providing passages for the adsorbate into the interior mesopores and micropores (Ryu et al., 1999).

2.6.6. Chemical Properties of Activated Carbon Fibres

X-ray diffraction (XRD) data indicates that the activated carbons are usually graphitic in nature (Toles et al. 1997). Small polyaromatic sheets with only a few aromatic rings per cluster exist in a disordered state relative to each other. They are thought to be cross linked by oxygen atoms between the polyaromatic sheets (Solum et al. 1995). These polyaromatic sheets often contain unpaired electrons and unsaturated valences on or near their edges, where oxygen-bearing functional groups are thought to be located. Hetero atoms provide the charged groups in the carbon structure residing either on sheet edges or forming heterocyclic rings within the sheets. These hetero atoms are basically derived from the precursor and they arise as a result of imperfect carbonisation or through activation.

The oxygen-bearing functional groups generally referred to as surface functional groups include carboxyls, phenols, lactones, hydroxyls, carbonyls, quinones, carboxylic anhydrides and lactols (Boehm 1994). Acidic hydrogen atoms on carboxylic and hydroxyl groups occurring on the surface of activated carbons appear to be more available for ion exchange possibly as a result of electron density diversion to \( \pi \)-bond system of the graphite planes. Activated carbons are usually classified into
two categories based on the acid-base behaviour of the carbon. H-type and L-type carbons are differentiated on the basis of the pH of the carbon, with L-type carbons being more acidic and H-type being more basic. Since activated carbons are produced from hydrocarbons, the dangling bonds at the edges of the carbon layers are saturated mostly by hydrogen. Boehm (1994) found large polycyclic aromatic ring systems that can be extracted with hot solvents e.g. xylene. Other elements like oxygen, sulphur, phosphorus and nitrogen are also found in activated carbon. The most important of these elements is oxygen which is chemisorbed on heating the carbon in air or oxygen or by treatment with oxidising media such as nitric acid, whereas sulphur, nitrogen and phosphorus originate from the precursor. The surface oxides formed have a pronounced effect on the surface properties of the carbon and are normally bound to the edges of the carbon layers.

2.6.6.1. Acidic surface functional groups

Carbons can show basic or acidic pH values in aqueous dispersions. The dispersions become more acidic for carbons with higher oxygen content. The acidic surface properties are due to the presence of acidic surface functional groups. Such carbons have cation exchange properties. Carbons with a low oxygen content show basic surface properties and so have anion exchange behaviour. The basic properties are ascribed to the presence of basic surface oxides.

Figure 2.1 below (Boehm 1994) presents several structures of oxygen functional groups that might be found at the edges of the graphene layers. The most important ones are the carboxyl (a), carbonyl (f) and single hydroxyl (phenolic) (e) groups. Other groups can be generated from a combination of these ones. Carboxyl groups can form carboxylic anhydrides (b) if they are close together. In close neighbourhood, hydroxyl groups and carboxyl groups are joined to produce lactones (c) and lactols (d) are formed when carboxyl and carbonyl groups are joined. Carbonyl groups can also be present on the surface of the carbon as conjugated structures called quinone (g). Ether type structures (h), which are stable even at high temperatures, can also be found on the activated carbon surfaces.
Figure 2.1 Possible structures of surface oxygen groups (Boehm, 1994).

2.6.6.2. Basic surface functional groups

Basic surface oxides are always present on carbon surfaces. Voll and Boehm (1971) heated carbon up to 1273 K in vacuum or under an inert gas and found that the existing surface compounds almost completely decomposed. When they exposed the heated carbon to dry oxygen after cooling to room temperature some oxygen was chemisorbed. After submersing it under aqueous acids, the same quantity of oxygen was taken up and approximately one equivalent of acid per chemisorbed oxygen atom is bound at the same time. The bound anion of the acid can be exchanged for other anions implying that the carbon had some basic functionality. They also put forward
the idea of the existence of some pyrone structures to explain the adsorption of acids. This idea has been widely accepted and is shown in Figure 2.2 below.

![Chemical structure](image)

**Figure 2.2 Proton addition to Y-Pyron like structures (Boehm, 1994).**

Contrary to the experimental observation of Voll and Boehm, Puri (1970) observed that carbons that were out gassed at 1473 K in vacuum and cooled without exposure to oxygen were better adsorbers of acids. Therefore, basic character of carbon could not be attributed only to oxygen containing surface structures. Leon y Leon et al. (1992) also made an intensive study of the nature of surface basicity of two series of chemically and thermally pre-treated carbons. They showed that carbons with low oxygen content exhibited electron donor-acceptor interactions of the following type:

\[
C_{\pi} + H_3O^+ \rightleftharpoons C_{\pi}H_3O^+ \tag{2.10}
\]

It was postulated that the \( C_{\pi} \) sites were located at the \( \pi \) electron rich regions of the basal planes of the carbon situated far from the edges. The interaction of \( C_{\pi} \) with \( H_3O^+ \) ions resulted in localisation of the \( \pi \) electron pair associated with the donor-acceptor complex. They therefore concluded that only the pyrone type group was responsible for the basicity of carbon as had been proposed by Voll and Boehm (1971) and that the basicity of carbon surfaces arises from the combination of the electron donor-acceptor and pyrone type interactions. Figure 2.3 below (Boehm 1994) presents some basic surface oxides which are ether and carbonyl groups.
Figure 2.3 Possible structures of basic surface sites on graphene layer (Boehm, 1994).
2.7. MODIFICATION OF ADSORBENTS

There have been several reports showing that activated carbons offer a great potential for the removal of organic and inorganic micro pollutants. Pradhan and Sandle (1999) showed that in the case of the adsorption of inorganic compounds onto activated carbon from aqueous solution, the chemical nature of the adsorbent, determined by the amount and nature of the surface complexes, has in general more influence than the surface area and porosity of the adsorbent. This can be significantly improved by surface modification. There are different techniques that modify the interfacial region of carbons that multiply contact points or increase the reactivity of the region by developing functional groups on the carbon surface. These techniques maybe classified as follows:

i) Wet chemical oxidation, using different reagents such as nitric acid, acidic potassium permanganate, sodium hypochlorite, hydrogen peroxide and phosphoric acid.

ii) Dry oxidation, by oxygen, air and ozone at different temperatures.

iii) Anodic oxidation, by an electrochemical process using different electrolytes, like, ammonium bicarbonate, potassium hydroxide, potassium chloride, Sodium hydroxide, potassium nitrate and nitric acid.

iv) Thermal treatments, e.g. annealing or applying hot briquetting method (Miura et al., 2000).

v) Pyrolytic carbon coating and polymer grafting (Donnet and Bansal, 1984).

The most common methods to oxidise carbonaceous materials have been air at high temperature and nitric acid. Other oxidants such as ozone and hydrogen peroxide have also been used to a lesser extent (Deitz and Bitner, 1972). In this section some methods of modification of carbonaceous materials and other adsorbents will be discussed.

2.7.1. Ozone Modification of Adsorbents

The surface modification of activated carbon has received much attention due to the great importance of their surface chemistry in a number of industrial applications. Although reports of surface modification of activated carbon with ozone can be found in literature, there is a lack of detailed investigation on the surface effects of this treatment in adsorption processes. Some relevant publications on ozone modification of adsorbents are reviewed and presented in this section.
Papirer et al. (1967) oxidised carbon black with ozone gas of 6 vol% in oxygen at 298 K for 8 h and found that while ozone treatment significantly increased the surface oxygen concentration of carbon black, it had little effect on the specific surface area. They also found that the surface oxygen concentration increased with increase in the voltage of the ozone generator. Increasing the flow rate of oxygen decreased the ozone concentration but increased the carbon surface oxygen concentration. This was attributed to the increase in total volume of ozone produced at the higher flow rates used. The surface oxygen concentration also increased steadily with time. They also concluded that the dominant functional groups introduced by ozone oxidation were carboxylic acid groups. The ozone treatment however caused etching on the surface of the carbon black and also decreased the tensile strength of the carbon black.

Deitz and Bitner (1972) modified steam activated coconut shell charcoal and steam activated coal-based charcoal with ozone concentrations varied from 0.2 vol% in oxygen to 2.5 vol% in oxygen at 299 K. They contacted the activated carbon with ozone for various times and observed an immediate increase in weight which passed through a maximum and then decreased slowly. This behaviour was explained by a three-model reaction of ozone with carbon represented as follows:

\[ C_xO_y + O_3 \rightarrow C_{x-2}O_{y-1} + 2CO_2 \quad (III) \]

\[ C_xO_y + O_2 \rightarrow CO_2 + C_{x-1}O_{y+1} \quad (II) \]

\[ C_xO_{y+1} + O_2 \rightarrow C_xO_{y+1} + O_2 \quad (I) \]

Reaction (I) represents the chemisorption of oxygen atoms without lost in weight. This is followed by the carbon gasification resulting from reactions (II) and (III) when progressive etching takes place. Reaction (II) generates less carbon loss than reaction (III). However, the amount of oxygen groups continuously increased. They found an elaborate etching of the carbonaceous material during ozone oxidation which resulted in a large increase of the surface area. Elemental analysis showed a continuous decrease in carbon and a continuous increase in oxygen. The oxygen content increased from 5.4 wt% for unoxidised charcoal to 50.3 wt% for ozone oxidised charcoal at 30 h while the carbon content decreased from 94.1 wt% for unoxidised charcoal to
45.7 wt% for ozone oxidised charcoal at 30 h. However, they observed 35% weight loss for the ozone oxidised charcoal. This was attributed to significant etching of the charcoal during ozone oxidation.

Sutherland et al. (1996) oxidised carbon black in ozone gas of 3 vol% in oxygen at 298 K for 0.25 h. They studied the effect of ozone oxidised carbon black on rubber reinforcement and found that ozone oxidised carbon black decreased the tensile strength for non-polar rubber but increased the tensile strength for polar rubber. FTIR analysis detected that the dominant functional groups introduced by ozone oxidation were carboxylic acid groups. However, the oxidation method decreased the tensile strength of carbon black.

Fu et al. (1998) modified isotropic-pitch-based carbon fibres (ACF) by stirring different ACFs for 24 h at room temperature in 2 N acetic acid, 2 N hydrogen peroxide, 1.5 N sodium hydroxide or 1.5 N nitric acid and then water washed the ACFs and dried at 393 K. The ACFs were then exposed to ozone gas of 0.6 vol% in oxygen for 5 min at 433 K. They observed an increase in oxygen content from 13.5% for unoxidised ACF to 24% for ozone oxidised ACF. They also observed that the ozone treatment changed the surface oxygen from C—O configuration to C=O configuration that is chemically more active, thereby increasing the bond strength between the ACF and cement paste and causing the contact angle between the ACF and water to decrease to zero. Therefore, ozone oxidation of ACF increased the reinforcement of cement.

Gomez-Serrano et al. (2002) oxidised cherry stone-based activated carbon with ozone, from 298 to 523 K for 1 h. The system was heated from room temperature to the maximum heat treatment temperature and held at this temperature for 1 h and then cooled down to room temperature. The initial dynamic heating and final cooling stages were all performed in nitrogen. Ozone was produced from air in a Constrena SLO ozone generator to provide air-ozone mixture containing 2.5 vol% of ozone at most. They observed that the concentration of hydroxyl groups in the ozone oxidised carbon was about twice that of quinonic structures or carboxylic acid groups. The highest content of various oxygen complexes was obtained at 373 K. However, the content of
lactonic structures was found to be very low. Elemental analysis showed an increase in oxygen content from 4.01 wt% for unoxidised cherry stone-based activated carbon to 5.5 wt% for ozone oxidised cherry stone-based activated carbon. They also found that due to the thermal decomposition of ozone, its content in the gas stream was very sensitive to increase in temperature. The amount of ozone that interacted with the carbon was largest at 373 K, therefore, they concluded that 373 K is the most suitable temperature for ozone oxidation of activated carbon. They also observed an increase in cation exchange capacity (sodium capacity) from 0.25 mmol/g for unoxidised cherry stone-based activated carbon to 1.89 mmol/g for ozone oxidised cherry stone-based activated carbon at 373 K. Finally, FTIR analysis detected the presence of hydroxyl and carboxyl functional groups on the ozone oxidised cherry stone-based activated carbon.

Rangel-Mendez and Streat (2002b) studied the influence of surface oxidation on the adsorption of cadmium by polyacrylonitrile-based activated carbon cloth (ACC). They oxidised 1gm of ACC by passing dry air at the rate of 1000 cm$^3$ min$^{-1}$ through an ozone generator with the voltage set at 9 V. The oxidation was carried out at 294 K for 1, 2 and 3 h. The oxygen content of the ozone oxidised ACC increased from 12.1% for unoxidised ACC to 19.3% for ozone oxidised ACC at 3 h. They observed that the point of zero charge (PZC) shifted to lower pH values as the degree of oxidation increased due to the introduction of acidic functional groups. The PZC of the unoxidised ACC was at pH 4.2 whereas it was at pH 2.8 for the ozone oxidised ACC at 3 h. An increase in cation exchange (sodium) capacity from 1.58 mmol/g for unoxidised ACC to 5.4 mmol/g for ozone oxidised ACC at 3 h was also observed. They also observed an increase in maximum cadmium adsorption capacity from 0.075 mmol/g for unoxidised ACC to 1.15 mmol/g for ozone oxidised ACC at 3 h. This was attributed to the introduction of carboxyl functional groups, detected by X-ray photoelectron spectroscopy analysis, onto the ACC during ozone oxidation. However, using scanning electron microscopy, they noticed very significant physical damage to the ozone oxidised ACC.

Ko et al. (2004) oxidised phenolic resin-based activated carbon fibre in ozone at a concentration of 0.1 gO$_3$/m$^3$ inert O$_2$ gas dispersed in 1 M sodium hydroxide or 3 M hydrogen peroxide solution at 298 K for 1 h. They observed a decrease in BET surface
area of the ozone oxidised ACF in 1 M sodium hydroxide from 1516 m²/g for unoxidised ACF to 1364 m²/g for ozone oxidised ACF in sodium hydroxide. This was attributed to some pore-blocking by the sodium ions. However, an increase in BET surface area of the ozone oxidised ACF in 3 M hydrogen peroxide from 1516 m²/g for unoxidised ACF to 1706 m²/g for ozone oxidised ACF in hydrogen peroxide was observed. This was attributed to the oxidation of carbon atoms of ACF by hydroxyl radical to produce carbon dioxide continuously, which resulted in the increase in surface area. Carboxyl and phenol functional groups were detected on all the ozone oxidised ACFs. Changes in PZC from pH 3 to pH 2.4 and pH 2.2 for ACFs oxidised with ozone in sodium hydroxide and hydrogen peroxide, respectively, were also observed. They also observed an increase in sodium capacity from 0.63 mmol/g for unoxidised ACF to 0.76 and 0.82 mmol/g for ACFs oxidised with ozone in sodium hydroxide and hydrogen peroxide, respectively. They also studied chromium(VI) and copper(II) adsorption onto the unoxidised ACF and ACFs oxidised with ozone in sodium hydroxide and hydrogen peroxide at different solution pH but at constant temperature 298 K. They observed increase in chromium(VI) adsorption capacities from 0.558 mmol/g for unoxidised ACF to 0.732 and 0.821 mmol/g at solution pH 2, which is below the PZC values for the oxidised ACFs, for ACFs oxidised with ozone in sodium hydroxide and hydrogen peroxide, respectively. However, they observed a decrease in chromium(VI) adsorption capacities at solution pH above the PZC values for the ozone oxidised ACFs. This was attributed to the ozone oxidised ACFs being positively and negatively charged below and above the PZC, respectively. Finally, they observed an increase in copper(II) adsorption capacities from 0.393 mmol/g for unoxidised ACF to 0.502 and 0.412 mmol/g at solution pH 6, which is above the PZC values for the oxidised ACFs, for ACFs oxidised with ozone in sodium hydroxide and hydrogen peroxide, respectively. This was attributed to the ozone oxidised ACFs being negatively charged above the PZC and since copper(II) ions exist in cationic forms, they were attracted and adsorbed onto the ozone oxidised ACFs.

2.7.1.1. Conclusions
Table 2.5 shows the comparison of ozone modification conditions, surface properties of different ozone modified adsorbents and the different applied processes for the ozone modified adsorbents shown in the literature review in this section. From the publications on ozone oxidation shown in the literature review in this section it can be
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Vol% O₃ in O₂</th>
<th>Temp. (K)</th>
<th>Time (h)</th>
<th>PZC</th>
<th>Functional group</th>
<th>Applied process</th>
<th>Effect on surface morphology and weight loss</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>6</td>
<td>298</td>
<td>8</td>
<td>-</td>
<td>Carboxyl</td>
<td>-</td>
<td>Etching and decreased tensile strength.</td>
<td>Papirer et al. (1967)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>2.5</td>
<td>299</td>
<td>24</td>
<td>-</td>
<td>Oxygen containing</td>
<td>-</td>
<td>Elaborate etching and 35% wt. loss</td>
<td>Deitz and Bitner (1972)</td>
</tr>
<tr>
<td>Carbon black</td>
<td>3</td>
<td>298</td>
<td>0.25</td>
<td>-</td>
<td>Reinfocing rubber</td>
<td>-</td>
<td>Decreased tensile strength</td>
<td>Sutherland et al. (1996)</td>
</tr>
<tr>
<td>Pitch-based ACF</td>
<td>0.6</td>
<td>433</td>
<td>0.083</td>
<td>-</td>
<td>C=O</td>
<td>Reinforcing cement</td>
<td>No effect</td>
<td>Fu et al. (1998)</td>
</tr>
<tr>
<td>Cherry stone-based</td>
<td>2.5</td>
<td>373</td>
<td>1</td>
<td>-</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na⁺ sorption capacity (1.89 mmol/g)</td>
<td>No effect</td>
<td>Gomez-Serrano et al. (2002)</td>
</tr>
<tr>
<td>PAN-based ACC</td>
<td>10</td>
<td>294</td>
<td>3</td>
<td>pH 2.8</td>
<td>Carboxyl</td>
<td>Na⁺ sorption capacity (5.8 mmol/g) Cd²⁺ sorption capacity (1.15 mmol/g)</td>
<td>Elaborate etching</td>
<td>Rangel-Mendez and Streit (2002b)</td>
</tr>
<tr>
<td>Phenolic resin-based</td>
<td>1</td>
<td>298</td>
<td>1</td>
<td>pH 2.4</td>
<td>Carboxyl, Pheno</td>
<td>Na⁺ sorption capacity (0.82 mmol/g) Cu²⁺ sorption capacity (0.51 mmol/g) Cr⁶⁺ sorption capacity (0.82 mmol/g)</td>
<td>No effect</td>
<td>Ko et al. (2004)</td>
</tr>
</tbody>
</table>

Table 2.5. Comparison of ozone modification conditions, surface properties of different ozone modified adsorbents and the different applied processes for the ozone modified adsorbents.

concluded that ozone is one of the strongest gaseous oxidant that seriously damages the physical structure of carbon, which is undesirable for any potential adsorption process even though in this literature review the highest cation exchange capacity of 5.4 mmol/g was observed for ozone oxidised PAN-based activated carbon cloth.
(Rangel-Mendez and Streat, 2002b). However, this oxidising reagent may be useful to
generate oxidised carbons with lower sorption capacity and good mechanical
properties provided parameters such as temperature, oxidation time and ozone
concentration are carefully controlled during the oxidation process. Therefore, it is
necessary to find another method of modification of activated carbon fibre that will
enhance its metal ion sorptive capacity but will not damage the physical structure of
the activated carbon fibre. This is the main objective of this research.

2.7.2. Chemical Modification of Adsorbents

The main aim of modification of adsorbent surface is to obtain a more hydrophilic
surface structure with a relatively large number of oxygen-containing surface groups.
In general these surface groups behave as acids or bases. In the last few years the
modification of adsorbents, such as granular activated carbons, carbon fibres and other
adsorbents have been carried out using different reagents and methodologies. Some
relevant publications on chemical modification of adsorbents are reviewed and
presented in this section.

2.7.2.1. Nitric acid modification of adsorbents

Kuzin and Strashko (1967) modified granular activated carbon by oxidising 1.4 g of
granular activated carbon in nitric acid at 353 K for different oxidation times. They
observed an increase in sodium capacity for the nitric acid oxidised granular activated
carbon with increase in oxidation time. The maximum sodium capacity for the nitric
acid oxidised granular activated carbon was 4.2 mmol/g.

Otake and Jenkins (1993) modified granular activated carbon (GAC) by oxidising the
GAC in concentrated nitric acid at different temperatures (320-360 K) for different
oxidation times (0.25-28.5 h). They observed carboxylic functional groups on the
oxidised granular activated carbon. They also observed that the sodium capacity
increased with increase in time of nitric acid oxidation. Maximum sodium capacity of
3.39 mmol/g was observed for nitric acid oxidised granular activated carbon at 340 K
for 28.5 h. They studied Ba$^{2+}$ adsorption from aqueous solutions onto nitric acid
oxidised GAC and observed maximum quantity of Ba$^{2+}$ adsorbed onto nitric acid
oxidised GAC as 1.61 mmol/g.
Vinke et al. (1994) chemically modified peat-based granular activated carbon (GAC) and wood-based GAC by oxidising 15 g of the GAC in 65% w/w nitric acid at 348 K for 4 h. FTIR analysis detected the presence of hydroxyl groups and carboxylic acid groups on the nitric acid oxidised GACs. They observed cation exchange capacities of 2.5 and 5 mmol/g for nitric acid oxidised peat-based GAC and nitric acid oxidised wood-based GAC, respectively. The PZC changed from pH 8 and 3 for unoxidised peat-based GAC and wood-based GAC, respectively to pH 1.6 and 1.9 for nitric acid oxidised peat-based GAC and nitric acid oxidised wood-based GAC, respectively. However, they observed weight loss of 32.61% and 30.33% for nitric acid oxidised peat-based GAC and nitric acid oxidised wood-based GAC, respectively. They finally proposed that nitric acid oxidation of carbons may be analogous to oxidation of aromatic hydrocarbons, with the aliphatic side chains of molecules being susceptible to oxidation to produce an arylcarboxylic acid as shown in Figure 2.4 below.

\[
\text{Figure 2.4 Nitric acid oxidation of a hydrocarbon (Vinke et al., 1994).}
\]

Moreno-Castilla et al. (1995) modified almond shell-based granular activated carbon (GAC) by oxidising 1 g of the almond shell-based GAC in 10 ml of 13.9 M nitric acid at 353 K until dryness. FTIR analysis detected carboxylic functional groups, nitro and nitrate groups on the nitric acid oxidised GAC. They observed an increase in oxygen content for the nitric acid oxidised GAC from 0.6% for unoxidised GAC to 20.6% for nitric acid oxidised GAC. They also observed a change in PZC for the nitric acid oxidised GAC from pH 10.6 for unoxidised GAC to pH 2.4 for nitric acid oxidised GAC. This was attributed to the formation of oxygen containing functional groups onto the GAC by nitric acid oxidation.
Wu et al. (1995) modified PAN-based activated carbon fibre (ACF) by oxidising 30 g of the PAN-based ACF in 300 ml of 71% w/w nitric acid at 388 K for 20-90 min and investigated the effects of subsequent treatment in aqueous sodium hydroxide. They found that nitric acid oxidation created acidic functional groups on the carbon fibre which increased with nitric acid oxidation time. They observed an increase in cation exchange capacity from 0.002 mmol/g for unoxidised ACF to 0.09 mmol/g for nitric acid oxidised ACF. This was attributed to generation of acidic functional groups on the ACF by nitric acid oxidation. However, they observed 15% tensile strength loss and 0.96% weight loss for the nitric acid oxidised ACF. They also observed that subsequent treatment with sodium hydroxide removed partially oxidised graphitic fragments as shown by decrease in cation exchange capacity from 0.09 mmol/g for nitric acid oxidised ACF without subsequent treatment with sodium hydroxide to 0.009 mmol/g for nitric acid oxidised ACF with subsequent treatment with sodium hydroxide.

Barton et al. (1997) modified granular activated carbon (GAC) by oxidising the GAC in 6 M nitric acid at 368 K for 2 h. They observed PZC at pH 9.16 for unoxidised GAC and at pH 2.5 for nitric acid oxidised GAC. They also observed an increase in cation exchange capacity from 0.232 mmol/g for unoxidised GAC to 3.36 mmol/g for nitric acid oxidised GAC. This was attributed to the introduction of carboxylic acid functional groups onto the GAC by nitric acid oxidation.

Pittman Jr. et al. (1997) modified PAN-based activated carbon fibre (ACF) by oxidising the ACF in 70% nitric acid at 388 K for 1.5 h and found that carboxyl and phenolic surface groups were mainly introduced during oxidation. They observed an increase in oxygen content from 19.2% for unoxidised ACF to 26.4% for nitric acid oxidised ACF. They also observed an increase in the cation exchange capacity from 0.005 mmol/g for unoxidised ACF to 0.048 mmol/g for nitric acid oxidised ACF. This was attributed to the formation of carboxylic acid groups on the ACF by nitric acid oxidation.

Figueiredo et al. (1999) modified Norit Rox activated carbon in 5 M nitric acid at 353 K for 6 h or in 10 M hydrogen peroxide at room temperature. They observed that
nitric acid oxidation increased the concentration of carboxylic acid surface groups on
the Norit Rox activated carbon.

Pradhan and Sandle (1999) modified activated charcoal cloth (ACC) and granular
activated charcoal (GAC) by oxidising 1 g of ACC or GAC in 10 ml of 1 M nitric acid
at 353 K for 24 h. They observed an increase in oxygen content from 9.3% for
unoxidised ACC to 27.4% for nitric acid oxidised ACC. They also observed an
increase in oxygen content from 11.6% for unoxidised GAC to 28.1% for nitric acid
oxidised GAC. This was attributed to formation of carboxylic acid groups on the ACC
and GAC by nitric acid oxidation. Finally, they observed an increase in the sodium
capacity from 1.6 mmol/g for unoxidised ACC to 5.67 mmol/g for nitric acid oxidised
ACC and an increase in the sodium capacity from 0.6 mmol/g for unoxidised GAC to
1.88 mmol/g for nitric acid oxidised GAC.

Yue et al. (1999a) modified PAN-based activated carbon fibre (ACF) by oxidising the
ACF in 71% nitric acid at 388 K for different oxidation times. They studied Ag⁺
adsorption from aqueous solutions onto nitric acid oxidised ACFs at different
oxidation times and observed an increase in Ag⁺ adsorption with increase in nitric acid
oxidation time. The maximum quantity of Ag⁺ adsorbed onto nitric acid oxidised ACF
was 0.625 mmol/g at 1.75 h of oxidation. However, comparing the Ag⁺ adsorbed onto
nitric acid oxidised ACF from aqueous solutions with Ag⁺ adsorbed onto
electrochemically oxidised ACF in 1 %wt potassium nitrate from aqueous solutions
showed that the electrochemically oxidised ACF adsorbed a prodigious amount of
Ag⁺, which was 3.7 mmol/g for ACF electrochemically oxidised at 5652 c/g extent of
oxidation. Therefore, they concluded that electrochemical oxidation enhanced the
cation exchange capacity much more than nitric acid oxidation.

Goyal et al. (2001) modified granular activated carbon (GAC) and activated carbon
fibre (ACF) by heating 5 gm of GAC or ACF in 150 ml nitric acid at 353 K. The
heating continued until 140 ml of the solution evaporated. They observed an increase
in oxygen content from 7.6% for unoxidised ACF to 22.77% for nitric acid oxidised
ACF. They also observed an increase in oxygen content from 5.12% for unoxidised
GAC to 20.52% for nitric acid oxidised GAC. They studied the adsorption of
copper(II) ions from aqueous solutions by the unoxidised and nitric acid oxidised ACF
and GAC and observed an increase in maximum copper(II) adsorption capacity for the nitric acid oxidised ACF from 0.14 mmol/g for unoxidised ACF to 0.51 mmol/g for nitric acid oxidised ACF. They also observed an increase in maximum copper(II) adsorption capacities for the nitric acid oxidised GAC from 0.47 mmol/g for unoxidised GAC to 0.63 mmol/g for nitric acid oxidised GAC. The increase in maximum copper(II) adsorption capacities for nitric acid oxidised ACF and GAC was attributed to the introduction of oxygen containing functional groups onto the ACF and GAC surfaces by nitric acid oxidation.

Saha et al. (2001b) modified coal-based granular activated carbon (GAC) by oxidising the GAC in 70% concentrated nitric acid in distilled water at 363 K for 9 and 24 h. They observed a decrease in BET surface area from 1210 m²/g for unoxidised GAC to 765 m²/g for nitric acid oxidised GAC. This was attributed to chemical reaction and etching by the oxidation processes. However, an increase in sodium capacity for nitric acid oxidised GACs was observed. The sodium capacity increased from 0.5 mmol/g for unoxidised GAC to 3.1 mmol/g for nitric acid oxidised GAC. FTIR analysis detected the presence of carboxylic acid groups on the nitric acid oxidised GAC. The PZC was observed at pH 6.83 for unoxidised GAC, whereas it shifted to pH 1.98 for nitric acid oxidised GAC. Finally, a drop in isoelectric point from pH 4.95 for unoxidised GAC to pH 1.07 for nitric acid oxidised GAC was observed.

Shim et al. (2001) modified pitch-based activated carbon fibre (ACF) by oxidising the ACF in 1 M nitric acid at 356 K for 2 h. FTIR analysis detected the presence of carboxylic acid groups on the nitric acid oxidised ACF. The PZC of the unoxidised ACF was observed at pH 6, whereas it changed to pH 4 for nitric acid oxidised ACF. They studied the adsorption of Cu²⁺ and Ni²⁺ from aqueous solutions by the unoxidised ACF and nitric acid oxidised ACF at solution pH 6.5 and 298 K and observed an increase in maximum Cu²⁺ and Ni²⁺ adsorption capacities from 0.14 and 0.03 mmol/g, respectively, for unoxidised ACF to 0.51 and 0.18 mmol/g, respectively, for nitric acid oxidised ACF.

Ania et al. (2002) modified granular activated carbon (GAC) by boiling 1 g of GAC in 10 ml of 60% v/v nitric acid until dryness. They found that, although treatment with nitric acid preserved the texture of the original activated carbon and resulted in huge
increase in its oxygen content, severe oxidation caused substantial textural and chemical changes. They therefore concluded that changes in the physical morphology of the carbon during oxidation depend on the strength of the oxidising agent and operating conditions. Severe oxidation at extreme conditions practically destroyed the porous structure of the carbon due to erosion of the pore walls while oxidation carried out in moderate conditions promoted slight modification but preserved the texture of the carbon. They also observed that the PZC shifted to lower values after oxidation. It was at pH 9.16 for unoxidised GAC, whereas it shifted to pH 4.2 for nitric acid oxidised GAC. They also observed an increase in oxygen content from 1.94% for unoxidised GAC to 14.96% for nitric acid oxidised GAC. However, in the study of adsorption of phenol from aqueous solutions by the nitric acid oxidised and unoxidised GAC they observed a decrease in the maximum phenol adsorption capacity from 2.47 mmol/g for unoxidised GAC to 0.91 for nitric acid oxidised GAC, indicating that the adsorption of phenol requires the presence of basic surface oxygen groups.

Rangel-Mendez and Streat (2002b) modified PAN-based activated carbon cloth (ACC) by oxidising 2 g of ACC in 80 ml of 8 M nitric acid at 363 K. Oxidation time was varied for 1, 2 and 3 h. The PZC of the unoxidised ACC was observed at pH 4.2, whereas it changed to pH 2.4 for nitric acid oxidised ACC. They observed an increase in oxygen content also from 29.32% for the unoxidised ACC to 32.3% for nitric acid oxidised ACC. It was also observed that the sodium capacity increased with time of oxidation, although it did not increase beyond 2 h of oxidation. The sodium capacity increased from 1.41 mmol/g for unoxidised ACC to 3.67 mmol/g for nitric acid oxidised ACC. This was attributed to the introduction of oxygen containing functional groups onto the ACC by nitric acid oxidation, since XPS analysis detected carbonyl and carboxyl functional groups on the nitric acid oxidised ACC. They also studied the adsorption of cadmium(II) from aqueous solutions by the unoxidised ACC and nitric acid oxidised ACC and observed an increase in maximum cadmium(II) adsorption capacity from 0.075 mmol/g for the unoxidised ACC to 0.89 mmol/g for nitric acid oxidised ACC.

Strelko and Malik (2002) modified granular activated carbon (GAC) by oxidising the GAC in 20% (v/v) nitric acid at 363 K for 15 h. The carbon-to-acid ratio was 1:3 (v/v). They observed an increase in oxygen content calculated from Boehm's titration
results, from 0.9% for unoxidised GAC to 7.21% for nitric acid oxidised GAC. They also observed an increase in cation exchange capacity from 0.358 mmol/g for unoxidised GAC to 2.941 mmol/g for nitric acid oxidised GAC. The point of zero charge shifted from pH 8.1 for unoxidised GAC to pH 2.5 for nitric acid oxidised GAC, while the isoelectric point shifted from pH 5.8 for unoxidised GAC to pH 1.3 for nitric acid oxidised GAC. They also studied the sorption of \( \text{Mn}^{2+} \), \( \text{Co}^{2+} \), \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) onto unoxidised GAC and nitric acid oxidised GAC from aqueous solutions and observed an increase in maximum \( \text{Mn}^{2+} \), \( \text{Co}^{2+} \), \( \text{Ni}^{2+} \), \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) adsorption capacities from 0.0063, 0.0064, 0.0375, 0.0812 and 0.0062 mmol/g, respectively, for unoxidised GAC to 0.144, 0.15, 0.156, 0.291 and 0.131 mmol/g, respectively, for nitric acid oxidised GAC. This was attributed to introduction of acidic functional groups onto the GAC surface by nitric acid oxidation.

El-Hendawy (2003) modified corncob-based granular activated carbon (GAC) by oxidising 5 g of GAC in 50 ml of 65% nitric acid at 333 K for 1 h. They observed an increase in oxygen content from 20.22% for unoxidised GAC to 41.14% for nitric acid oxidised GAC. FTIR analysis detected phenol and carboxyl functional groups on the nitric acid oxidised GAC. They also studied the adsorption of lead(II) from aqueous solutions by unoxidised GAC and nitric acid oxidised GAC and observed a significant increase in lead(II) maximum adsorption capacity from 1.215 mmol/g for unoxidised GAC to 2.143 mmol/g for nitric acid oxidised GAC. However, a large erosive effect by nitric acid oxidation was detected by scanning electron microscopy.

Haydar et al. (2003) modified olive stone-based granular activated carbon (GAC) by oxidising 4 g of GAC in 80 cm\(^3\) of 15 M nitric acid. The solution was stirred at room temperature for 24 h. They observed an increase in oxygen content from 0.6% for unoxidised GAC to 11.72% for nitric acid oxidised GAC. This was attributed to introduction of oxygen containing functional groups onto GAC by the nitric acid oxidation process.

Park et al. (2003) modified pitch-based activated carbon fibre (ACF) by oxidising 1 g of ACF in 1 M nitric acid at 353 K for 2 h. They observed an increase in sodium capacity from 0.02 mmol/g for unoxidised ACF to 0.44 mmol/g for nitric acid oxidised ACF. This was attributed to the introduction of oxygen containing functional
groups onto the ACF by nitric acid oxidation. They also studied copper(II) and nickel(II) adsorptions onto the unoxidised ACF and nitric acid oxidised ACF from aqueous solutions in a subsequent study (Park et al., 2004b). They observed a significant increase in the specific surface areas, micropore volume and total pore volume of the fibres. This was attributed to the widening of the micropores on the porous ACF by acid erosion, consequently the average pore diameter increased. The isoelectric point was observed at pH 6 for unoxidised ACF, whereas it shifted to pH 4 for nitric acid oxidised ACF. Finally they observed an increase in maximum copper(II) and nickel(II) adsorption capacities from 0.143 and 0.031 mmol/g, respectively, for unoxidised ACF to 0.243 and 0.077 mmol/g, respectively for nitric acid oxidised ACF. This was attributed to increase in oxygen containing functional groups on the ACF by nitric acid oxidation.

Saha et al. (2003) modified pine wood-based granular activated carbon (GAC) by oxidising the GAC in 15.8 M nitric acid at 363 K for 9 h. FTIR analysis detected the presence of hydroxyl groups on the unoxidised GAC and nitric acid oxidised GAC and the presence of weakly acidic groups (carboxyl) on the nitric acid oxidised GAC. They observed a decrease in BET surface area from 672 m$^2$/g for the unoxidised GAC to 619 m$^2$/g for the nitric acid oxidised GAC. This was attributed to the blockage of pores by oxygen functional groups produced by nitric acid oxidation. The IEP and PZC shifted from pH 2 and 4.4, respectively, for unoxidised GAC to pH 1.4 and 3.4, respectively, for nitric acid oxidised GAC. They also studied the adsorption of copper(II) from aqueous solutions onto the nitric acid oxidised GAC at solution pH 4.7 and observed the maximum copper(II) adsorption capacity of 0.47 mmol/g for nitric acid oxidised GAC. This was attributed to the addition of oxygen containing weakly acidic functional groups onto the surface of the GAC by nitric acid oxidation. However, erosive effect by nitric acid oxidation was detected by scanning electron microscopy.

Xiao and Thomas (2004) modified a coconut shell-based nanoporous granular activated carbon (GAC) by oxidising the GAC in 7.5 M nitric acid at 368 K for 72 h. They observed an increase in oxygen content from 2.95% for unoxidised GAC to 22.36% for nitric acid oxidised GAC. FTIR analysis detected the presence of hydroxyl groups on the unoxidised GAC and the presence of hydroxyl, nitrate and carboxyl
groups on the nitric acid oxidised GAC. A change in PZC from pH 8.14 for unoxidised GAC to pH 2.53 for nitric acid oxidised GAC was also observed. An increase in sodium capacity from 0.08 mmol/g for unoxidised GAC to 5.44 mmol/g for nitric acid oxidised GAC was observed. They also studied the adsorption of Ca$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ from aqueous solutions onto the unoxidised GAC and nitric acid oxidised GAC and observed an increase in the maximum Ca$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ adsorption capacities by a factor of 5 due to the nitric acid oxidation. The maximum Ca$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ adsorption capacities increased from 0.048, 0.0614, 0.1146 and 0.259 mmol/g, respectively, for unoxidised GAC to 0.24, 0.307, 0.573 and 1.293 mmol/g, respectively, for nitric acid oxidised GAC.

Chingombe et al. (2005) modified coal-based granular activated carbon (GAC) by oxidising the GAC in nitric acid and distilled water at a ratio of 1:1 (v/v) at 363 K and stirring for 9 h. They observed disintegration of the nitric acid oxidised GAC particles to small particles from scanning electron micrographs. This was attributed to cleavage of C-O bridging bonds on the GAC surface during the oxidation process. FTIR analysis detected the presence of hydroxyl groups on the unoxidised GAC and nitric acid oxidised GAC and the presence of carboxylic and nitrate groups on the nitric acid oxidised GAC. They observed changes in oxygen content from 10.06% for unoxidised GAC to 16.36% for nitric acid oxidised GAC. This was attributed to formation oxygen functional groups on the GAC by nitric acid oxidation. They also observed change in the PZC from pH 7.5 for unoxidised GAC to pH 4 for nitric acid oxidised GAC. Finally, increase in sodium capacity from 0.3 mmol/g for the unoxidised GAC to 2.5 mmol/g for nitric acid oxidised GAC was observed. This was attributed to formation carboxylic functional groups on the GAC by nitric acid oxidation.

Zhao et al. (2005) modified coal-based granular activated carbon (GAC) by oxidising GAC in different concentrations of nitric acid at 373 K for 1 h. Some of the nitric acid oxidised samples were then heat treated at different temperatures to improve their anion exchange capacities. They calculated the amount of carboxylic acid and lactonic groups on the GACs from Boehm titrations and observed an increase in the calculated carboxylic groups from 2.125 mmol/g for unoxidised GAC to 2.626 mmol/g for nitric acid oxidised GAC. However, heat treatment after oxidation removed all the carboxylic groups on nitric acid oxidised GAC. In contrast, heat treatment after
oxidation increased the lactonic groups on nitric acid oxidised GAC. The lactonic groups increased from 0.13 mmol/g for nitric acid oxidised to 3.38 mmol/g for heat treated nitric acid oxidised GAC. They also studied the adsorption of Cr(VI) from aqueous solutions onto unoxidised GAC and heat treated nitric acid oxidised GAC and observed an increase in maximum Cr(VI) adsorption capacity from 0.21 mmol/g for unoxidised GAC to 0.28 mmol/g for heat treated nitric acid oxidised GAC. This was attributed to reduction of carboxylic groups and an increase in lactonic groups by heat treatment after nitric acid oxidation, therefore, resulting in an increase in basic sites on the surfaces of the GACs.

2.7.2.1.1. Conclusions

Table 2.6 shows the comparison of nitric acid modification conditions, surface properties of different nitric acid modified adsorbents and the different maximum adsorption capacities for the nitric acid modified adsorbents shown in the literature review in this section. From Table 2.6 it is obvious that the highest cation exchange capacity of 5.44 mmol/g in the literature reviewed in this section was observed for nitric acid oxidised granular activated carbon (Xiao and Thomas 2004). However, significant surface etching, tensile strength loss and weight loss were observed for some of the nitric acid oxidised granular activated carbons and activated carbon fibres by some researchers as shown in the publications reviewed in this section (Vinke et al., 1994, Wu et al., 1995; Saha et al., 2001b, El-Hendawy, 2003; Saha et al., 2003). It can be concluded that nitric acid is one of the strongest liquid oxidant and that it may seriously damage the physical structure of carbon, which is undesirable for any potential adsorption process. From Table 2.6 it is obvious that nitric acid oxidised adsorbents without any effect on the surface morphology were oxidised under low temperature, oxidation time and nitric acid concentration. However, the sorption capacities of these adsorbents are very low, therefore, this oxidising reagent maybe useful to generate oxidised carbons with lower sorption capacities and good mechanical properties provided parameters such as temperature, oxidation time and nitric acid concentration are reduced and carefully controlled during the oxidation process. Therefore, it is necessary to find another method of modification of activated carbon fibre that will greatly enhance its metal ion sorptive capacity but will not damage the physical structure of the activated carbon fibre. This is the main objective of this research.
## MODIFICATION CONDITIONS SURFACE PROPERTIES DUE TO MODIFICATION

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Conc. Of nitric acid</th>
<th>Temp. (K)</th>
<th>Time (h)</th>
<th>PZC</th>
<th>IEP</th>
<th>Functional group</th>
<th>Maximum adsorption capacity ($q_e$) (mmol/g)</th>
<th>Effect on surface morphology and wt. loss</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>4 M</td>
<td>340</td>
<td>28.5</td>
<td>-</td>
<td>-</td>
<td>Carboxyl</td>
<td>Na$^+$ 3.39, Ba$^{2+}$ 1.61</td>
<td>Etching</td>
<td>Otake and Jenkins (1993)</td>
</tr>
<tr>
<td>Wood-based GAC</td>
<td>65%</td>
<td>348</td>
<td>4</td>
<td>pH 1.9</td>
<td>-</td>
<td>Carboxyl</td>
<td>Na$^+$ 5</td>
<td>30.33% wt. loss</td>
<td>Vinke et al. (1994)</td>
</tr>
<tr>
<td>PAN-based ACF</td>
<td>71%</td>
<td>398</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>Carboxyl</td>
<td>Na$^+$ 0.09</td>
<td>0.96% wt. loss</td>
<td>Wu et al. (1995)</td>
</tr>
<tr>
<td>PAN-based ACF</td>
<td>71%</td>
<td>388</td>
<td>1.75</td>
<td>-</td>
<td>-</td>
<td>Ag$^+$</td>
<td>0.625</td>
<td>No effect</td>
<td>Yue et al. (1999a)</td>
</tr>
<tr>
<td>ACF</td>
<td>3 M</td>
<td>353</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>Carboxyl</td>
<td>Cu$^{2+}$ 0.51</td>
<td>No effect</td>
<td>Goyal et al. (2001)</td>
</tr>
<tr>
<td>Coal-based GAC</td>
<td>70%</td>
<td>363</td>
<td>24</td>
<td>pH 1.98</td>
<td>pH 1.1</td>
<td>Carboxyl, Nitrate</td>
<td>Na$^+$ 3.1</td>
<td>Etching</td>
<td>Saha et al. (2001b)</td>
</tr>
<tr>
<td>Pitch-based ACF</td>
<td>1 M</td>
<td>356</td>
<td>2</td>
<td>pH 4</td>
<td>-</td>
<td>Carboxyl, Phenol</td>
<td>Na$^+$ 1.768, Cu$^{2+}$ 0.511, Ni$^{2+}$ 0.183</td>
<td>No effect</td>
<td>Shim et al. (2001)</td>
</tr>
<tr>
<td>PAN-based ACF</td>
<td>8 M</td>
<td>363</td>
<td>3</td>
<td>pH 2.4</td>
<td>-</td>
<td>Carboxyl, Carbonyl</td>
<td>Na$^+$ 3.67, Cd$^{2+}$ 0.89</td>
<td>No effect</td>
<td>Rangel-Mendez and Streat (2002b)</td>
</tr>
<tr>
<td>GAC</td>
<td>20%</td>
<td>363</td>
<td>15</td>
<td>pH 2.5</td>
<td>pH 1.3</td>
<td>Carboxyl, Phenol</td>
<td>Na$^+$ 2.941, Cu$^{2+}$ 0.291, Mn$^{2+}$ 0.144, Co$^{2+}$ 0.15, Ni$^{2+}$ 0.156, Zn$^{2+}$ 0.131</td>
<td>No effect</td>
<td>Strelko and Malik (2002)</td>
</tr>
<tr>
<td>Cornocob-based GAC</td>
<td>65%</td>
<td>333</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>Carboxyl, Phenol</td>
<td>Pb$^{2+}$ 2.143</td>
<td>Large erosion</td>
<td>El-Hendawy (2003)</td>
</tr>
<tr>
<td>Pine wood-based GAC</td>
<td>16 M</td>
<td>363</td>
<td>9</td>
<td>pH 3.4</td>
<td>pH 1.4</td>
<td>Carboxyl, Hydroxyl</td>
<td>Cu$^{2+}$ 0.47</td>
<td>Large erosion</td>
<td>Saha et al. (2003)</td>
</tr>
<tr>
<td>Coconut shell-based GAC</td>
<td>7.5 M</td>
<td>368</td>
<td>72</td>
<td>pH 2.53</td>
<td>-</td>
<td>Carboxyl, Nitrate, Hydroxyl</td>
<td>Na$^+$ 5.44, Ca$^{2+}$ 0.24, Cd$^{2+}$ 0.307, Pb$^{2+}$ 0.573, Hg$^{2+}$ 1.293</td>
<td>Etching</td>
<td>Xiao and Thomas (2004)</td>
</tr>
</tbody>
</table>

Table 2.6. Comparison of nitric acid modification conditions, surface properties of different nitric acid modified adsorbents and the different maximum adsorption capacities for the nitric acid modified adsorbents.
2.7.2.2. Modification of adsorbents in different chemicals

Moreno-Castilla et al. (1995) modified almond shell-based granular activated carbon (GAC) by oxidising 1 g of the almond shell-based GAC in 10 ml of 9.8 M hydrogen peroxide at 298 K for 48 h or 10 ml of saturated solution of ammonium sulphate in 1 M sulphuric acid at 298 K for 48 h. FTIR analysis detected carboxyl, ketone and ether groups on the hydrogen peroxide oxidised GAC and ammonium sulphate oxidised GAC. They observed an increase in oxygen content for the oxidised GACs from 0.6% for unoxidised GAC to 9.5% and 3.5% for ammonium sulphate oxidised GAC and hydrogen peroxide oxidised GAC, respectively. They also observed a change in PZC for the oxidised GACs from pH 10.4 for unoxidised GAC to pH 1.4 and 4.8 for ammonium sulphate oxidised GAC and hydrogen peroxide oxidised GAC, respectively. This was attributed to the formation of oxygen containing functional groups onto the oxidised GACs by oxidation.

Moreno-Castilla et al. (1998) modified olive stone-based granular activated carbon (GAC) by stirring 1 g of the olive stone-based GAC in 10 ml concentrated hydrochloric acid or hydrogen fluoride at 333 K for 1 h. They observed an increase in oxygen content calculated from the amount of carbon monoxide and carbon dioxide evolved after heating the samples at 1250 K in helium flow, from 1.9% for unmodified GAC to 2.6% for hydrogen fluoride modified GAC. However, no increase in oxygen content was observed for hydrochloric acid modified GAC.

Lopez-Ramon et al. (1999) modified olive stone-based granular activated carbon (GAC) by oxidising 1 g of GAC in 10 ml of 9.8 M hydrogen peroxide for 24 h or 1 g of GAC in 10 ml of saturated solution of ammonium peroxydisulphate in 1 M sulphuric acid at 298 K for 24 h. They observed the maximum increase in sodium capacity on the ammonium peroxydisulphate oxidised GAC, which increased from 0.11 mmol/g for unoxidised GAC to 2.72 and 1.1 mmol/g for ammonium peroxydisulphate oxidised GAC and hydrogen peroxide oxidised GAC, respectively. They also observed that the PZC changed from pH 10.9 for unoxidised GAC to pH 2.2 and pH 4.2 for ammonium peroxydisulphate oxidised GAC and hydrogen peroxide oxidised GAC, respectively. This was attributed to formation of carboxyl functional groups on the surfaces of the oxidised GACs by the oxidation processes.
Pradhan and Sandle (1999) modified activated charcoal cloth (ACC) and granular activated charcoal (GAC) by oxidising 1 g of ACC or GAC in 10 ml of 30% hydrogen peroxide for 48 h or 10 ml of saturated ammonium peroxydisulphate in 4 M sulphuric acid for 48 h. They observed an increase in oxygen content from 9.3% for unoxidised ACC to 24.7% and 29.5% for hydrogen peroxide oxidised ACC and ammonium peroxydisulphate oxidised ACC, respectively. They also observed an increase in oxygen content from 11.6% for unoxidised GAC to 15.1% and 30.2% for hydrogen peroxide oxidised GAC and ammonium peroxydisulphate oxidised GAC, respectively. This was attributed to formation of carboxylic acid groups on the ACC and GAC by oxidation. Finally, they observed an increase in the sodium capacity from 1.6 mmol/g for unoxidised ACC to 1.64 and 4.96 mmol/g for hydrogen peroxide oxidised ACC and ammonium peroxydisulphate oxidised ACC, respectively and an increase in the sodium capacity from 0.6 mmol/g for unoxidised GAC to 1.02 and 1.6 mmol/g for hydrogen peroxide oxidised GAC and ammonium peroxydisulphate oxidised GAC, respectively.

Shim et al. (2001) modified pitch-based activated carbon fibre (ACF) by oxidising the ACF in 1 M sodium hydroxide at 393 K for 2 h. FTIR analysis detected the presence of lactone and phenol groups on the sodium hydroxide oxidised ACF. The PZC of the unoxidised ACF was observed at pH 6, whereas it changed to pH 10 for sodium hydroxide oxidised ACF, respectively. They studied the adsorption of Cu$^{2+}$ and Ni$^{2+}$ from aqueous solutions by the unoxidised ACF and sodium hydroxide oxidised ACF and observed an increase in maximum Cu$^{2+}$ and Ni$^{2+}$ adsorption capacities from 0.14 and 0.03 mmol/g, respectively, for unoxidised ACF to 0.42 and 0.16 mmol/g, respectively, for sodium hydroxide oxidised ACF.

Ania et al. (2002) modified 1 g of granular activated carbon (GAC) in saturated solution of ammonium peroxydisulphate in 4 N sulphuric acid for 24 h. They found that, although treatment with ammonium peroxydisulphate preserved the texture of the original activated carbon and resulted in huge increase in its oxygen content, severe oxidation caused substantial textural and chemical changes. They therefore concluded that changes in the physical morphology of the carbon during oxidation depend on the strength of the oxidising agent and operating conditions. Severe oxidation at extreme conditions practically destroyed the porous structure of the carbon due to erosion of
the pore walls while oxidation carried out in moderate conditions promoted slight modification but preserved the texture of the carbon. They also observed that the PZC shifted to lower values after oxidation. It was at pH 9.16 for unoxidised GAC, whereas it shifted to pH 2.28 for ammonium peroxydisulphate oxidised GAC. They also observed an increase in oxygen content from 1.94% for unoxidised GAC to 10.28% for ammonium peroxydisulphate oxidised GAC. However, in the study of adsorption of phenol from aqueous solutions by the ammonium peroxydisulphate oxidised and unoxidised GACs, they observed a decrease in maximum phenol adsorption capacity from 2.47 mmol/g for unoxidised GAC to 1.5 mmol/g for ammonium peroxydisulphate oxidised GAC, indicating that the adsorption of phenol requires the presence of basic surface oxygen groups.

Monser and Adhoum (2002) modified powdered activated carbon (PAC) by agitating 2.5 g of PAC in 50 ml of 1000 mg/L tetrabutyl ammonium (TBA) at 298 K for 72 h or 12 g of PAC in 0.0053 M sodium diethyl dithiocarbamate (SDDC) at 323 K for 72 h. They studied the adsorption of CN⁻ onto TBA modified PAC from wastewater and observed an increase in the maximum CN⁻ adsorption capacity from 0.025 mmol/g to 1.12 mmol/g for TBA modified PAC. This was attributed to the formation of positively charged TBA ammonium groups on the PAC by TBA modification. They also studied the adsorption of Cu²⁺, Zn²⁺ and Cr³⁺ onto SDDC modified PAC from wastewater and observed an increase in maximum Cu²⁺, Zn²⁺ and Cr³⁺ capacities from 0.15, 0.038 and 0.066 mmol/g, respectively, for unmodified PAC to 0.6, 0.15 and 0.132 mmol/g, respectively for SDDC modified PAC. This was attributed to the formation of negatively charged thiol groups on the PAC during SDDC modification and so more Cu²⁺, Zn²⁺ and Cr³⁺ ions were electrostatically attracted and adsorbed onto the SDDC modified PAC.

Park and Jang (2002) modified coconut shell-based granular activated carbon (GAC) by soaking 1 g of GAC in 35 wt% hydrochloric acid or 35 wt% sodium hydroxide for 24 h. They observed an increase in sodium capacity from 1.2 mmol/g for unmodified GAC to 2.77 mmol/g for hydrochloric acid modified GAC and a decrease in chloride capacity from 0.173 mmol/g for unmodified GAC to 0.069 mmol/g for hydrochloric acid modified GAC. In contrast, a decrease in sodium capacity from 1.2 mmol/g for unmodified GAC to 0.15 mmol/g for sodium hydroxide modified GAC and an
increase in chloride capacity from 0.173 mmol/g for unmodified GAC to 0.42 mmol/g for sodium hydroxide modified GAC were observed. They also observed a shift in PZC from pH 7.9 for unmodified GAC to pH 2.5 and pH 10.2 for hydrochloric acid modified GAC and sodium hydroxide modified GAC, respectively. This is attributed to introduction of acidic oxygen containing groups onto the surface of the GAC by hydrochloric acid modification and introduction of basic oxygen containing groups onto the surface of the GAC by sodium hydroxide modification.

Chen et al. (2003) modified granular activated carbon by reacting 4 g of granular activated carbon in 25 ml of 1 M citric acid at 323 K for 24 h. They observed a shift of PZC from pH 7.07 for unoxidised granular activated carbon, to pH 6.54 for citric acid oxidised granular activated carbon. They also studied the adsorption of copper(II) from aqueous solutions by the unoxidised granular activated carbon and citric acid oxidised activated carbon and observed an increase in copper(II) maximum adsorption capacity from 0.097 mmol/g for unoxidised granular activated carbon to 0.24 mmol/g for citric acid oxidised granular activated carbon.

Haydar et al. (2003) modified olive stone-based granular activated carbon (GAC) by oxidising 4 g of GAC in 80 cm³ of 15 M sodium hypochlorite. The solution was stirred at room temperature for 24 h. They observed an increase in oxygen content from 0.6% for unoxidised GAC to 10.06% for sodium hypochlorite oxidised GAC. This was attributed to introduction of oxygen containing functional groups onto GAC by the sodium hypochlorite oxidation process.

Goel et al. (2005) modified coconut shell-based granular activated carbon (GAC) by immersing 99.5 g of GAC in a minimum quantity of distilled water containing 0.5 g of sodium sulphide for 24 h. The mixture was then heated to dryness at 383 K for 4 h. FTIR analysis detected the presence of hydroxyl and aldehyde groups on the unmodified GAC and the sodium sulphide modified GAC and the presence of sulphur functional groups on the sodium sulphide modified GAC. They observed an increase in sulphur content from 0.56% for unmodified GAC to 7.86% for sodium sulphide modified GAC. In contrast they observed a decrease in oxygen content from 29.6% for unmodified GAC to 27.1% for sodium sulphide modified GAC. A shift in PZC from pH 5.3 for unmodified GAC to pH 4.5 for sodium sulphide modified GAC was also
observed. They also studied the adsorption of Pb(II) from aqueous solutions onto unmodified GAC and sodium sulphide modified GAC and observed an increase in maximum Pb(II) adsorption capacity from 0.105 mmol/g for unmodified GAC to 0.142 mmol/g for sodium sulphide modified GAC. The small increase in Pb(II) adsorption capacity was attributed to the sodium sulphide modified GAC being slightly more acidic than the unmodified GAC as shown by the PZC values. However, scanning electron micrographs showed some significant etching on the surface of the GAC by sodium sulphide modification.

Zhao et al. (2005) modified coal-based granular activated carbon (GAC) by oxidising GAC in different concentrations of hydrogen peroxide or iron(III) nitrate at 373 K for 1 h. Some of the oxidised samples were then heat treated at different temperatures to improve their anion exchange capacities. They calculated the amount of carboxylic acid and lactonic groups on the GACs from Boehm titrations and observed a decrease in the carboxylic groups from 2.125 mmol/g for unoxidised GAC to 0.75 and 0.375 mmol/g for hydrogen peroxide oxidised GAC and iron(III) nitrate oxidised GAC, respectively. However, heat treatment after oxidation removed all the carboxylic groups on iron(III) nitrate oxidised GAC, but increased the carboxylic groups on hydrogen peroxide oxidised GAC to 1.25 mmol/g. In contrast, heat treatment after oxidation increased the lactonic groups on all oxidised GACs. The lactonic groups increased from 1.44 and 1.88 mmol/g for hydrogen peroxide oxidised GAC and iron(III) nitrate oxidised GAC, respectively, to 1.75 and 4.81 mmol/g for heat treated hydrogen peroxide oxidised GAC and heat treated iron(III) nitrate oxidised GAC, respectively. They also studied the adsorption of Cr(VI) from aqueous solutions onto unoxidised GAC and heat treated oxidised GACs and observed an increase in maximum Cr(VI) adsorption capacity from 0.21 mmol/g for unoxidised GAC to 0.26 and 0.3 mmol/g for heat treated hydrogen peroxide oxidised GAC and heat treated iron(III) nitrate oxidised GAC, respectively. This was attributed to reduction of carboxylic groups and an increase in lactonic groups by heat treatment after oxidation, therefore, resulting in an increase in basic sites on the surfaces of the GACs.

Luo et al. (2006) modified powdered marine brown algae (biomass) by cross linking 10 g of the biomass with 20 ml of epichlorohydrin at 293 K for 2 h or oxidising 10 g of the biomass in 0.01 M potassium permanganate at 303 K for 30 min. They studied
the adsorption of Pb(II) from aqueous solutions at solution pH 5.3 and 298 K onto the unmodified biomass, epichlorohydrin modified biomass and potassium permanganate modified biomass and observed an increase in the maximum Pb(II) adsorption capacity from 1.21 mmol/g for unmodified biomass to 1.67, and 1.54 mmol/g for epichlorohydrin modified biomass and potassium permanganate modified biomass, respectively. The highest maximum Pb(II) capacity observed for epichlorohydrin modified biomass was attributed to the unique mixture of polysaccharides, mainly alginates and fucoidan. The increase in maximum Pb(II) adsorption capacity for potassium permanganate modified biomass was attributed to the production of carboxylated alginic acid by oxidation reaction of alginates with potassium permanganate.

Xuan et al. (2006) modified dried ground orange peel (GOP) by stirring 20 g of GOP in 750 ml of 20% isopropyl alcohol solution at room temperature for 24 h. 10 g of the GOP modified in 20% isopropyl alcohol was further modified by stirring in 100 ml of 0.1 mol/L sodium hydroxide at room temperature for 1 h. 5 g of the GOP modified in 0.1 mol/L sodium hydroxide was further modified by stirring in 100 ml of 0.6 mol/L citric acid at 353 K for 2 h. They studied the adsorption of Pb(II) from aqueous solutions onto the unmodified GOP and modified GOPs at solution pH 5.3 and 298 K and observed an increase in maximum Pb(II) adsorption capacity from 0.55 mmol/g for unmodified GOP to 0.61, 0.97 and 1.22 mmol/g for isopropyl alcohol modified GOP, sodium hydroxide modified GOP and citric acid modified GOP, respectively. The highest maximum Pb(II) capacity observed for citric acid modified GOP was attributed to the introduction of carboxyl groups onto the GOP by reaction of citric acid anhydride with cellulosic hydroxyl groups of the GOP.

Basha et al. (2007) modified crushed oven-dried seaweed by stirring 10 g of the crushed oven-dried seaweed in 150 ml of dimethyl sulphoxide at room temperature for 24 h. 20 ml of epichlorohydrin was then added to the mixture and stirred at 327 K for 5 h. They also oxidised 10 g of crushed oven-dried seaweed in 150 ml of 0.01 M of potassium permanganate at 303 K for 30 min. FTIR analysis detected the presence of hydroxyl groups on the unmodified crushed oven-dried seaweed and potassium permanganate modified crushed oven-dried seaweed. The presence of ether and hydroxyl groups were detected on the epichlorohydrin modified crushed oven-dried
seaweed. They studied the adsorption of chromium(VI) from aqueous solutions at solution pH 3 and 298 K onto the unmodified and modified crushed oven-dried seaweeds and observed an increase in the maximum chromium(VI) adsorption capacity from 0.34 mmol/g for unmodified crushed oven-dried seaweed, to 0.47 and 0.39 mmol/g for epichlorohydrin and potassium permanganate modified crushed oven-dried seaweeds respectively. The highest maximum chromium(VI) capacity observed for epichlorohydrin modified crushed oven-dried seaweed was attributed to the introduction of ether groups that are more basic than hydroxyl groups onto the crushed oven-dried seaweed by epichlorohydrin modification.

Gunay et al. (2007) modified ground clinoptilolite by soaking the ground clinoptilolite in 2 M sodium chloride at 295 K for 24 h. They studied the adsorption of Pb(II) from aqueous solutions at solution pH 4.5 and 295 K onto the unmodified ground clinoptilolite and sodium chloride modified ground clinoptilolite and observed an increase in the maximum Pb(II) adsorption capacity from 0.391 mmol/g for the unmodified ground clinoptilolite to 0.591 mmol/g for sodium chloride modified ground clinoptilolite. The adsorption of Pb(II) onto unmodified ground clinoptilolite was attributed to the presence of oxygen atoms on the surface of the ground clinoptilolite in the forms of SiO₂, Al₂O₃ and K₂O that made the adsorption of Pb(II) onto the unmodified ground clinoptilolite possible. The increase in the maximum Pb(II) adsorption capacity for sodium chloride modified ground clinoptilolite was attributed to improvement of the surface properties of the ground clinoptilolite by sodium chloride modification.

Mugisidi et al. (2007) modified coconut shell-based granular activated carbon (GAC) by reacting it with 10% or 15% sodium acetate for 72 h. They studied the adsorption of Cu(II) from aqueous solutions onto the unmodified GAC and modified GACs and observed an increase in the maximum Cu(II) adsorption capacity from 0.022 mmol/g for unmodified GAC to 0.035 and 0.047 mmol/g for 10% sodium acetate modified GAC and 15% sodium acetate modified GAC, respectively. This was attributed to the introduction of carboxylic groups onto the surface of GAC by sodium acetate modification.
Unuabonah et al. (2007) modified kaolinite clay by impregnating the kaolinite clay by stirring it in sodium tripolyphosphate (TPP) at 298 K for 6 h. They observed an increase in cation exchange capacity from 0.135 mmol/g for unmodified kaolinite clay to 1.287 mmol/g for TPP modified kaolinite clay. They studied the adsorption of Pb(II) and Cd(II) from aqueous solutions at solution pH 5.5 and 298 K onto the TPP modified kaolinite clay and observed maximum Pb(II) and Cd(II) adsorption capacities of 0.61 and 1.01 mmol/g, respectively, for TPP modified kaolinite clay. This was attributed to the formation of P-OH and O-P-O functional groups on the surface of the kaolinite clay by TPP modification that are the active sites for the adsorption of Pb(II) and Cd(II) from aqueous solutions.

Yu et al. (2007) modified baker’s yeast (biomass) by cross-linking 1 g of the biomass in 100 ml of 0.5 wt% glutaraldehyde and stirred at room temperature for 24 h and then by grafting polyamic acid onto 0.5 g of cross linked biomass in a solution of 1 g of pyromellitic dianhydride and 0.3 g of lysine in 30 ml of N,N-dimethylacetamide and stirred at 323 K for 3 h. FTIR analysis detected the presence of hydroxyl and amine groups on the unmodified biomass and the presence of carboxylate groups on the modified biomass. They studied the adsorption of Pb(II) and Cd(II) from aqueous solutions at solution pH 5 and 298 K onto unmodified and modified biomass and observed an increase in maximum Pb(II) and Cd(II) adsorption capacities from 0.11 and 0.059 mmol/g, respectively, for unmodified biomass to 0.98 and 0.85 mmol/g, respectively, for modified biomass. This was attributed to formation of carboxylate groups on the surface of the biomass by polyamic acid modification.

2.7.2.2.1 Conclusions

Table 2.7 shows the comparison of modification conditions in different chemicals, surface properties of adsorbents modified in different chemicals and the different maximum adsorption capacities for the chemically modified adsorbents shown in the literature review in this section. From Table 2.7 it is obvious that the highest cation exchange (sodium) capacity of 2.77 mmol/g was observed for hydrochloric acid oxidised shell-based GAC (Park and Jang 2002). However, this cation exchange capacity is lower than the highest cation exchange capacity of 5.44 mmol/g obtained by nitric acid oxidation (Table 2.6) with surface etching. There was no etching on the surfaces of all the modified adsorbents. However, it is obvious that all maximum metal
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Chemical used and conc. Of chemical</th>
<th>Temp. (K)</th>
<th>Time (h)</th>
<th>PZC</th>
<th>Functional group</th>
<th>Maximum adsorption capacity ($q_c$) (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive stone-based GAC</td>
<td>Concentrated ($\text{NH}_4$)$_2\text{S}_2\text{O}_8$ in 1 M H$_2$SO$_4$</td>
<td>298</td>
<td>24</td>
<td>pH 2.2</td>
<td>Carboxyl, Phenol, Lactone</td>
<td>Na$^+$ 2.72</td>
<td>Lopez-Ramon et al. (1999)</td>
</tr>
<tr>
<td>Pitch-based ACF</td>
<td>1 M Sodium hydroxide</td>
<td>393</td>
<td>2</td>
<td>pH 10</td>
<td>Phenol, Lactone</td>
<td>Na$^+$ 0.59, Cu$^{2+}$ 0.42, Ni$^{2+}$ 0.16</td>
<td>Shim et al. (2001)</td>
</tr>
<tr>
<td>Powdered activated carbon</td>
<td>0.0053 M Sodium diethyl dithiocarbonate</td>
<td>298</td>
<td>24</td>
<td></td>
<td>Thiol</td>
<td>Cu$^{2+}$ 0.6, Zn$^{2+}$ 0.15, Cr$^{3+}$ 0.13</td>
<td>Monser and Adhoum (2002)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>35 wt% Hydrochloric acid</td>
<td>298</td>
<td>24</td>
<td>pH 2.5</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na$^+$ 2.77, Cl$^-$ 0.07</td>
<td>Shim et al. (2001)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>35 wt% Sodium hydroxide</td>
<td>298</td>
<td>24</td>
<td>pH 10.2</td>
<td>Ether, Hydroxyl</td>
<td>Na$^+$ 0.15, Cl$^-$ 0.42</td>
<td>Park and Jang (2002)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>1 M Citric acid</td>
<td>323</td>
<td>24</td>
<td>pH 6.54</td>
<td></td>
<td>Na$^+$ 0.07, Cl$^-$ 0.42</td>
<td>Park and Jang (2002)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>4 M Sodium sulphide</td>
<td>383</td>
<td>4</td>
<td>pH 4.5</td>
<td>Sulphur, Hydroxyl</td>
<td>Pb$^{2+}$ 0.14</td>
<td>Goel et al. (2005)</td>
</tr>
<tr>
<td>Powdered brown algae</td>
<td>Cross linking with epichlororhodrin</td>
<td>293</td>
<td>2</td>
<td></td>
<td></td>
<td>Pb$^{2+}$ 1.67</td>
<td>Luo et al. (2006)</td>
</tr>
<tr>
<td>Ground orange peel</td>
<td>0.01 M Potassium permanganate</td>
<td>303</td>
<td>0.5</td>
<td></td>
<td></td>
<td>Pb$^{2+}$ 1.54</td>
<td>Luo et al. (2006)</td>
</tr>
<tr>
<td>Ground orange peel</td>
<td>20% Isopropyl alcohol</td>
<td>298</td>
<td>24</td>
<td></td>
<td></td>
<td>Pb$^{2+}$ 0.61</td>
<td>Xuan et al. (2006)</td>
</tr>
<tr>
<td>Ground orange peel</td>
<td>0.1 M Sodium hydroxide</td>
<td>298</td>
<td>1</td>
<td></td>
<td></td>
<td>Pb$^{2+}$ 0.97</td>
<td>Xuan et al. (2006)</td>
</tr>
<tr>
<td>Ground orange peel</td>
<td>0.6 Citric acid</td>
<td>353</td>
<td>2</td>
<td></td>
<td></td>
<td>Pb$^{2+}$ 1.22</td>
<td>Xuan et al. (2006)</td>
</tr>
<tr>
<td>Crushed seaweed</td>
<td>Cross linking with epichlororhodrin</td>
<td>327</td>
<td>5</td>
<td></td>
<td></td>
<td>Cr$^{6+}$ 0.47</td>
<td>Basha et al. (2007)</td>
</tr>
<tr>
<td>Crushed seaweed</td>
<td>0.01 M Potassium permanganate</td>
<td>303</td>
<td>0.5</td>
<td></td>
<td></td>
<td>Cr$^{6+}$ 0.39</td>
<td>Basha et al. (2007)</td>
</tr>
<tr>
<td>Kaolinite clay</td>
<td>Sodium tripolyphosphate</td>
<td>298</td>
<td>6</td>
<td></td>
<td></td>
<td>Na$^+$ 1.29, Pb$^{2+}$ 0.61, Cd$^{2+}$ 1.01</td>
<td>Unuabona et al. (2007)</td>
</tr>
<tr>
<td>Baker's yeast</td>
<td>0.5 wt% Glutaraldehyde</td>
<td>298</td>
<td>24</td>
<td></td>
<td></td>
<td>Na$^+$ 0.19, Pb$^{2+}$ 1.01, Cd$^{2+}$ 0.85</td>
<td>Yu et al. (2007)</td>
</tr>
</tbody>
</table>

Table 2.7. Comparison of modification conditions in different chemicals, surface properties of adsorbents modified in different chemicals and the different maximum adsorption capacities for the chemically modified adsorbents.
adsorption capacities of all the chemically modified adsorbents, that is shown in Table 2.7 are very low, except the sodium capacities observed for HCl oxidised shell-based GAC (Park and Jang 2002) and olive stone-based GAC modified with concentrated (NH₄)₂S₂O₈ in 1 M H₂SO₄ (Lopez-Ramon et al. 1999). The highest maximum adsorption of other metals, apart from sodium capacities, is 1.67 mmol/g and was observed for powdered brown algae cross linked with epichlorohydrin. As discussed in chapter 1, powdered adsorbents and granular adsorbents are economically favourable, but with technically difficult processes when compared to activated carbon fibre. Very low cation exchange (sodium) capacity of 0.59 mmol/g was observed for NaOH modified pitch-based ACF (Shim et al. 2001). Therefore, it is necessary to find another method of modification of activated carbon fibre that will greatly enhance its metal ion sorptive capacity but will not damage the physical structure of the activated carbon fibre. This is the main objective of this research.

2.7.2.3. Modification of adsorbents in gases

Otake and Jenkins (1993) modified granular activated carbon by oxidising the granular activated carbon (GAC) in flowing air at different temperatures (473-723 K) for different oxidation times (0.5-41 h). They observed carboxylic functional groups on the air oxidised GAC. They also observed that sodium capacity increased with increase in time of air oxidation. Maximum sodium capacity of 3.22 mmol/g was observed for air oxidised GAC at 698 K for 11 h. They also studied the adsorption of Ba²⁺ from aqueous solutions onto the air oxidised GAC and observed the maximum Ba²⁺ adsorption capacity of 1.55 mmol/g for air oxidised GAC. This was attributed to the addition of oxygen containing weakly acidic functional groups onto the surface of the GAC by air oxidation.

Figueiredo et al. (1999) modified Norit Rox activated carbon in 5% oxygen in nitrogen at 698 K for different oxidation times or in 50% nitrogen oxide in nitrogen at 773 K for 8 h. They observed that oxidation in oxygen in nitrogen and nitrogen oxide in nitrogen increased the concentration of hydroxyl and carbonyl surface groups.

Goyal et al. (2001) modified granular activated carbon (GAC) and activated carbon fibre (ACF) by modifying 5 g of GAC or ACF in a flow of 2 L/h of pure and dry oxygen at 623 K for 4 h. They observed an increase in oxygen content from 7.6% for
unoxidised ACF to 11.02% for oxygen oxidised ACF. They also observed an increase in oxygen content from 5.12% for unoxidised GAC to 10.4% for oxygen oxidised GAC. The cation exchange (sodium) capacity increased from 0.24 mmol/g for unoxidised ACF to 3.05 mmol/g for oxygen oxidised ACF and 0.48 mmol/g for unoxidised GAC to 1.22 mmol/g for oxygen oxidised GAC. They studied the adsorption of copper(II) ions from aqueous solutions by the unoxidised and oxygen oxidised ACF and GAC and observed an increase in maximum copper(II) adsorption capacities for the oxygen oxidised ACF from 0.14 mmol/g for unoxidised ACF to 0.24 mmol/g for oxygen oxidised ACF. They also observed an increase in maximum copper(II) adsorption capacities for the oxygen oxidised GAC from 0.47 mmol/g for unoxidised GAC to 0.51 mmol/g for oxygen oxidised GAC. The increase in maximum copper(II) adsorption capacities for oxygen oxidised ACF and GAC was attributed to the introduction of oxygen containing functional groups onto the ACF and GAC surfaces by oxygen oxidation.

Saha et al. (2001b) modified coal-based granular activated carbon (GAC) by oxidising the GAC in flowing air at 693 K for 24 h. They observed a decrease in BET surface area from 1210 m²/g for unoxidised GAC to 916 m²/g for air oxidised GAC. This was attributed to chemical reaction and etching by the air oxidation process. However, an increase in sodium capacity for air oxidised GAC was observed. The sodium capacity increased from 0.5 mmol/g for unoxidised GAC to 2.1 mmol/g for air oxidised GAC. FTIR analysis detected the presence of carboxylic acid groups on the air oxidised GAC. The PZC was observed at pH 6.83 for unoxidised GAC, whereas it shifted to pH 4.07 for air oxidised GAC. Finally, a drop in isoelectric point from pH 4.95 for unoxidised GAC to pH 1.25 for air oxidised GAC was observed.

Saha et al. (2003) modified pine wood-based granular activated carbon (GAC) by oxidising the GAC in flowing air at 693 K for 24 h. FTIR analysis detected the presence of hydroxyl groups on the unoxidised GAC and air oxidised GAC and the presence of weakly acidic groups on the air oxidised GAC. They observed a slight increase in BET surface area from 672 m²/g for the unoxidised GAC to 686 m²/g for the air oxidised GAC. No significant difference in isoelectric point was observed for the unoxidised GAC and air oxidised GAC (isoelectric points are close to pH 2). The PZC shifted from pH 4.4 for the unoxidised GAC to pH 3.6 for air oxidised GAC.
They also studied the adsorption of copper(II) from aqueous solutions at solution pH 4.7 and 298 K onto the air oxidised GAC and observed the maximum copper(II) adsorption capacity of 0.38 mmol/g for air oxidised GAC. This was attributed to the addition of oxygen containing weakly acidic functional groups onto the surface of the GAC by air oxidation.

2.7.2.3.1. Conclusions

Table 2.8 shows the comparison of modification conditions in different gases, surface properties of adsorbents modified in different gases and the different maximum adsorption capacities for the adsorbents modified in gases shown in the literature review in this section. It is obvious that the highest cation exchange (sodium) capacity of 3.22 mmol/g was observed for air oxidised GAC (Otake and Jenkins 2002). However, this cation exchange capacity is lower than the highest cation exchange

<table>
<thead>
<tr>
<th>MODIFICATION CONDITIONS</th>
<th>SURFACE PROPERTIES DUE TO MODIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent</td>
<td>Gas used</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>Flowing air</td>
</tr>
<tr>
<td>Activated carbon fibre</td>
<td>Dry oxygen flowing at 2 L/h</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>Dry oxygen flowing at 2 L/h</td>
</tr>
<tr>
<td>Coal-based GAC</td>
<td>Flowing air</td>
</tr>
<tr>
<td>Pine wood-based GAC</td>
<td>Flowing air</td>
</tr>
</tbody>
</table>

Table 2.8. Comparison of modification conditions in different gases, surface properties of adsorbents modified in different gases and the different maximum adsorption capacities for the adsorbents modified in gases.
exchange capacity of 5.44 mmol/g obtained by nitric acid oxidation (Table 2.6) with surface etching. There was no etching on the surfaces of all the modified adsorbents. However, it is obvious that maximum metal adsorption capacities of all the adsorbents modified in gases that are shown in Table 2.8 are very low, except the maximum $\text{Ba}^{2+}$ adsorption capacity of 1.55 mmol/g for air oxidised GAC (Otake and Jenkins 2002). As discussed in chapter 1, granular activated carbon is economically favourable, but with technically difficult process when compared to activated carbon fibre. Very low maximum $\text{Cu}^{2+}$ adsorption capacity of 0.24 mmol/g was observed for oxygen oxidised ACF (Goyal et al., 2001). Therefore, it is necessary to find another method of modification of activated carbon fibre that will greatly enhance its metal ion sorptive capacity but will not damage the physical structure of the activated carbon fibre. This is the main objective of this research.

2.7.3. Electrochemical Oxidation of Adsorbents

In recent years many research studies dealing with environmental applications of electrochemistry have demonstrated that many compounds can be treated by electrochemical oxidation instead of traditional methods like chemical oxidation, dry oxidation and thermal treatments. Electrochemical oxidation has been reported to result in oxygenated products or in electrophilic species that react with unsaturated compounds, depending on the experimental conditions (Park and Kim, 2001). The oxidised carbons possess some unique properties caused by oxygen-containing functional groups such as carboxylic, lactonic and phenolic groups on their surfaces (Boehm, 1966; Park and Jang, 2002). These surface functional groups make the carbon surfaces hydrophilic and increase their adsorption capacities and adsorption rates in liquid phase so that these carbons are potential adsorbents for the removal of metal ions from industrial and domestic wastewaters. Another reason for electrochemical oxidation of carbon fibres in recent years is to improve their adhesion characteristics in composite materials. The properties of composite materials are not only governed by the individual components but also by the interface separating them. Good interfacial bonding between composite constituents is necessary to couple their properties and enable adequate stress transfer. Carbon fibres represent an important class of composite reinforcement due to the specific strength and stiffness of the carbon fibres (Waseem et al., 1998). These properties are derived from the graphitic microstructure of the fibres and the preferential alignment of graphitic crystallites.
along the fibre axis. Unfortunately, the adhesion characteristics of carbon fibres are often poor due to the high percentage of graphitic basal planes on the surfaces (Waseem et al., 1998). These basal planes are quite inactive chemically and so it is necessary to modify the carbon fibre surfaces in order to enhance the adhesive properties. Surface treatments may be beneficial to carbon fibre surfaces in several ways, e.g. by removing weak boundary layers and impurities, a more robust fibre surface is exposed. The fibre surface roughness may also be increased, promoting physical interlocking with the matrix. Surface modification may also enhance the surface density of reactive functional groups. Depending upon the specific composite system, these functional groups may contribute to adhesion by enhancing the wetting characteristics of the fibres and creating the potential for chemical reaction with components in the matrix, which is particularly important with respect to improving adhesion. Phenol, hydroxyl and carboxyl groups on the oxidised carbon fibre surfaces can react with epoxy functions or amine curing agents present in the matrix to form fibre to matrix covalent bonds. So the adhesive strength at the interface region of a composite is normally controlled by surface oxidation of the carbon fibre. To develop an oxidative treatment method and to determine the relationship between the degree of oxidation and adhesive strength is therefore very important in order to obtain the desirable mechanical properties of carbon fibre-reinforced plastic. Various surface oxidation treatments, such as dry gaseous oxidation, anodic oxidation, chemical oxidation and plasma treatment have been used for this purpose. Among these surface treatment methods, the anodic oxidation process is normally employed for commercial use, because it is easy to control and suitable for continuous oxidation processes (Yumitori and Nankanishi, 1996a). Some relevant publications on electrochemical oxidation are reviewed and presented in this section.

Horita et al. (1996) oxidised 100 mg of carbon black electrochemically in 0.1 M potassium hydroxide solution with a constant current of 6 mA for 10 min to produce a high functional surface for use in battery electrodes. They observed that the surface of the sample changed from hydrophobic to hydrophilic with the treatment. This was attributed to the formation of surface oxides by the treatment. They also observed an increase in pore volume from 0.75 cm$^3$/g to 0.87 cm$^3$/g due to the oxidation.
Yumitori and Nankanishi (1996a) compared the effect of anodic oxidation in two electrolytes of coal tar pitch-based carbon fibres on adhesion in epoxy matrix. The electrolytes used were 0.05 M sulphuric acid and 0.05 M sodium hydroxide. They oxidised the carbon fibres at electrical charge of $1.5 \times 10^4$-18.4 $\times 10^4$ c/mm$^2$. The current density was controlled at 0.03 mAm$^{-2}$. After oxidation the fibres electrochemically oxidised in sodium hydroxide were neutralised with 0.1 M hydrochloric acid and those electrochemically oxidised in sulphuric acid were neutralised with 0.1 M sodium hydroxide. They observed that the oxygen content of the acid treated fibre was twice as high as that of the base treated fibre. They also observed that hydroxyl and carboxyl groups increased with an increase in the extent of oxidation in both solutions while carbonyl group decreased with an increase in the extent of oxidation. Disordered structures were observed on the surfaces of both oxidised fibres, although it was more on the acid treated fibres. In a subsequent study Yumitori and Nankanishi (1996b) also compared the effect of anodic oxidation on carbon fibres in three alkaline solutions. They used 0.05 mol/L sodium hydroxide, saturated sodium bicarbonate and saturated sodium carbonate solutions as electrolytes. They electrochemically oxidised the carbon fibres in each electrolyte at different electrical charge, $1.23 \times 10^4$-1.73 $\times 10^3$ c/mm$^2$. The current density was controlled at 0.03 mAm$^{-2}$. The highest oxygen content was observed on the fibres electrochemically oxidised in sodium hydroxide while those electrochemically oxidised in sodium carbonate had the lowest oxygen content. They also observed degradation of fibres due to electrochemical oxidation in the following order NaOH > NaHCO$_3$ > Na$_2$CO$_3$.

Waseem et al. (1998) studied the adhesive properties of electrochemically oxidised PAN-based activated carbon fibres in 1 or 2 wt% potassium nitrate at various extent of electrochemical oxidation (e.g. 96-4294 c/g). They noticed the presence of hydroxyl, carboxyl and carbonate groups on the oxidised fibre surfaces. They observed that the oxygen content increased with an increase in the extent of oxidation. An increase in hydroxyl groups in the outermost layers was noticed on fibres oxidised at 112 c/g while an increase in carboxyl groups was noticed in fibres oxidised at 4,112 c/g. An increase in sodium capacity from 0.00264 mmol/g for the unoxidised fibre to 1.078 mmol/g for fibre oxidised at 4,294 c/g was also observed. The sodium capacity increased with an increase in the extent of oxidation. However, the detected acidic group by sodium hydroxide titration was much higher than those detected by X-ray
photoelectron spectroscopy (XPS) experiment. This was attributed to the fact that the surface titration experiments quantify an absolute number of acidic groups per gram of carbon fibre to the depth that is governed by the characteristic dimensions of the fibre porosity and microstructure, which is unlike XPS experiment that measures the relative concentration of oxygen and carbon within a sampling depth of approximately 10 nm. So an increase in oxidation had occurred beyond the XPS sampling depth. They also observed an increase in BET surface area from 0.67 m²/g for unoxidised fibres to 2.9 m²/g for fibres oxidised at 4,294 c/g.

Bismark et al. (1999a) electrochemically oxidised PAN based carbon fibres to study their surface and mechanical characteristics and their effect on the adhesion properties to a polycarbonate matrix. They oxidised the PAN-based fibres, using 1:1 mixture of 0.1 M potassium hydroxide and 0.5 M potassium carbonate (K₂CO₃/KOH) or 0.1 M potassium hydroxide and 0.5 M potassium nitrate (KNO₃/KOH) electrolyte solution. They oxidised the fibres at 10 A/g for 2.5, 5 and 10 min giving a maximum extent of electrochemical oxidation of 6000 c/g. Mass loss was detected more in K₂CO₃/KOH treated fibres (16% mass loss) than in KNO₃/KOH treated fibres (15.3% mass loss). Carbon fibres oxidised in KNO₃/KOH showed a gradual increase in oxygen content with an increase in the oxidation time. They observed that potassium began to appear on the carbon fibre after 5 min of electrochemical oxidation and increased with an increase in the time of oxidation. This was attributed to the formation of the carboxylic groups which reacted with the electrolyte solution by an acid-base reaction to form the potassium salts of these groups. They also observed that the unoxidised fibre had 3.6% oxygen content, while the KNO₃/KOH treated fibre had 24% oxygen content and the K₂CO₃/KOH treated fibre had 15.3% oxygen content. Compared to the unoxidised fibre the relative concentration of carbonyl and carboxyl groups increased drastically. The isoelectric point (the pH at which there is no charge on the external surface of the adsorbent) for unoxidised fibre was at pH 4. The K₂CO₃/KOH and KNO₃/KOH treated fibres shifted to more acidic values due to the higher surface functionalisation by dissociable acidic groups. However, the isoelectric points for the K₂CO₃/KOH and KNO₃/KOH treated fibres were not measurable because the proton concentration of the bulk electrolyte solution used for the zeta potential measurement is too low. The negative zeta potential plateau-values increased indicating further oxidation of carbonyl (C=O) and hydroxyl (C-OH) groups to carboxyl (COOH) groups. In the case
of KNO₃/KOH treated fibres, the negative zeta potential plateau-values decreased with an increase in the time of oxidation due to formation of some carboxylate (COO⁻K⁺) groups which reduced the concentration of dissociable functional groups on the surface.

Park et al. (1999b) electrochemically oxidised phenol-based activated carbon fibres to increase their Cr(VI) adsorption rate and amount. They used 35 wt% sodium hydroxide as the electrolyte and oxidation was performed at 398 K and different current densities of 5-450 mA/m². They observed that BET specific surface area and micropore volume of the oxidised carbon fibres were similar to those of the unoxidised fibres. An increase in the NaOH uptake from 0.325 mmol/g for the unoxidised fibre to 0.812 mmol/g for fibre oxidised at 450 mA/m² was also observed. FTIR analysis detected the presence of hydroxyl groups on the unoxidised fibre and electrochemically oxidised fibre. However, the presence of ether was also detected on electrochemically oxidised fibre. This was attributed to electrochemical oxidation in basic electrolyte, that is, sodium hydroxide. They also studied the adsorption of chromium(VI) from aqueous solutions onto the unoxidised fibre and electrochemically oxidised fibre and observed an increase in maximum chromium(VI) adsorption from 0.293 mmol/g for unoxidised fibre to 0.372 mmol/g at solution pH 3 and 298 K for the electrochemically oxidised fibre. The slight increase in maximum chromium(VI) adsorption capacity was attributed to the introduction of ether groups that are more basic than hydroxyl groups by electrochemical oxidation of the fibre in sodium hydroxide. Therefore at solution pH 3 the electrochemically oxidised fibre was more protonated than the unoxidised fibre and so attracted and adsorbed more negatively charged chromium(VI) ions. They concluded that anodic oxidation of carbon fibres leads to an increase in the surface functional groups without significantly changing the surface area.

Pittman Jr. et al. (1999a) electrochemically oxidised PAN-based activated carbon fibres to study the effect of the oxidation on the surface area and pore size distribution of the fibres. They used 1 wt% potassium nitrate as electrolyte at different constant currents, from 0.1-1 A for different oxidation times to give 200-10600 c/g extent of oxidation. They observed that electrochemical oxidation alters both the surface chemistry and pore structure of the fibres. They related these alterations to the
introduction of surface oxygen functional groups and the removal of carbon atoms through gasification. XPS results showed that mild electrochemical oxidation leads to a significant external surface enrichment in oxygen up to a level which remains essentially constant with an increase in the severity of oxidation. They observed that this was in contrast with sodium hydroxide uptake results which increased linearly with an increase in the severity of oxidation. The sodium hydroxide uptake results were 0.0097 mmol/g for unoxidised carbon fibre, 1.19 and 2.5 mmol/g for fibres electrochemically oxidised at 4,237.9 and 10,600 c/g, respectively. The difference in the two results was attributed to the fact that sodium hydroxide neutralisation probes chemically and physically accessible acidic sites such as carboxyl, lactone and phenol functional groups (Boehm, 1966; Leon y Leon and Radovic, 1994). The XPS result alone cannot account for the changes in the quality and quantity of acidic groups located on the surface of the carbon fibre, since at an electron take-off angle of 30°, XPS can only probe the external fibre surface down to a depth of 4 nm of the fibre surface (Gardner et al., 1996; Pittman Jr. et al., 1997; Pittman Jr. et al., 1998). Also sodium hydroxide titrates accessible acidic functional groups which may reside in pore walls located well below the external fibre surface. They suggested that sodium hydroxide uptake would give high acidic surface group content if:

1. Each sodium hydroxide equivalent was able to titrate more than one acidic group.

2. Sodium hydroxide exposed more surfaces by leaching out additional oxidation products, e.g. benzene hexacarboxylic acid from water-washed fibres.

3. Intercalating forces managed to overcome solvation forces upon oxidation due to increase in average graphene interlayer distances.

They concluded that sodium hydroxide uptake results indicate that the electrochemical oxidation process introduces acidic groups which are homogeneously spread throughout the fibre surface. In contrast, other oxidation treatments are known to introduce functional groups which are not uniformly distributed throughout the surfaces of porous carbons, with their external surfaces being richer in oxygen than their internal surfaces (Leon y Leon and Radovic, 1994; Menendez et al. 1995; Gardner et al., 1996). In a subsequent study Pittman Jr. et al. (1999b) electrochemically oxidised PAN-based carbon fibres to enhance their properties for composite reinforcement. They oxidised the fibres in 1 wt% potassium nitrate at different applied currents, 0.1-0.6 A for different oxidation times, 10-180 min. They
observed an increase in sodium hydroxide uptake as the applied current was increased at constant oxidation time. Sodium hydroxide uptake also increased as the oxidation time was increased at constant applied current. The sodium hydroxide uptake was 1.15 mmol/g at 6,360 c/g extent of oxidation and 2.5 mmol/g at 10,600 c/g extent of oxidation. They suggested that aqueous sodium hydroxide was able to swell some of the porous internal surfaces via powerful exothermic solvation forces, which include ionisation of acidic sites, solvation of the resulting ions and significant capillarity between the aqueous phase and the hydrophilic oxygenated pore surfaces. Therefore ultra micropores could be opened and penetrated by aqueous sodium hydroxide. They observed the presence of carbonyl, carboxyl, ether and ester groups on the oxidised carbon surfaces. They concluded that electrochemical oxidation generates acidic and other oxygenated functions on the surfaces of a microporous region which extends below the outer depth of the fibres considerably in excess of 50 Å. So electrochemical oxidation penetrates increasingly deeper into the carbon fibres as the extent of oxidation increases. They also observed that adsorption of silver, methylene blue and iodine increased with an increase in the extent of oxidation for the electrochemically oxidised fibre. However, the silver adsorption capacity was much higher than methylene blue and iodine adsorption capacities. The maximum silver, methylene blue and iodine adsorption capacities were 3.5, 0.5 and 0.25 mmol/g, respectively at solution pH 10 and 298 K.

Yue et al. (1999b) observed a similar difference between XPS and sodium hydroxide uptake results when they electrochemically oxidised PAN-based activated carbon fibres for surface characterisation. They also used 1 wt% potassium nitrate as electrolyte but electrochemically oxidised at 133-10,600 c/g extent of oxidation. XPS analysis showed that the surface oxygen concentration rose rapidly to 24% after initial electrochemical oxidation at 133 c/g and then remained at this level with an increase in the extent of oxidation up to 10,600 c/g. However, the total amount of oxygen containing acidic functional groups detected by sodium hydroxide titration increased from 0.003 mmol/g for unoxidised carbon fibre to 1.06 mmol/g for carbon fibre electrochemically oxidised at 6,360 c/g and then finally increased to 2.48 mmol/g for carbon fibre electrochemically oxidised at 10,600 c/g. They inferred that the large increase in acidic functional groups that accompanied fibre weight loss means that the overall oxygen content should have continually increased with progressive oxidation.
This deduction contrasts sharply with the XPS result, therefore they concluded that electrochemical oxidation continually generates micropore, void and slit structures that penetrate increasingly deeper below the outer fibre surface as oxidation progresses. They proposed that, since XPS analysis can only sample the outer 50 Å of the fibre, further increase in carboxylic and phenolic groups by electrochemical oxidation primarily occurred below the sampling depth of XPS experiment. They also concluded that oxygen functional groups mainly exist on the internal pore slit and void surfaces and not within graphitic sheets and most likely, lateral planes are oxidised progressively forming pores and slits which interconnect and link as they move increasingly deeper into the fibre. This was also confirmed with FTIR studies that showed an increase in ketone and carboxyl groups within the fibre with increase in extent of oxidation. In a previous study, Yue et al. (1999a) also electrochemically oxidised carbon fibres in 1 wt% potassium nitrate at different extents of oxidation, 133-9,540 c/g. They compared the adsorption capacity of silver (Ag⁺) for electrochemically oxidised fibres with those for oxygen plasma-treated carbon fibres and nitric acid treated fibres. They observed a slight decrease in the quantity of Ag⁺ adsorbed onto oxygen plasma-treated carbon fibre from 0.0386 mmol/g for unmodified fibre to 0.0378 mmol/g. The BET surface area remained approximately constant as plasma oxidation continued. For nitric acid oxidised fibres an increase in Ag⁺ adsorption was observed from 0.0386 mmol/g for the unmodified fibre to 0.631 mmol/g. In contrast to oxygen plasma and nitric acid treated fibres, electrochemically oxidised carbon fibres adsorbed a prodigious amount of Ag⁺ with progressive oxidation. The amount of Ag⁺ adsorbed reached 3.75 mmol/g at 6000 c/g extent of oxidation. They therefore, concluded that extensive electrochemical oxidation produced special, highly porous carbon fibres with high Ag⁺ adsorption capacity. Such fibres might have potential uses in precious metal recovery. They also compared the Ag⁺ adsorption capacity with gold (Au³⁺) adsorption capacity for the electrochemically oxidised fibres. They observed that the amount of Ag⁺ adsorbed was always about three times that of Au³⁺ adsorbed. This was attributed to the fact that based on stoichiometry, Au³⁺ needs three electrons to produce Au⁰ but Ag⁺ needs only one to give Ag⁰. However, the amount of Au³⁺ adsorbed also increased with an increase in the extent of oxidation. The amount of Au³⁺ adsorbed onto the electrochemically oxidised fibre reached 0.741 mmol/g at 6000 c/g extent of electrochemical oxidation. They further conducted XPS analysis of the oxidised fibres.
after Ag$^+$ and Au$^{3+}$ adsorption and observed the presence of Ag$^0$ and Au$^0$ on the outermost surface of the fibres. So redox adsorption of Au$^{3+}$ and Ag$^+$ onto the electrochemically oxidised fibres as Au$^0$ and Ag$^0$ was confirmed by X-ray diffraction. Reduction of precious metal ions by various activated carbon surfaces has been reported by other researchers (Ehrburger et al., 1987; Heal and Mkayula 1988; Fu et al., 1993; Fu et al., 1994; Fu et al., 1995).

Rangel-Mendez and Streat (2002a) studied mercury and cadmium sorption performance of a weakly acidic fibrous ion exchanger (K-4) and wood-based granular activated carbon (WHK). They electrochemically oxidised the granular activated carbon at a current density of 3 mA/m$^2$ using different electrolytes, 0.5 M potassium chloride (KCl), potassium nitrate (KNO$_3$), ammonium bicarbonate (NH$_4$HCO$_3$) or nitric acid (HNO$_3$). The K-4 already had weakly acidic functional groups on it, therefore needed no further oxidation. It had sodium capacity of 4.28 mmol/g while the unoxidised WHK had sodium capacity of 1.27 mmol/g. However, a significant increase in sodium capacity for the WHK was obtained after electrochemical oxidation. The sodium capacities for the electrochemically oxidised WHKs were observed as 1.37 mmol/g for KNO$_3$ oxidised WHK, 1.39 mmol/g for NH$_4$HCO$_3$ oxidised WHK, 1.69 mmol/g for HNO$_3$ oxidised WHK and 2.57 mmol/g for KCl oxidised WHK. Since the highest sodium capacity was obtained for the KCl oxidised WHK and sodium capacity data gives an indication of the cation exchange capacity of adsorbents in aqueous solutions, they concluded that adsorbents electrochemically oxidised in KCl will be potential adsorbents for trace metal removal from wastewater. They attributed the increase in sodium capacity to the introduction of weakly acidic functional groups on the carbon surface by electrochemical oxidation. They also concluded that the WHK was more strongly oxidised in KCl than other electrolytes because the chlorine and hypochlorous acid (HOCl) that is formed when chlorine is present in water are well known strong oxidants (Chernow and Vallasi, 1993). XPS analysis showed that the highest concentration of surface functional group on the electrochemically oxidised WHK was a lactone group, followed by carbonyl, carboxyl and phenol groups. So the high sodium capacities for the electrochemically oxidised WHK and K-4 were attributed to the presence of carboxylic acid functional groups on the surfaces of WHK and K-4. The isoelectric points (IEP) for unoxidised and electrochemically oxidised WHK in KCl were observed at pH 2.19 and pH 0.96
respectively. They noticed that BET surface area decreased from 1,935 m$^2$/g for unoxidised WHK to 702 m$^2$/g for electrochemically oxidised WHK in KCl. This was attributed to blockage of pores by broken graphene planes, surface oxygen complexes and solid by-products generated during electrochemical oxidation. This was confirmed by elemental analysis that showed an increase in oxygen content from 21.62% for unoxidised WHK to 32.84% for electrochemically oxidised WHK in KCl. They evaluated the sorption capacity of K-4, the unoxidised WHK and the electrochemically oxidised WHK in KCl for cadmium and mercury. They observed that the maximum cadmium sorption capacity increased from 0.08 mmol/g for the unoxidised WHK to 1.2 mmol/g for the electrochemically oxidised WHK in KCl. This was 15 times greater than the maximum cadmium sorption capacity for the unoxidised WHK. The maximum mercury sorption capacity also increased from 0.15 mmol/g for the unoxidised WHK to 1.4 mmol/g for the electrochemically oxidised WHK in KCl, which was 9.3 times greater than the mercury sorption capacity for the unoxidised carbon. They also noticed that the maximum cadmium sorption capacity for K-4 was 1.8 mmol/g while the maximum mercury sorption capacity was 1 mmol/g. They therefore, concluded that K-4 is more effective for the removal of cadmium than mercury. In a subsequent study Rangel-Mendez and Streat (2002b) also oxidised PAN-based activated carbon cloth (ACC), by ozone oxidation, nitric acid oxidation or electrochemical oxidation, to enhance its adsorption capacity. They used 0.5 M potassium chloride as electrolyte for electrochemical oxidation and current density of 3 mA/m$^2$ for 1, 2 and 3 h at 298 K. For nitric acid oxidation, 2 g of the ACC was oxidised in 80 ml of 8 M nitric acid at 363 K for 1, 2 and 3 h. For ozone oxidation, 1 g of ACC was oxidised in air/ozone mixture from ozonator at 294 K for 1, 2 and 3 h. They observed a decrease in BET surface area after 3 h of oxidation from 973 m$^2$/g for the unoxidised ACC to 627 and 730 m$^2$/g for electrochemically oxidised ACC and nitric acid oxidised ACC, respectively. The reduction in surface area was attributed to erosion by nitric acid oxidation and blockage of pores by oxygen functional groups produced during electrochemical oxidation. However, the oxygen content increased from 12.1% for unoxidised ACC to 15.7, 19.3 and 20.4% for nitric acid oxidised ACC, ozone oxidised ACC and electrochemically oxidised ACC, respectively. They observed that PZC for the unoxidised ACC was at pH 4.2 whereas it shifted to pH 2.4 for nitric acid oxidised ACC, pH 2.8 for ozone oxidised ACC and pH 2.25 for electrochemically oxidised ACC. The PZC is defined as the pH value at which the
surface charge is zero at a particular ambient temperature, applied pressure and aqueous solution composition (Garrison, 1998; Babic et al., 1999). They therefore, concluded that the PZC depended on the level of oxidation. It shifted to lower values as the degree of oxidation increased due to the introduction of acidic groups such as carboxyl, phenol, carbonyl and lactone groups (Donnet and Bansal, 1984). They concluded that the surface of the ACC is positively charged at solution pH values below the PZC since the oxygen-containing groups are not dissociated and are protonated, so the adsorbent will remove anionic species from solutions under these conditions. On the other hand at solution pH values above the PZC, the surface of the ACC becomes negatively charged due to dissociation of acidic oxygen-containing groups. The acidic oxygen-containing groups start dissociating at different solution pH values and the dissociation increases with increase in solution pH e.g. carboxylic groups dissociate between solution pH 2 and 6. Thus the adsorbent surface is able to attract and exchange cations in solution. They also observed that sodium capacity increased with an increase in the time of oxidation. The maximum sodium capacity results were obtained for ACCs oxidised for 3 h and were 3.8 mmol/g for nitric acid oxidised ACC, 5.27 mmol/g for ozone oxidised ACC and 6.13 mmol/g for electrochemically oxidised ACC. No visual change in surface morphology was observed on the electrochemically oxidised ACCs up to 3 h of electrochemical oxidation. However, surface etching was observed for ozone oxidised ACC and nitric acid oxidised ACC. The surface etching was more severe for ozone oxidised ACC. They also observed that the maximum cadmium sorption capacity of the electrochemically oxidised ACC increased by a factor of 13. This was attributed to the increase in oxygen-containing groups as detected by the XPS analysis. The maximum cadmium adsorption capacities at solution pH 5 increased from 0.1 mmol/g for unoxidised ACC to 0.95 mmol/g for nitric acid oxidised ACC, 1.075 mmol/g for ozone oxidised ACC and 1.325 mmol/g for electrochemically oxidised ACC. They finally concluded that electrochemically oxidised ACC in potassium chloride has considerable potential as an adsorbent for large-scale removal of trace metal pollutants from water and aqueous effluent at neutral or near-neutral solution pH values.

2.7.3.1. Conclusions

Table 2.9 shows the comparison of electrochemical oxidation conditions in different electrolytes, surface properties of different electrochemically oxidised adsorbents and
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Electrolyte</th>
<th>Current density (mAm⁻²) or extent of oxidation (c/g)</th>
<th>PZC</th>
<th>Functional group</th>
<th>Applied process Max. metal adsorption capacity (mmol/g)</th>
<th>Effect on surface morphology and wt. loss</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal tar pitch-based ACF</td>
<td>0.05 M H₂SO₄</td>
<td>0.03 mAm⁻²</td>
<td>Hydroxyl, Carboxyl</td>
<td>Adhesion in epoxy matrix</td>
<td>Highly disordered structure</td>
<td>Yumitori and Nankanishi (1996a)</td>
<td></td>
</tr>
<tr>
<td>Coal tar pitch-based ACF</td>
<td>0.05 M NaOH</td>
<td>0.03 mAm⁻²</td>
<td>Carboxyl, Carbonyl</td>
<td>Adhesion in epoxy matrix</td>
<td>disordered structure</td>
<td>Yumitori and Nankanishi (1996a)</td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF 2 wt% KNO₃</td>
<td>4294 c/g</td>
<td></td>
<td>Hydroxyl, Carboxyl</td>
<td>Na⁺ 1.078</td>
<td>No effect</td>
<td>Waseem et al. (1998)</td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF   0.1 M KOH and 0.5 M K₂CO₃</td>
<td>6000 c/g</td>
<td>Carboxyl</td>
<td>Adhesion in epoxy matrix</td>
<td>16% wt. loss</td>
<td>Bismark et al. (1999a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF 0.1 M KOH and 0.5 M K₂NO₃</td>
<td>6000 c/g</td>
<td>Carboxyl</td>
<td>Adhesion in epoxy matrix</td>
<td>15.3% wt. loss</td>
<td>Bismark et al. (1999a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF   1 wt% KNO₃</td>
<td>4238 c/g</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na⁺ 1.19</td>
<td>No effect</td>
<td>Pittman Jr. et al. (1999a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF   1 wt% KNO₃</td>
<td>6360 c/g</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na⁺ 1.15</td>
<td>No effect</td>
<td>Pittman Jr. et al. (1999b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol-based ACF 35 wt% NaOH</td>
<td>450 mAm⁻²</td>
<td>Ether, Hydroxyl</td>
<td>Na⁺ 0.812</td>
<td>No effect</td>
<td>Park et al. (1999b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF   1 wt% KNO₃</td>
<td>6000 c/g</td>
<td>Carboxyl, Hydroxyl</td>
<td>Ag⁺ 3.75</td>
<td>No effect</td>
<td>Yue et al. (1999a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACF   1 wt% KNO₃</td>
<td>10600 c/g</td>
<td>Carboxyl, Ketone</td>
<td>Na⁺ 2.476</td>
<td>No effect</td>
<td>Yue et al. (1999b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood-based GAC  0.5 M KCL</td>
<td>3 mAm⁻²</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na⁺ 2.57</td>
<td>No effect</td>
<td>Rangel-Mendez and Streat (1999)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood-based GAC  0.5 M NH₂HCO₃</td>
<td>3 mAm⁻²</td>
<td>Carboxyl, Carbonyl</td>
<td>Na⁺ 1.39</td>
<td>No effect</td>
<td>Rangel-Mendez and Streat (1999)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood-based GAC  0.5 M HNO₃</td>
<td>3 mAm⁻²</td>
<td>Carboxyl, Hydroxyl</td>
<td>Na⁺ 1.69</td>
<td>No effect</td>
<td>Rangel-Mendez and Streat (1999)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN-based ACC  0.5 M KCL</td>
<td>3 mAm⁻²</td>
<td>pH Carboxyl, Hydroxyl</td>
<td>Na⁺ 6.13</td>
<td>No effect</td>
<td>Rangel-Mendez and Streat (1999)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.9. Comparison of electrochemical oxidation conditions in different electrolytes, surface properties of different electrochemically oxidised adsorbents and the different applied processes for the electrochemically oxidised adsorbents.
the different applied processes for the electrochemically oxidised adsorbents shown in
the literature review in this section. From Table 2.9 it is obvious that high cation
exchange capacities were observed for electrochemically oxidised adsorbents in
potassium chloride and potassium nitrate, with highest cation exchange capacity of
6.13 mmol/g observed for electrochemically oxidised PAN-based activated carbon
cloth in potassium chloride (Rangel-Mendez and Streat, 2002b). It is also obvious that
surface etching that produced some disordered structures and weight losses were
observed for electrochemically oxidised coal tar pitch-based activated carbon fibres
and PAN-based activated carbon fibres in sodium hydroxide, sulphuric acid and
potassium hydroxide (Yumitori and Nankanishi, 1996a; Bismark et al., 1999a), with
highly disordered structure on electrochemically oxidised coal tar pitch-based
activated carbon fibre in sulphuric acid. However, no surface etching and weight loss
were observed on electrochemically oxidised pitch-based activated carbon fibre and
PAN-based activated carbon fibres in potassium chloride and potassium nitrate. It can
be concluded that electrochemical oxidation of carbon fibre using base or acid as
electrolyte damages the physical structure of carbon fibre, which is undesirable for any
potential adsorption process. However, it can be concluded that electrochemical oxidation of carbon fibre using salt as electrolyte and oxidising the carbon fibre under
conditions that produce carbon fibre with very high cation exchange capacity does not
damage the physical structure of carbon fibre, which is desirable for any potential
adsorption process. Rangel-Mendez and Streat (2002a) electrochemically oxidised
wood-based granular activated carbons under the same electrochemical oxidation
conditions, but using potassium chloride, potassium nitrate, ammonium bicarbonate or
nitric acid as electrolyte. The sodium capacities for the electrochemically oxidised
wood-based granular activated carbons were observed as 1.37 mmol/g for potassium
nitrate oxidised wood-based granular activated carbon, 1.39 mmol/g for ammonium
bicarbonate oxidised wood-based granular activated carbon, 1.69 mmol/g for nitric
acid oxidised wood-based granular activated carbon and 2.57 mmol/g for potassium
chloride oxidised wood-based granular activated carbon. Since the highest sodium
capacity was obtained in the potassium chloride oxidised wood-based granular
activated carbon and sodium capacity data gives an indication of the cation exchange
capacity of adsorbents in aqueous solutions, it can be concluded that potassium
chloride is the best electrolyte for electrochemical oxidation of granular activated
 carbons and activated carbon fibres to enhance the cation exchange capacities of
granular and fibrous activated carbons. However, no determination of optimum current and electrochemical oxidation time at an extent of electrochemical oxidation of activated carbon fibre that will enhance its metal ion sorptive capacity but will not damage its physical structure was done. Therefore, it is necessary to find optimum current and electrochemical oxidation time at an extent of electrochemical oxidation of activated carbon fibre that will enhance its metal ion sorptive capacity but will not damage the physical structure of the activated carbon fibre. This is the main objective of this research.

2.7.4. Final Conclusions

Table 2.10 shows the comparison of maximum cation exchange capacities obtained by different modification processes and adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Modification section</th>
<th>Modification conditions</th>
<th>PZC</th>
<th>Effect on surface morphology</th>
<th>Maximum adsorption capacity ((q_e)) (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN-based ACC</td>
<td>Ozone modification</td>
<td>10 vol% (O_3) in (O_2) at 294 K for 3 h</td>
<td>pH 2.8</td>
<td>Elaborate etching</td>
<td>(Na^+) 5.8; (Cd^{2+}) 1.15</td>
<td>Rangel-Mendez and Streat (2002b)</td>
</tr>
<tr>
<td>Coconut shell-based GAC</td>
<td>Nitric acid modification</td>
<td>7.5 M (HNO_3) at 368 K for 72 h</td>
<td>pH 2.53</td>
<td>Etching</td>
<td>(Na^+) 5.44; (Ca^{2+}) 0.24; (Cd^{2+}) 0.307; (Pb^{2+}) 0.573; (Hg^{2+}) 1.293</td>
<td>Xiao and Thomas (2004)</td>
</tr>
<tr>
<td>Shell-based GAC</td>
<td>Modification in different chemicals</td>
<td>35 wt% (HCL) at 298 K for 24 h</td>
<td>pH 2.5</td>
<td>No effect</td>
<td>(Na^+) 2.77; (Cl^-) 0.07</td>
<td>Park and Jang (2002)</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>Modification in gases</td>
<td>Flowing air at 698 K for 11 h</td>
<td>No effect</td>
<td>(Na^+) 3.22; (Ba^{2+}) 1.55</td>
<td>Otake and Jenkins (1993)</td>
<td></td>
</tr>
<tr>
<td>PAN-based ACC</td>
<td>Electrochemical oxidation</td>
<td>0.5 M (KCL) with current density of 3 mAm(^{-2})</td>
<td>pH 2.25</td>
<td>No effect</td>
<td>(Na^+) 6.13; (Cd^{2+}) 1.325</td>
<td>Rangel-Mendez and Streat (2002a)</td>
</tr>
</tbody>
</table>

Table 2.10. Comparison of maximum cation exchange capacities obtained by ozone modification of adsorbents, modification of adsorbents in different chemicals, modification of adsorbents in gases and electrochemical oxidation of adsorbents.
ozone modification of adsorbents, nitric acid modification of adsorbents, modification of adsorbents in different chemicals, modification of adsorbents in gases and electrochemical oxidation of adsorbents and surface properties of adsorbents with maximum cation exchange capacities obtained by the different methods of modification from the articles reviewed in all the sections of modification of adsorbents. From Table 2.10 it is obvious that the highest cation exchange capacity of 6.13 mmol/g was observed for electrochemically oxidised PAN-based activated carbon cloth in potassium chloride without etching. This observation confirm that among all the modified adsorbents in this review, the highest cation exchange capacity was observed for modified activated carbon cloth that is economically favourable, with technically easy process, as shown in chapter 1. However, very few reports of electrochemical oxidation of adsorbents to enhance the cation exchange capacities of the adsorbents can be found in the literature. There is a lack of detailed investigation on the surface effects of this treatment in adsorption processes. Finally, no report of electrochemical reduction of adsorbent to enhance the anion exchange capacity of the adsorbent is found in literature and no determination of optimum current and electrochemical oxidation time at an extent of electrochemical oxidation of activated carbon fibre that will enhance its metal ion sorptive capacity but will not damage its physical structure was found in literature. Therefore, the objectives of this research are as shown in section 1.3.

From the total 33 publications of literature reviewed in sections 2.2 and 2.3, 24 publications showed increase in Pb\(^{2+}\) and Cu\(^{2+}\) adsorption with increase in solution pH. Therefore, it can be concluded that the solution pH plays a very important role on the adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) onto adsorbents and the adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) onto adsorbents increased with an increase in solution pH. However, the opposite was observed for the adsorption of chromium(VI) that exist as anions (CrO\(_4^{2-}\)) as discussed in section 1.1.3. From the total 18 publications of literature reviewed in section 2.5, 13 publications showed decrease in chromium(VI) adsorption with increase in solution pH. Therefore, it can be concluded that the solution pH plays a very important role on the adsorption of chromium(VI) ions onto adsorbents and the adsorption of chromium(VI) ions onto adsorbents decreased with an increase in solution pH. Finally, it can be concluded that adsorption of cations increase with an increase in solution pH, while adsorption of anions decrease with an increase in solution pH.
3. ADSORPTION THEORY

3.1. INTRODUCTION
This chapter covers some theoretical aspects of adsorption. Different types of adsorption and some conventional adsorption isotherms are discussed.

3.2. DIFFERENT TYPES OF ADSORPTION
Adsorption is the use of solids for removing substances from either gaseous or liquid solutions. It involves the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid. The adsorbing phase is the adsorbent and the material adsorbed at the surface of the adsorbing phase is the adsorbate. Adsorption is different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a solution. The term sorption is a general expression encompassing both processes. A substance present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the substance in the fluid-solid boundary region is higher than that in the bulk of the fluid. After some time, the adsorbent and the surrounding fluid equilibrate. The tendency of molecules from the fluid phase to adhere to the interface originates from the attractive forces between the molecules. More specifically, adsorption takes place to reduce the imbalance of attractive forces. Thermodynamically, adsorption is accompanied by a decrease in free energy as well as a decrease in entropy of the system (Puri, 1970). If accumulation at the interface arises from dispersion forces the phenomenon is known as physical adsorption (physisorption) and if it occurs as a consequence of exchange or sharing of electrons, giving rise to ionic or covalent bonds, the phenomenon is known

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forces of adsorption</td>
<td>By van der Waals forces</td>
<td>Chemical bonds formation</td>
</tr>
<tr>
<td>Identity of adsorbate</td>
<td>Retained</td>
<td>Altered</td>
</tr>
<tr>
<td>Temperature of adsorption</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Nature of adsorbed phase</td>
<td>Monolayer or multilayer</td>
<td>Monolayer only</td>
</tr>
</tbody>
</table>

Table 3.1. Comparison of physisorption and chemisorption.
as chemical adsorption (chemisorption). Puri (1970) stated that the enthalpy of adsorption is often used to differentiate between physical adsorption in which the value is usually less than 33 kJ/mole and chemical adsorption in which the value is much higher, usually between 84-418 kJ/mole. Comparison of the two processes is shown in Table 3.1.

### 3.2.1. Physisorption

Physical adsorption or physisorption occurs due to the presence of strong, non-specific van der Waals forces between adsorbate molecules and the atoms which compose the adsorbent surface. The van der Waals forces can induce dipole-dipole interaction and it can involve polar and non-polar molecules. Also, adsorption can be favoured by London interactions (hydrophobic bonding) between adsorbent and adsorbate or by dipole-dipole interactions of the polar molecules with one another and with polar groups of the adsorbent. In a case where non-polar molecules are involved, the attractive forces are due to instantaneous dipole caused by momentary distortion of the distribution of charge on one of the molecules. The electron motion in a molecule or an atom could lead to a rapidly oscillating dipole moment. The lack of symmetry of the electron distribution about the nucleus imparts a transient dipole moment to an atom or molecule. When in close proximity to a solid surface, each instantaneous dipole of an approaching molecule induces an oriented dipole moment in the surface molecule. The moments then interact to produce an instantaneous attraction between the positive end of one polar molecule to the negative end of a neighbouring polar molecule. Also, in physisorption the adsorbate may form monomolecular or multimolecular layers. Multimolecular layer formation starts at pressures approaching the saturation pressure of the adsorbate.

### 3.2.2. Chemisorption

Chemical adsorption or chemisorption occurs through the formation of chemical bonds. In chemisorption electrostatic bonding occurs through the process of ion exchange. The most important specific interactions are those between the counter ions and fixed ionic groups. Ion pairs and covalent bonds are formed when anions or cations in solution are adsorbed onto the ion exchange material and are replaced by equivalent quantities of ions of the same charge released by the ion exchange material. A prerequisite for chemisorption is the dissociation of all or part of the molecules in
the fluid phase and the dissociation of the functional groups of the adsorbent. However, the interactions between the counter ions and fixed ionic groups do not necessarily involve the formation of chemical bonds. The counter ions may be merely localised in the neighbourhood of the fixed ionic groups by the electrostatic attraction between charges of opposite sign. As a consequence, forces result from the electric charge of the individual atoms (Sweetland, 1997). A chemisorbed layer is only one molecule thick because the adsorbate molecules are linked to the surface by valency bonds. In carbons, the fraction which exists in the form of disordered, single, unstacked graphite-like layers is more susceptible to chemisorption, while the fraction which shows some degree of well-ordered parallel stacking is less susceptible to chemisorption. The disordered fraction is higher in microcrystalline carbons than crystalline carbons. At the same time there are many exposed defects, dislocations and discontinuities in the layer planes of the microcrystalline carbons, apart from the edges of the carbon layers. Such sites, called the active sites, are associated with high concentrations of unpaired electron spin centre and are expected to play a significant role in chemisorption. The surface carbon atoms located at the active sites, due to residual valences, show a strong tendency to chemisorb other elements like oxygen, nitrogen, chlorine, bromine, iodine and sulphur. This produces nonstoichiometric stable surface compounds called surface complexes. Many of the surface reactions of carbon arise either due to their tendency to chemisorb other elements or due to the existence of a superficial layer of chemically bonded elements (Puri, 1970). Oxygen is chemisorbed more readily than many other elements and the carbon-oxygen complexes are by far the most important in influencing surface reactions, surface behaviour, wetability and electrical and catalytic properties of carbon.

Toles et al. (1999) observed that metal uptake is a function of polar or acidic surface groups on the carbon. X-ray diffraction (XRD) in their study showed that activated carbons are usually graphitic in nature and small polyaromatic sheets with only a few aromatic rings per cluster exist in a disordered state relative to each other. The polyaromatic sheets are thought to be cross linked by oxygen atoms between them (Solum et al., 1995). These polyaromatic sheets often contain unpaired electrons and unsaturated valences on or near their edges where oxygen-bearing functions are thought to be located. Heteroatoms provide the charged groups in the carbon structure residing either on sheet edges or forming heterocyclic rings within the sheets. Acidic
hydrogen atoms on carboxyl and hydroxyl groups occurring on the surface of activated carbon appear to be more labile. They attributed this to electron density diversion to the $\pi$-bond system of the graphitic planes. The acid or base character of activated carbon is largely a function of oxidation of the carbon. Activated carbons are usually classified into two categories based on the acid-base behaviour of the carbon, H-type and L-type (Toles et al., 1999). The L-type carbons are acidic while the H-type carbons are basic.

### 3.3. ADSORPTION ISOTHERMS.

The two important properties in an adsorption system are the adsorption capacity of a given amount of adsorbent for a particular adsorbate and the adsorption rate at which the adsorbate is taken out of the solution by the adsorbent. These properties describe the adsorption process sufficiently and can be obtained from adsorption isotherms and adsorption kinetics of the system. The adsorption rate depends on the size, porous structure and chemical properties of the adsorbent. It also depends on the size and structure of the adsorbate molecule and the concentration and temperature of the solution. The adsorption capacity of an adsorbent depends on its surface area, porosity and chemical properties. It also depends on the concentration, pH and temperature of the solution. The adsorption capacity of an adsorbent is best described graphically in the form of adsorption isotherms. An adsorption isotherm is the relationship between the quantity of adsorbate per unit mass of adsorbent ($q_e$) and the equilibrium concentration of adsorbate in solution ($C_e$). A wide variety of adsorption isotherms have been proposed to model different types of adsorption systems. However, the most commonly employed adsorption isotherms in gas and liquid systems are Langmuir and Freundlich isotherms (Langmuir, 1918; Freundlich, 1926).

#### 3.3.1. Langmuir Isotherm.

The Langmuir isotherm is a gas adsorption model. Langmuir equation is restricted to type 1 isotherm. It is derived from simple mass-action kinetics, assuming that sorption is chemisorption (Seader and Henley, 2006). Langmuir (1918) studied the adsorption of gases on plane surfaces of glass, mica and platinium and derived the isotherm as follows:

If $\theta$ is the fraction of the surface covered by adsorbed molecules, therefore, $1-\theta$ is the fraction of the bare surface. The net rate of adsorption is the difference between the
rate of adsorption of the molecules onto the bare surface and the rate of desorption of
the adsorbed molecules from the covered surface. Therefore, the net rate of adsorption
is represented as follows:
\[
\frac{dq}{dt} = k_aP(1 - \theta) - k_d\theta
\] (3.1)
where \( q \) is the equilibrium loading or amount adsorbed/unit mass of adsorbent, \( t \) is the
time for adsorption, \( P \) is the equilibrium partial pressure of the component in gas, \( k_a \) is
the adsorption constant and \( k_d \) is the desorption constant.

At adsorption equilibrium \( \frac{dq}{dt} = 0 \) and equation (3.1) reduces to:
\[
\theta = \frac{KP}{1 + KP}
\] (3.2)
where \( K \) is the adsorption equilibrium constant, \( K = \frac{k_a}{k_d} \).

Also, \( \theta = \frac{q}{q_m} \) (3.3)
where \( q_m \) is the maximum loading corresponding to complete coverage of the surface
by the gas. Combining equations (3.2) and (3.3) gives the Langmuir adsorption
isotherm:
\[
q = \frac{q_mKP}{1 + KP}
\] (3.4)
Langmuir isotherm is therefore based on the following assumptions (Duong, 1998;
Seader and Henley, 2006):
(1) Adsorption of adsorbate molecules takes place at well defined localised sites,
assuming that there is a finite number of binding sites.
(2) The adsorption energy is constant over all the sites, implying that the sites are
equivalent and are homogeneously distributed over the adsorbent surface.
(3) Each site accommodates only one adsorbate molecule, assuming that maximum
adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent
surface.
(4) There are no lateral interactions (i.e. interactions between neighbouring adsorbed
adsorbate molecules).

When porous adsorbent particles are immersed in a pure gas, the pores are filled with
the gas and the amount of gas adsorbed is determined by decrease in total pressure. If
the adsorbent particles are immersed in liquid, the pressure does not change. If the liquid is a homogeneous binary mixture, it is customary to designate one component as the solute and the other as the solvent. Therefore, the change in composition of the bulk liquid in contact with the porous solid is due to adsorption of the solute. It is therefore common to fit the data with concentration forms of the Langmuir equation. Therefore, Langmuir isotherm can be expressed as:

$$q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e}$$  \hspace{1cm} (3.5)

where $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), $C_e$ is the equilibrium concentration of the adsorbate (mmol/L), $q_{\text{max}}$ and $b$ are empirical constants, $q_{\text{max}}$ is the maximum value of $q_e$ obtainable with an increase in $C_e$ and $b$ is the constant related to the free adsorption energy which gives an indication of the strength of bonding between the adsorbate and the adsorbent. The constants $q_{\text{max}}$ and $b$ are characteristics of the Langmuir equation and can be determined from the linearised form of Equation (3.5) represented by Equation (3.6).

$$\frac{1}{q_e} = \frac{1}{q_{\text{max}} b C_e} + \frac{1}{q_{\text{max}}}$$  \hspace{1cm} (3.6)

A plot of $1/q_e$ versus $1/C_e$ gives a straight line of slope $1/q_{\text{max}} b$ and intercept $1/q_{\text{max}}$. Although this model is a gas adsorption model, it has been used to model isotherms from liquid solutions successfully by several researchers (Faur-Brasquet et al., 2002; Li et al., 2003; Xiao and Thomas, 2004; Saha et al., 2004; Chen and Wu, 2004). The Langmuir isotherm assumes monolayer adsorption behaviour, which is different from the Freundlich isotherm that assumes multilayer adsorption.

### 3.3.2. Freundlich Isotherm.

The Freundlich isotherm is a gas adsorption model. When gas is adsorbed by an adsorbent, it is expected that the amount of gas adsorbed by a given weight of adsorbent should be proportional to the equilibrium pressure as follows:

$$q = KP$$  \hspace{1cm} (3.7)

where $q$ is the amount adsorbed/unit mass of adsorbent, $P$ is the equilibrium partial pressure of the component in the gas. This is Henry’s law called the linear isotherm. However, Freundlich (1926) studied the adsorption of gases and found that experimentally, Henry’s law does not appear to hold even at low pressure. As higher
amount of the gas is adsorbed Freundlich discovered that the amount adsorbed/unit mass of adsorbent becomes proportional to a power of the equilibrium partial pressure of the component in the gas that is smaller than unity. Therefore, Freundlich isotherm is empirical and nonlinear in pressure and is expressed as:

\[ q = KP^{1/n} \]  

(3.8)

where \( q \) is the amount adsorbed/unit mass of adsorbent, \( P \) is the equilibrium partial pressure of the component in the gas, \( K \) and \( n \) are temperature dependent constants. Generally, \( n \) is greater than 1 and the Freundlich isotherm is an exponential equation. If \( n \) is equal to 1 the Freundlich isotherm reduces to the Henry’s law.

Freundlich isotherm is therefore based on the following assumptions (Duong, 1998; Seader and Henley, 2006): Equilibrium at heterogeneous surfaces, which assumes multilayer adsorption. It is therefore based on the assumption of non-uniform energy distribution and the adsorption energy is not constant over all the sites, implying that the sites are not equivalent and are heterogeneously distributed over the adsorbent surface. In contrast, whilst the Langmuir isotherm predicts surface saturation by the adsorbate, the Freundlich isotherm is mathematically unlimited. With the difference in adsorption of gas and adsorption of solutes from liquid as discussed in the Langmuir isotherm section, it is also common to fit the data with concentration forms of the Freundlich equation. Therefore the Freundlich isotherm can be expressed as:

\[ q_e = k_f C_e^{1/n} \]  

(3.9)

where \( q_e \) is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), \( C_e \) is the equilibrium concentration of the adsorbate (mmol/L), \( k_f \) is an approximate indicator of adsorption capacity while \( 1/n \) is a function of the strength of adsorption. A high value of \( n \) indicates high adsorption of solute at high solute concentration and poor adsorption of solute at low solute concentration. The constants \( K_f \) and \( 1/n \) can be determined from the linearised form of Equation (3.9) represented by Equation (3.10).

\[ \log q_e = \frac{1}{n} \log C_e + \log K_f \]  

(3.10)

A plot of \( \log q_e \) versus \( \log C_e \) gives a straight line of slope \( 1/n \) and intercept \( \log K_f \). Although this model is a gas adsorption model, it has been used to model isotherms from liquid solutions successfully by several researchers (Faur-Brasquet et al., 2002; Li et al., 2003; Xiao and Thomas, 2004; Saha et al., 2004; Chen and Wu, 2004).
3.3.3. Sips Isotherm.

Sips isotherm is a combination of the Langmuir and Freundlich isotherms and so it is also known as Langmuir-Freundlich isotherm. Sips (1948) studied the adsorption of gas by catalyst in the molecular state, that is, without dissociation and derived the isotherm as follows:

It is well known that experimental results may be expressed with a remarkable accuracy by using Freundlich isotherm:

\[
\theta = KP^{1/n}
\]  

(3.11)

\(\theta\) is the fraction of the surface covered by adsorbed molecules, therefore, \((1-\theta)\) is the fraction of the bare surface. \(P\) is the equilibrium partial pressure of the component in the gas, \(K\) and \(n\) are constants at a definite temperature. Freundlich isotherm assumes that the quantity of gas adsorbed increases indefinitely with pressure. This is possible only if the number of available sites is infinite. In fact it is well known that, if the pressure is high enough, the catalyst surface becomes saturated, which means that for high values of \(P\), \(\theta\) tends asymptotically towards unity. The simplest way to express this is to assume that the actual form of the isotherm is given by:

\[
\theta = \frac{KP^{1/n}}{1 + KP^{1/n}}
\]  

(3.12)

If \(P\) is small \(KP^{1/n}\) is negligible compared to unity and equation (3.12) reduces to equation (3.11). In the Langmuir isotherm section it has been shown that \(\theta = \frac{q}{q_m}\)

where \(q\) is the equilibrium loading or amount adsorbed/unit mass of adsorbent and \(q_m\) is the maximum loading corresponding to complete coverage of the surface by the gas. Therefore the Sips model can be written as:

\[
q = \frac{q_mKP^{1/n}}{1 + KP^{1/n}}
\]  

(3.13)

With the difference in adsorption of gas and adsorption of solutes from liquid as discussed in the Langmuir isotherm section, it is also common to fit the data with concentration forms of the Sips equation. Therefore the Sips isotherm can be expressed as:

\[
q_e = \frac{q_mKC_e^{1/n}}{1 + KC_e^{1/n}}
\]  

(3.14)
where \( q_e \) is the amount of adsorbate adsorbed per unit mass of adsorbent (mmol/g), \( C_e \) is the equilibrium concentration of the adsorbate (mmol/L), \( q_{\text{max}} \) and \( b \) are empirical constants, \( q_{\text{max}} \) is the maximum value of \( q_e \) obtainable with an increase in \( C_e \) and \( K \) is the constant related to the free adsorption energy which gives an indication of the strength of bonding between the adsorbate and the adsorbent. At low adsorbate concentrations \( KC_e^{1/n} \) is negligible compared to unity and the Langmuir-Freundlich isotherm (i.e., Sips isotherm) reduces to the Freundlich isotherm. For homogeneous adsorbent surfaces \( (n = 1) \) and it reduces to the Langmuir isotherm. Finally, at high adsorbate concentrations it predicts monolayer adsorption capacity characteristic of homogeneous adsorbent surfaces \( (n = 1) \) and so reduces to the Langmuir isotherm.

3.3.4. Multicomponent Isotherms.

Commercial applications of adsorption involve mixtures rather than pure gases. If the adsorption of all components in the gas except one (A) is negligible, then the adsorption of A is estimated from its pure gas adsorption isotherm using equilibrium partial pressure of A. If the adsorption of two or more components in the mixture is significant, the solution is quite complicated. Experimental data show that one component can increase, decrease or have no influence on the adsorption of the other, depending on the interactions of the adsorbed molecules. Markham and Benton (1931) studied the adsorption of gas mixtures by silica and derived a simple theoretical multicomponent isotherm which is the extension of the Langmuir isotherm, based on the assumption that the only effect is the reduction of the vacant surface area for the adsorption of A because of the adsorption of other components, as follows:

Considering a binary gas mixture of A and B. If \( \theta_A \) is the fraction of the surface covered by A and \( \theta_B \) is the fraction of the surface covered by B then, \( (1 - \theta_A - \theta_B) \) is the fraction of vacant surface. At equilibrium:

\[
(K_A)_e P_A (1 - \theta_A - \theta_B) = (K_A)_d \theta_A
\]

(3.15)

Where \( P_A \) is the equilibrium partial pressure of A, \( (K_A)_e \) is the adsorption constant of A and \( (K_A)_d \) is the desorption constant of A.

\[
(K_B)_e P_B (1 - \theta_A - \theta_B) = (K_B)_d \theta_B
\]

(3.16)
Where \( P_b \) is the equilibrium partial pressure of B, \((K_B)_a\) is the adsorption constant of B and \((K_B)_d\) is the desorption constant of B.

In the Langmuir isotherm section it has been defined that \( K = \frac{k_a}{k_d} \), also, \( \theta = \frac{q}{q_m} \) where q is the equilibrium loading or amount adsorbed/unit mass of adsorbent and \( q_m \) is the maximum loading corresponding to complete coverage of the surface by the gas. Solving equations (3.15) and (3.16) simultaneously and combining the results with the definitions of \( K \) and \( \theta \) gives:

\[
q_A = \frac{(q_A)_m K_A P_A}{1 + K_A P_A + K_B P_B} \tag{3.17}
\]

\[
q_B = \frac{(q_B)_m K_B P_B}{1 + K_A P_A + K_B P_B} \tag{3.18}
\]

Equations (3.17) and (3.18) are readily extended to multicomponent mixture of \( j \) components:

\[
q_i = \frac{(q_i)_m K_i P_i}{1 + \sum_j K_j P_j} \tag{3.19}
\]

Where \((q_i)_m\) is the maximum amount of adsorption of species i for coverage of the entire surface.

Yon and Turnock (1971) studied multicomponent adsorption equilibria on molecular sieves and extended the Langmuir-Freundlich isotherm to a multicomponent isotherm, using the same method used by Markham and Benton (1931). The multicomponent Langmuir-Freundlich isotherm for gas mixtures derived was presented by Yon and Turnock (1971) as:

\[
q_i = \frac{(q_i)_0 K_i P_i^{1/n_i}}{1 + \sum_j K_j P_j^{1/n_j}} \tag{3.20}
\]

Where \((q_i)_0\) is the maximum loading, which may differ from \((q_i)_m\) for a monolayer.

When porous adsorbent particles are immersed in pure gas mixtures, the pores are filled with the gas components and the amount of gas component adsorbed is determined by decrease in total pressure. If the adsorbent particles are immersed in liquid mixtures, the pressure does not change. If the liquid mixtures are homogeneous it is customary to designate one component as the solvent and the others as the solutes.
Therefore, the change in composition of the bulk liquid in contact with the porous solid is due to adsorption of the solutes. It is therefore common to fit the data with concentration forms of the multicomponent isotherms.

Therefore, the extended Langmuir isotherm derived by Markham and Benton (1931) can be expressed as:

\[
(q_i)_e = \frac{(q_i)_m K_i (C_i)_e}{1 + \sum_j K_j (C_j)_e} \tag{3.21}
\]

The extended Langmuir-Freundlich isotherm for gas mixtures derived by Yon and Turnock (1971) can be expressed as:

\[
(q_i)_e = \frac{(q_i)_o K_i (C_i)_e^{1/n}}{1 + \sum_j K_j (C_j)_e^{1/n}} \tag{3.22}
\]

where \((q_i)_e\) is the amount of different species in solution adsorbed per unit mass of adsorbent (mmol/g), \((C_i)_e\) and \((C_j)_e\) are the equilibrium concentrations of different species in the bulk liquid (mmol/L).

Unfortunately, Broughton (1948) has shown that the extended Langmuir isotherm lacks thermodynamic consistency. Since the extended Langmuir-Freundlich isotherm was derived by the same method it also lacks thermodynamic consistency. Therefore both multicomponent isotherms are frequently referred to as nonstoichiometric isotherms (Seader and Henley, 2006).

### 3.3.5. Brunauer-Emmet-Teller (BET) Isotherm.

Physical characteristics of porous materials, such as surface area and pore structure are extremely important when applied in catalytic and sorption processes. The surface is a reactive zone where chemisorption and/or physisorption occur. Alternatively, pore size and shape will define the process performance since kinetics are directly related to adsorbate intraparticle diffusion. Brunauer-Emmet-Teller (BET) isotherm is the most widely used isotherm for the determination of the surface area of porous materials. Brunauer et al. (1938) studied the adsorption of gases in multimolecular layers and made assumption that adsorption is conducted on sites of uniform energy, with the molecules adsorbed in the first layer acting as active sites for the formation of the next layers. With this assumption they were able to derive an isotherm for multimolecular layers that is similar to Langmuir's isotherm for unimolecular layers as follows:
So, $S_1$, $S_2$... represent the surface area that is covered by only 0, 1, 2... layers of adsorbed molecules. At equilibrium $S_0$ remains constant, so the rate of condensation on the bare surface is equal to the rate of evaporation from the first layer:

$$a_1PS_0 = b_1S_1e^{-E_1/kT}$$  \hspace{1cm} (3.23)

Where $P$ is the pressure, $E_1$ is the heat of adsorption of the first layer, $a_1$ and $b_1$ are constants with the assumption that $E_1$, $a_1$ and $b_1$ are independent of the number of adsorbed molecules already present in the first layer. Extending the same argument to $S_i$ layer and $S$ layer gives:

$$a_1PS_{i+1} = b_{i+1}S_{i+1}e^{-E_{i+1}/kT}$$  \hspace{1cm} (3.24)

The total surface area of the adsorbent is:

$$A = \sum_{i=0}^{\infty} S_i$$  \hspace{1cm} (3.25)

The total volume adsorbed is:

$$V = V_0 \sum_{i=0}^{\infty} iS_i$$  \hspace{1cm} (3.26)

Where $V_0$ is the volume of gas adsorbed on 1 cm$^2$ of the adsorbent surface when it is covered with a complete unimolecular layer of adsorbed gas. It follows that:

$$\frac{V}{AV_0} = \frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} iS_i}{\sum_{i=0}^{\infty} S_i}$$  \hspace{1cm} (3.27)

Where $V_m$ is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

Assuming that the evaporation-condensation properties of the molecules in the second and higher adsorbed layers are the same as those of the liquid state, that is:

$$E_2 = E_3 = \ldots E_i = E_L$$  \hspace{1cm} (3.28)

Where $E_L$ is the heat of liquefaction and

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \ldots \frac{b_i}{a_i} = g$$  \hspace{1cm} (3.29)

Where $g$ is an appropriate constant. $S_1$, $S_2$, $S_3$... $S_i$ can now be expressed in terms of $S_0$ using equations (3.23) and (3.24):

$$S_i = xS_{i-1} = x^{i-1}S_1 = yx^{i-1}S_0 = cx^i S_0$$  \hspace{1cm} (3.30)
Where $c = \frac{y}{x} = \frac{a_1 g}{b} e^{\frac{\delta_1 \xi_1}{RT}}$  \hspace{0.5cm} (3.31)

Substituting equation (3.31) into equation (3.27) and solving it gives:

$$\frac{V}{V_m} = \frac{cx}{(1-x)(1-x+cx)}$$  \hspace{0.5cm} (3.32)

If the adsorption is on a free surface, then at the saturation pressure of the gas, $P^0$, an infinite number of layers can build upon the adsorbent. From equation (3.32) to make $V = \infty$, when $P = P^0$, $x$ must be equal to unity, therefore,

$$x = \frac{P}{P^0}$$  \hspace{0.5cm} (3.33)

Substituting equation (3.33) into equation (3.32) gives the isotherm equation:

$$V = \frac{V_m c P}{(P^0 - P)(1 + (c-1)(\frac{P}{P^0})}$$  \hspace{0.5cm} (3.34)

If $P \ll P^0$ equation (3.34) reduces to a special form of the Langmuir equation:

$$V = \frac{(V_m c P)}{P^0}$$  \hspace{0.5cm} (3.35)

Rearranging equation (3.34) gives:

$$\frac{P}{V(P^0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P^0}$$  \hspace{0.5cm} (3.36)

The BET model can also be represented by replacing the volume of gas adsorbed ($V$) with the moles of gas adsorbed as follows:

$$\frac{P}{n(P^0 - P)} = \frac{1}{n_m c} + \frac{(c-1)P}{n_m c P^0}$$  \hspace{0.5cm} (3.37)

Where $n$ is the adsorption capacity of the adsorbent (mmol/g), $c$ is the dimensionless constant related to the enthalpy of adsorption in the first adsorbed layer, $P$ is the pressure (Pa), $n_m$ is the monolayer adsorption capacity (mmol/g) and $P^0$ is the saturated pressure of the system (Pa). The monolayer adsorption capacity ($n_m$) is very useful in the evaluation of the specific surface area of the adsorbent. If the Avogadro number is multiplied by $n_m$, the number of molecules involved in the monolayer surface coverage can be evaluated. Evaluation of the specific surface area requires knowledge of the average molecular cross sectional area occupied by the adsorbate molecule in the monolayer. The most common adsorbate for this purpose is nitrogen with cross
sectional area of 162 nm². Even though the BET method is the most widely used method for the determination of surface area of porous material, Sing et al. (1985) reported that the range of linearity is restricted to a limited part of the isotherm and for most materials the range lies within relative pressures (P/P°) of 0.05-0.3.

3.4. CONCLUSIONS

From the articles reviewed in this chapter, it can be concluded that sorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Classical sorption models, such as Langmuir and Freundlich models have been extensively used to describe the equilibrium established between adsorbed metal ions on the adsorbent and the metal ions remaining in solution at constant temperature. Therefore, one of the objectives of this research is to correlate the equilibrium data by conventional theoretical models, such as Langmuir and Freundlich models.
4. MATERIALS AND METHODS

4.1. INTRODUCTION

This chapter describes the sources and qualities of the materials used in this research and details of experimental methods used for electrochemical oxidation and electrochemical reduction of a viscose rayon based activated carbon cloth (ACC). The details of experimental methods of various conventional techniques used to characterise the electrochemically oxidised, electrochemically reduced and as-received ACCs are described in this chapter. Finally details of experimental methods used for the studies of competitive and noncompetitive lead(II) and copper(II) sorption onto electrochemically oxidised and as-received ACCs and chromium(VI) sorption onto electrochemically reduced, electrochemically oxidised and as-received ACCs are also described in this chapter.

4.2. MATERIALS

A viscose rayon based activated carbon cloth (ACC), ZORFLEX$^R$ FM 10 (supplied by Charcoal Cloth International) was used as a starting material for this research. The standard solutions used to obtain all the calibration curves on atomic absorption spectrophotometer and all other chemicals used in this research were of analytical grade and volumetric standard and were obtained from Fisher Scientific, U.K.

4.3. EXPERIMENTAL

4.3.1. Conversion of Activated Carbon Cloth (ACC) to Hydrogen Form

Before use the viscose rayon based ACC was converted to hydrogen form by passing 2 L of 5 % (w/w) hydrochloric acid very slowly (for 48 h) through a column containing 20 g of the ACC. After conversion, the ACC was washed with 50 L of deionised water and the conductivity of the washed water was measured. Washing was continued until the conductivity of the washed water was the same as that of deionised water, which is 2.1 $10^{-6}$ Siemens. After washing, the ACC was dried in an oven at 383 K for 24 h. It was then put in a desiccator overnight and weighed. All converted samples were kept in sealed plastic bags to avoid any contamination.
4.3.2. Electrochemical Oxidation of ACC

Viscose rayon based activated carbon cloth, ZORFLEX® FM 10 in hydrogen form was modified electrochemically using 0.5 M potassium chloride as an electrolyte. The choice of potassium chloride as an electrolyte was based on the fact that studies of electrochemical oxidation in several electrolytes (Yumitori and Nankanishi, 1996b; Bismark et al. 1999b; Rangel-Mendez and Streat, 2002a) showed that activated carbon oxidised in potassium chloride had the highest cation exchange capacity. The electrochemical cell was immersed in a thermostatically controlled water bath regulated at 303 K. 1 gm of ACC was wrapped round the anode (platinised titanium) and immersed in 0.5 M potassium chloride for 1 h prior to the electrochemical oxidation process. The equipment used for electrochemical oxidation is shown in Figure 4.1 and the schematic of the electrochemical cell used for electrochemical

Figure 4.1. Equipment used for electrochemical oxidation.
oxidation is shown in Figure 4.2. The electrochemical cell is a two compartment cell with dimensions of 0.176 m in length, 0.08 m in width and 0.09 m in depth. Two cathodes (platinised titanium) were used as counter electrodes. As shown in Figure 4.2, the cathodes were placed at equal distances from the anode to achieve uniform surface oxidation of the ACC. The dimensions of the anode and cathodes are the same, with dimensions of 0.001 m in thickness, 0.063 m in length and 0.054 m in width, giving a surface area of 0.0034 m². The electrochemical oxidation was carried out at currents ranging from 0.55 to 8.8 A at different oxidation times (e.g. 0.25, 0.5, 0.75, 1, 2, 3, 4 and 6 h) to obtain different extents of electrochemical oxidation. The extent of electrochemical oxidation is defined as the product of current and electrochemical oxidation time in coulomb per gram (c/g) of ACC. For each oxidation the chosen current was kept constant by adjusting the voltage throughout the chosen oxidation time and using fresh electrolyte each time. After oxidation, the oxidised ACC was washed with deionised water until the conductivity of the washed water reached the same value as the conductivity of deionised water that is, 2.1 \times 10^6\text{Siemens}. The oxidised ACC was then dried in an oven at 383 K for 24 h, put in a desiccator overnight and then weighed.
4.3.3. Electrochemical Reduction of ACC

Viscose rayon based activated carbon cloth, ZORFLEX® FM 10 in hydrogen form was modified electrochemically using 0.5 M potassium chloride as an electrolyte. The electrochemical cell was immersed in a thermostatically controlled water bath regulated at 303 K. 1 gm of ACC was wrapped round the cathode (platinised titanium) and immersed in 0.5 M potassium chloride for 1 h prior to the electrochemical reduction process. The equipment used for electrochemical reduction is the same as that shown in Figure 4.1 and the schematic of electrochemical cell used for electrochemical reduction is shown in Figure 4.3. Two anodes (platinised titanium) were used as counter electrodes. The electrochemical cell is a two compartment cell with dimensions of 0.176 m in length, 0.08 m in width and 0.09 m in depth. The dimensions of the anodes and cathode are the same, with dimensions of 0.001 m in thickness, 0.063 m in length and 0.054 m in width, giving surface area of 0.0034 m². As shown in Figure 4.3, the anodes were placed at equal distances from the cathode to achieve uniform surface reduction of the ACC. The electrochemical reduction was carried out at different currents from 1.1 to 8.8 A at different reduction times (e.g. 0.5, 0.57, 0.67, 0.75, 0.8, 0.86, 1, 1.2, 1.33, 1.5, 1.71, 2, 2.4 3, 4, 6 and 12 h) to obtain different extents of electrochemical reduction. The extent of electrochemical reduction

Figure 4.3. Schematic of electrochemical cell used for electrochemical reduction.
is defined as the product of current and electrochemical reduction time in coulomb per gram (c/g) of ACC. For each reduction the chosen current was kept constant by adjusting the voltage throughout the chosen reduction time and using fresh electrolyte each time. After reduction, the reduced ACC was washed with deionised water until the conductivity of the washed water reached the same value as the conductivity of deionised water that is, $2.1 \times 10^{-6}$ Siemens. The reduced ACC was then dried in an oven at 383 K for 24 h, put in a desiccator overnight and then weighed.

4.3.4. Characterisation of ACCs

It is important to know the physical and chemical composition of adsorbents since these properties define their most efficient working conditions and hence electrochemically oxidised, electrochemically reduced and as-received ACCs were characterised by various conventional techniques. The quantity and nature of the surface functional groups on the surface of the ACCs were characterised by sodium capacity, chloride capacity, pH titration, zeta potential measurements, elemental analysis, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD), nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

4.3.4.1. Sodium capacity determination

The sodium sorption capacity determination experiments were performed in order to compare the cation exchange capacity of electrochemically oxidised ACC and as-received ACC in aqueous solution, since it is known that sodium sorption data gives an indication of the total cation exchange capacity of adsorbents in aqueous solution (Waseem et al., 1998; Saha et al., 2001b; Rangel-Mendez and Streat, 2002a; Saha et al., 2003). A series of experiments were conducted to determine the total sodium capacity of electrochemically oxidised ACC and as-received ACC in hydrogen form as follows: 0.2 g of electrochemically oxidised ACC or as-received ACC was placed in a 50 ml conical flask containing 25 ml of 0.1 M volumetric standard sodium hydroxide. The flasks were sealed with parafilm to avoid spillage and were agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 72 h. The solutions were then filtered and 10 ml of the supernatant solutions were back titrated with 0.1 M volumetric standard hydrochloric acid using methyl orange as an indicator. The final
concentration of sodium hydroxide ($C_{NaOH_{final}}$) in each conical flask after equilibration was determined using the following equation:

$$C_{NaOH_{final}} = \frac{C_{HCl} V_{HCl}}{V_{NaOH}}$$  \hspace{1cm} (4.1)$$

Where $C_{HCl}$ is the concentration of hydrochloric acid used for back-titration (0.1 M), $V_{HCl}$ and $V_{NaOH}$ are the volume of hydrochloric acid and the volume of the supernatant solution in the conical flask used for back-titration, respectively. The concentration of sodium hydroxide adsorbed was calculated using the following equation,

$$C_{NaOH_{adsorbed}} = C_{NaOH_{initial}} - C_{NaOH_{final}}$$  \hspace{1cm} (4.2)$$

Where $C_{NaOH_{initial}}$ is the initial concentration of sodium hydroxide used for the experiment (0.1 M) and $C_{NaOH_{final}}$ is the final concentration of sodium hydroxide. The sodium capacity ($q_{NaOH}$) was then calculated using the following equation:

$$q_{NaOH} = \frac{V_{initial} C_{NaOH_{adsorbed}}}{ACC_m}$$  \hspace{1cm} (4.3)$$

Where $ACC_m$ is the mass of ACC used (0.2 g) and $V_{initial}$ is the initial volume of the 0.1 M sodium hydroxide used for the sodium capacity determination (25 ml).

### 4.3.4.2 Chloride capacity determination

Chloride sorption capacity was determined in order to compare the anion exchange capacity of electrochemically reduced ACC and as-received ACC in aqueous solution. The chloride sorption capacity gives an indication of the total anion exchange capacity of adsorbents in aqueous solution which is related to the quantity of basic functional groups on the adsorbents (Natale et al., 2007; Jeffery, 1989; Park and Kim, 2001; Park and Jang, 2002; Leon y Leon et al., 1992). A series of experiments were conducted to determine the total chloride capacity of electrochemically reduced ACC and as-received ACC as follows: 0.2 g of the electrochemically reduced or as-received ACC was placed in a 50 ml conical flask containing 25 ml of 0.1 M volumetric standard hydrochloric acid. The flasks were sealed with parafilm to avoid spillage and were agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 72 h. The solutions were then filtered and 10 ml of the supernatant solutions were back titrated with 0.1 M volumetric standard sodium hydroxide using phenolphthalein as an indicator. The final concentration of hydrochloric acid ($C_{HCl_{final}}$) in each conical flask after equilibration was determined using the following equation:
Where \( C_{NaOH} \) is the concentration of sodium hydroxide used for back-titration (0.1 M), \( V_{NaOH} \) and \( V_{HCl} \) are the volume of sodium hydroxide and the volume of the supernatant solution in the conical flask used for back-titration, respectively. The concentration of hydrochloric acid adsorbed (\( C_{HCl adsorbed} \)) was calculated using the following equation:

\[
C_{HCl adsorbed} = C_{HCl initial} - C_{HCl final} \tag{4.5}
\]

Where \( C_{HCl initial} \) is the initial concentration of hydrochloric acid used for the experiment (0.1 M). The Chloride capacity (\( q_{HCl} \)) was then calculated using the following equation:

\[
q_{HCl} = \frac{V_{initial} C_{HCl adsorbed}}{ACC_m} \tag{4.6}
\]

Where \( ACC_m \) is the mass of ACC used (0.2 g) and \( V_{initial} \) is the initial volume of the 0.1 M hydrochloric acid used for the chloride capacity determination (25 ml).

4.3.4.3. pH Titration

This technique determines the acidic and basic properties of ion exchangers and the nature of the functional surface groups (Tai et al., 1999; Saha et al., 2001b; Rangel-Mendez and Streat, 2002a; Saha et al. 2003). 0.025 g of electrochemically oxidised, electrochemically reduced or as-received ACC was weighed using Sartorius BP 210 D balance (± 0.0005 g accuracy) and placed in a 50 ml conical flask. 20 ml of 0.1 M sodium chloride was added to each flask. A pre-determined volume of 0-2 ml of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain a shape of curve over a pH range of 2-12. The pH of the solution in each flask, prior to the addition of the adsorbent was measured using a Mettler-Toledo 340 digital pH meter. The flasks were sealed with parafilm and were agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 48 h. Blank experiments without adsorbent were also performed under otherwise identical conditions. The pH of the solutions with adsorbent and the solutions of the blank experiments were measured after 48 h. The solutions with the adsorbent were then filtered. The supernatant solutions and the solutions of the blank experiments were then back titrated with volumetric standard of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide using phenolphthalein as an indicator to obtain the amount of \( H^+ \) or \( OH^- \) released by the
adsorbent. The total $H^+$ or $OH^-$ ions released by the ACC at a particular pH value was calculated from the difference between the volume of sodium hydroxide or hydrochloric acid used to back titrate the supernatant solutions for the solutions with the ACC and the blank solutions using the following equation:

$$IR = \frac{C(V_b - V_a)}{ACC_m}$$ (4.7)

where $C$ is the titrant concentration (0.1 M), $IR$ is the ion released in mmol/g, $V_b$ is the volume of titrant used to back titrate the blank solution at a given pH, $V_a$ is the volume of titrant used to back titrate the supernatant solution of the solution with adsorbent at a given solution pH and $ACC_m$ is the mass of ACC (0.025 g).

4.3.4.4. Zeta potential measurement

Zeta potential measurements were performed on a Malvern Zetamaster 3000HSA. The electrochemically oxidised, electrochemically reduced or as-received ACC was cut to small pieces, finely ground and sieved to obtain particle size $< 45 \mu m$. 0.025 g of the finely ground electrochemically oxidised, electrochemically reduced or as-received ACC was weighed using a Sartorius BP 210 D balance ($\pm 0.0005$ g accuracy) and placed in a 50 ml conical flask. 20 ml of 0.1 M sodium chloride was added to each flask. A pre-determined volume (0-20 ml) of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain a shape of curve over a pH range of 1-12. The flasks were sealed with parafilm and were agitated in a Brunswick C25 series incubator shaker at 298 K and at 150 rpm for 48 h. The equilibrium pH of the solution in each flask was measured using a Mettler-Toledo 340 digital pH meter after which the zeta potential was measured. 5 ml aliquots of adsorbent suspensions were injected directly into the electrophoretic quartz cell with a plastic Luer syringe. Each sample was measured three times to provide an average reading. The cell was rinsed after each measurement with 40 ml of deionised water.

4.3.4.5. Elemental analysis

The ACC samples were analysed in the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK on a Perkin Elmer series II 2400 elemental analyser. Each sample was accurately weighed (1-2 mg) and wrapped in tin foil prior to analysis. The combustion of the sample was done in the combustion tube at 2073 K in a controlled environment in the presence of pure oxygen after purging the system.
with Helium carrier gas. The gaseous combustion products were further decomposed in the presence of a series of catalysts. A thermal conductivity detector quantified the percentage of carbon, hydrogen and nitrogen. The oxygen content was determined by difference.

4.3.4.6. Fourier transform infra red (FTIR) spectroscopy analysis
The surface chemistry of the ACCs was analysed by FTIR spectroscopy. The samples were dried at 383 K for 24 h and stored in a desiccator before use. All the samples were cut to small pieces and then finely crushed with a mortar and pestle. The samples were mixed with finely crushed spectroscopic grade potassium bromide in the ratio of 1:100. Thin pellets were prepared by subjecting the mixture of the samples and potassium bromide to a load of 10 tonnes. The Spectra were recorded on a Mattson 3000 FTIR spectrometer at a resolution of 4 cm⁻¹at 64 scans.

4.3.4.7. Surface area and pore size distribution
Brunauer-Emmet-Teller (BET) Surface area and pore size distribution measurements of ACCs were done by nitrogen adsorption and desorption method using a Micromeretics ASAP (Accelerated Surface Area and Porosimetry) 2000 surface analyser. The samples were weighed and then out-gassed at 393 K under a vacuum of less than 10 mm Hg on the degas ports of the analyser for a minimum period of 24 h. The adsorption isotherms were generated by dosing 99.99% pure nitrogen onto the samples within a bath of liquid nitrogen at a temperature of 77 K. The mass of the degassed sample was determined by subtracting the weight of the degassed empty tube from the nitrogen back-filled sample containing tube. The Density Functional Theory (DFT) model was used to determine the pore size distribution. The DFT model is a widely used and recognised powerful tool for calculating the pore size distribution of adsorbents in inhomogeneous fluids (Ross and Oliver, 1964; Evans, 1979; Walton and Quirke, 1986; Balbuena and Gubbins, 1992; Olivier, 1998; Tai et al., 1999; Rangel-Mendez and Streat, 2002b; Saha et al., 2003; Chingombe et al., 2006).

4.3.4.8. Scanning electron microscopy (SEM)
The surface morphology of each ACC was observed using SEM. The SEM of the ACCs were taken on a Carl Zeiss 1530 field emission microscopy at room temperature. The bath normal secondary electron mode was used at an accelerating
voltage of 5 kV. Prior to observation, the samples were dried in an oven at 383 K for 24 h and stored in a desiccator overnight. The samples were then attached onto aluminium platforms using PVA glue and coated with gold.

4.3.5 Adsorption Studies

4.3.5.1. Speciation of metal ions in aqueous solution

The knowledge of the relationship between the adsorbent surface chemistry and metal speciation is necessary to explain sorption mechanisms (Rangel-Mendez and Streat, 2002a; Faur-Brasquet et al., 2002; Saha et al., 2004). To verify that there was no precipitation of metal species in the pH range at which sorption of lead and copper onto electrochemically oxidised or as-received ACC was conducted, aqueous speciation of lead and copper as a function of solution pH was studied using JCHESS and CHESS software at concentrations of 0.0193 M lead(II) in lead(II) nitrate and 0.0157 M copper(II) in copper(II) nitrate which is higher than the maximum operating metal concentrations used in the batch sorption experiments. To verify that there was no precipitation of metal species in the pH range at which sorption of chromium(VI) onto electrochemically oxidised, electrochemically reduced or as-received ACC was conducted, aqueous speciation of chromium as a function of solution pH was studied using JCHESS and CHESS software at concentrations of 0.01 M chromium(VI) in sodium dichromate solution, which is higher than the maximum operating chromium(VI) concentration used in the batch sorption experiments.

4.3.5.2. Batch sorption experiments for copper(II) and lead(II)

Competitive and non-competitive sorption of copper(II) and lead(II) from nitrate solutions were studied in batch experiments to obtain isotherms at solution pH values of 3, 4 and 5. For non-competitive sorption experiments, 20 ml of copper(II) or lead(II) from nitrate solutions at several initial concentrations (0.03-7.87 mM), were added to several 50 ml conical flasks with 0.025 g of electrochemically oxidised or unoxidised ACC in each flask. For competitive sorption experiments, 20 ml of equimolar copper(II)-lead(II) from nitrate solutions at several initial concentrations (0.03-7.87 mM), were added to several 50 ml conical flasks with 0.025 g of electrochemically oxidised or unoxidised ACC in each flask. The pH values of the solutions were measured using a Mettler-Toledo 340 digital pH meter and were
adjusted to the required value by addition of 0.1 M sodium hydroxide or 0.1 M nitric acid. The flasks were then sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm. The original solution pH values were maintained at a regular interval by adding 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. The added volume of sodium hydroxide or nitric acid was recorded each time. This was continued until equilibrium was achieved i.e. when there was no significant change in solution pH for 48 h, this was about 5 days for unoxidised ACC and 8 days for electrochemically oxidised ACC. To investigate the effect of pH on the sorption capacity of electrochemically oxidised ACC, a series of non-competitive batch sorption experiments were conducted at original solution pH of 3, 4 and 5. All other batch sorption experiments were conducted at solution pH 5.

Figure 4.4. Varian AA 200 atomic absorption spectrophotometer (AAS).

Equilibrated solutions were filtered to remove ACC particles. The initial concentrations before the addition of ACC and the concentrations of the equilibrated supernatant solutions were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene-air flame emission mode. The AAS is shown in Figure 4.4. The quantity of metal ion adsorbed (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$
\[ q_e = \frac{C_i V_i - C_e V_e}{A_m ACC_m} \]  

(4.8)

Where \( q_e \) is the quantity of metal ion adsorbed per unit mass of ACC (mmol/g), \( C_i \) is the initial concentration of metal solution before addition of ACC (mg/L), \( C_e \) is the equilibrium concentration of metal solution (mg/L), \( V_i \) is the initial volume of aqueous metal solution (0.02 L), \( V_e \) is the final volume of aqueous metal solution at equilibrium, \( A_m \) is the atomic mass of metal, and \( ACC_m \) is the mass of ACC (0.025 g).

### 4.3.5.3. Batch sorption experiments for chromium(VI)

Sorption of chromium(VI) from sodium dichromate solutions was studied in batch experiments to obtain isotherms at solution pH of 4, 6 and 8. Equilibrium chromium(VI) ion sorption isotherms were obtained as follows: 20 ml of chromium(VI) from sodium dichromate solutions at several initial concentrations, (0.19-9.62 mM) were added to 50 ml conical flasks with 0.025 g of electrochemically reduced, electrochemically oxidised or as-received ACC in each flask. The initial pH values of the solutions were measured using a Mettler-Toledo 340 digital pH meter and adjusted to particular values by the addition of 0.1 M sodium hydroxide or 0.1 M nitric acid. The flasks were then sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm. The original solution pH values were maintained at a regular interval by adding 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. The added volume of sodium hydroxide or nitric acid was recorded each time. This was continued until equilibrium was achieved i.e., when there was no significant change in solution pH for 48 h, this was about 10 days. To investigate the effect of solution pH on the sorption capacity of ACC, a series of batch sorption experiments were conducted at original solution pH values of 4, 6 and 8. It is well known that chromium(VI) can easily be reduced to chromium(III) when in contact with adsorbents with hydroxyl functional groups, even in alkaline solutions (Selomulya et al., 1999; Aggarwal et al., 1999; Daneshvar et al., 2002; Smith and March, 2001; McMurry, 2000). The standard reduction potentials for several alcohols of -4.86 to -0.13 V are much lower than the standard reduction potential of 1.36 V for dichromate ion (Jeffery, 1989; Lide, 2006; Dean, 1999; Skoog et al., 1997). Therefore, alcohol groups are stronger reductants than sodium dichromate (Jeffery, 1989; Skoog et al., 1997) and can readily reduce chromium(VI) to chromium(III). The equilibrated solutions were filtered to remove ACC particles and the residual concentrations of
total chromium(VI) were determined by oxidising chromium(III) in the filtrate with excess of potassium permanganate (Clesceri et al., 1989) to chromium(VI). 5 ml of 0.1 M sulphuric acid was added to each conical flask with the filtrate and agitated and then 5 ml of 0.1 M potassium permanganate was added to each conical flask with the filtrate and heated for 5 min. The choice of potassium permanganate is based on the fact that the standard reduction potential of 1.51 V for manganate ion is higher than the standard reduction potential of 1.36 V for dichromate ion (Jeffery, 1989; Lide, 2006; Dean, 1999; Skoog et al., 1997). Therefore, potassium permanganate is a stronger oxidant than sodium dichromate (Jeffery, 1989; Skoog et al., 1997) and can readily oxidise chromium(III) to chromium(VI), especially at high temperature. This method has been confirmed by several researchers (Han et al., 2000; Selomulya et al., 1999; Daneshvar et al., 2002; Benhammou et al., 2005; Park et al., 2004a, Lazaridis and Charalambous, 2005; Aoyama, 2003). After the oxidation of chromium(III) to chromium(VI), the residual chromium(VI) concentrations were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene-air flame emission mode. The initial chromium(VI) concentrations before the addition of ACC was also determined using a Varian AA 200 AAS in acetylene-air flame emission mode. The AAS is shown in Figure 4.4. The quantity of metal ion adsorbed was calculated using the following equation:

\[ q_e = \frac{C_i V_i - C_f V_f}{A_m ACC_m} \]  

(4.9)

Where \( q_e \) is the quantity of chromium(VI) ion adsorbed per unit mass of ACC (mmol/g), \( C_i \) is the initial concentration of chromium(VI) solution before addition of ACC (mg/L), \( C_f \) is the final equilibrium concentration of chromium(VI) solution after oxidation of chromium(III) to chromium(VI) (mg/L), \( V_i \) is the initial volume of aqueous chromium(VI) solution (0.02 L), \( V_f \) is the final equilibrium volume of aqueous chromium(VI) solution after oxidation of chromium(III) to chromium(VI), \( A_m \) is the atomic mass of metal and \( ACC_m \) is the mass of ACC (0.025 g).
5. RESULTS AND DISCUSSIONS OF CHARACTERISATION OF ELECTROCHEMICALLY OXIDISED ACTIVATED CARBON CLOTH AND ADSORPTION STUDIES

5.1. INTRODUCTION
This chapter highlights the results of various conventional techniques used to characterise the electrochemically oxidised and as-received ACCs. The results from the studies of competitive and noncompetitive lead and copper sorption experiments onto electrochemically oxidised ACC and as-received ACC are also described in this chapter.

5.2. CHARACTERISATION OF ACCS
This section discusses the results of the experimental procedures used to physically and chemically characterise the as-received and electrochemically oxidised activated carbon cloth (ACC) used in this research. The quantity and nature of the surface functional groups on the surface of the ACCs were characterised by sodium capacity, pH titration, zeta potential measurements, elemental analysis, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD), nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

5.2.1. Sodium Capacity
The total cation exchange capacity (i.e. the quantity of acidic functional groups) was determined in sodium hydroxide solution. Since sodium hydroxide neutralisation is presumed to probe chemically and physically accessible acidic sites such as carboxyl, lactone and phenol functional groups (Boehm, 1966; Leon y Leon and Radovic, 1994; Pittman Jr. et al., 1997; Pittman Jr. et al., 1998; Pittman Jr. et al., 1999a), it follows that sodium hydroxide titrates the accessible functionalities which may reside in the pore walls located well below the external fibre surface. Oxygen-containing groups
such as carbonyl, carboxyl, phenol and lactone groups that are present on carbonaceous materials dissociate increasingly with an increase in solution pH values (Leon y Leon and Radovic, 1994). Therefore, these surface groups are completely dissociated in solutions at high pH and are available for ion exchange. Under this condition the total cation exchange capacity can be determined. A high sodium capacity is an indication of a high content of surface oxygen functional groups. Preliminary experiments measuring sodium capacity indicated that the best sorption capacity took place using a current of 1.1 A or 2.2 A. The sodium capacity results for the modified and as-received ACC are shown in Figure 5.1. The results in Figure 5.1 show that the sodium capacity of electrochemically oxidised ACC at 1.1 A for 6 h is 4.7 times higher than that of unoxidised ACC. This increase is attributed to the introduction of weakly acidic functional groups. The extent of oxidation on the carbon surface depends on the chemical composition of the electrolyte used for electrochemical oxidation (Rangel-Mendez and Streat, 2002a). Chlorine and hypochlorous acid (HOCl) that is formed when chlorine is present in water are strong oxidants (Chernow and Vallasi, 1993). Also from the electrochemical series of metals (Atkins and Paula, 2002) it is obvious that the potassium is a very strong reductant. Since the reduction and oxidation processes are responsible for the overall reaction in

![Figure 5.1. Sodium capacity result for unoxidised ACC (UO) and electrochemically oxidised ACC (EO) at different conditions.](image_url)
an electrolytic cell, the presence of strong oxidant and strong reductant explains why the ACC is strongly oxidised when potassium chloride is used as an electrolyte. The sodium capacity data gives an indication of the cation exchange capacity of the ACC in aqueous solution. So ACC, electrochemically oxidised in potassium chloride has a high potential for trace metal removal from aqueous solutions.

A plot of the sodium hydroxide uptake (sodium capacity) \textit{versus} the extent of electrochemical oxidation of ACC at a constant time of 4 h but at different currents of 0, 0.55, 1.1, 1.47, and 2.2 A is shown in Figure 5.2. The extent of electrochemical oxidation is defined as the product of current and electrochemical oxidation time in coulomb per gram (c/g) of ACC. However, it was observed that at 0.55 A the sodium capacity did not improve very significantly. This is shown in Figure 5.2 for 7,920 c/g extent of oxidation and this observation was confirmed by repeat experimental values. Above 7,920 c/g the sodium capacity increased in direct proportion to the extent of oxidation. This is attributed to an increase in the amount of weakly acidic functional groups introduced on the surface of the ACC as the oxidation process increased with increase in current. This also suggests that it is not just the current that passed through the electrolyte to the anode (i.e. the ACC) that is important. The chemical conditions

![Figure 5.2. NaOH uptake \textit{versus} extent of electrochemical oxidation for 4 h at different currents.](image-url)
at the anode are very complex. As potassium chloride was the electrolyte, chlorine, oxygen and hypochlorous acid were evolved at the anode (Horita et al., 1996). The composition of these products will depend on the current used as well as the diffusion processes at the electrodes. It would seem likely that the generation of exchangeable groups on the ACC depends on both current used for electrochemical oxidation as well as the total coulombs (i.e. product of current and oxidation time) passed through the solution. In order to observe the effect of oxidation time, a series of electrochemical oxidations of ACC were performed at a constant current of 1.1 A, but at different specific period of oxidation (0-8 h) to achieve different extents of oxidation. The plot of sodium hydroxide uptake versus the extent of oxidation at constant current is shown in Figure 5.3. It can be seen that the sodium capacity increased rapidly for 7,920 c/g extent of oxidation and then further increased at a rate directly proportional to the extent of oxidation at constant current of oxidation. This is attributed simply to the longer exposure of the ACC to the oxidising condition allowing a greater reaction time for the introduction of weakly acidic groups on the ACC. The process of manufacturing viscose rayon consists of the following steps: alkalisation, shredding, preripening i.e. ageing, xanthation, dissolving, maturing and viscose fibre spinning (see section 2.6.2.1.) (Wilks, 2001). At the spinning stage, the cellulose is regenerated from the viscose for the production of the viscose rayon filament. Therefore, the ACC

![Figure 5.3. NaOH uptake versus extent of electrochemical oxidation at 1.1 A for different oxidation times.](image-url)
matrix is composed of interlinking cellulose molecules. At short periods of oxidation, some of the cellulose molecules in the viscose rayon based ACC matrix will not be oxidised and so the amount of acidic functional groups to be introduced to the surface of the ACC will be less than the amount introduced at long periods of oxidation when more of the surface molecules are oxidised. The cation exchange capacity of electrochemically oxidised ACC depends on both the applied current and the time of oxidation, indicating that electrochemical oxidation is a current-dependent process and diffusion-dependent process, since it depends on the time of oxidation.

Two sets of experiments were performed by electrochemically oxidising ACCs at a specific oxidation time (e.g. 0-6 h) to establish the predominant factor (applied current or oxidation time) that influences the sodium hydroxide uptake of the ACC. The first set of ACCs were electrochemically oxidised at a constant current of 1.1 A for 2 h, 4 h, 6 h and 8 h to give 7,920, 15,840, 23,760 and 31,680 c/g extent of oxidation, respectively. The second set of ACCs were electrochemically oxidised at a constant current of 2.2 A for 1, 2, 3 and 4 h to give the same extent of oxidation as that of the first set, that is, 7,920, 15,840, 23,760 and 31,680 c/g extent of oxidation, respectively. This was to achieve data from the two sets of experiments for the same extent of oxidation at different oxidation time. Plots of sodium hydroxide uptake versus the extent of oxidation for the two different sets are presented in Figure 5.4.

![Figure 5.4. NaOH uptake versus extent of electrochemical oxidation at 1.1 and 2.2 A.](image-url)
The sodium capacity for the ACCs electrochemically oxidised at 1.1 A was higher than that for the set oxidised at 2.2 A at lower extent of oxidation. It was 1.7 times higher at 7,920 c/g extent of oxidation, i.e., 3.53 mmol/g and 2.106 mmol/g for ACCs electrochemically oxidised at 1.1 A and 2.2 A, respectively. However, this trend gradually decreased with an increase in the extent of oxidation up to 31,680 c/g. At this extent of oxidation, the same value of 6.313 mmol/g of sodium capacity was obtained for ACC electrochemically oxidised at 1.1 A and 2.2 A. The trend in sodium capacity for the two sets of electrochemically oxidised ACCs is attributed to the fact that at low extent of oxidation, ACC oxidised at 2.2 A did not have enough reaction time for a large number of cellulose molecules in the ACC matrix to be oxidised even though the current was higher. When the sodium hydroxide uptake was plotted against time of exposure to the oxidising condition (i.e. oxidation time) for the two sets of electrochemically oxidised ACC at 1.1 A and 2.2 A as shown in Figure 5.5, the sodium hydroxide uptake was similar for about 50% of the total improvement in sodium capacity. However, at oxidation time of about 4 h, the production of acidic functional groups that enhanced the sodium hydroxide uptake slowed down at the lower current of 1.1 A. It is therefore possible that the chemical condition at the ACC

![Figure 5.5. NaOH uptake versus oxidation time at 1.1 A and 2.2 A.](image)
surface is most significant in the early stages of oxidation whilst later in the oxidation process (i.e. at higher oxidation time) the current becomes more significant. As the current is the driving force for oxidation to occur (Atkins and Paula, 2002), the choice of current is very important. As shown in Figure 5.2, for any extent of oxidation, if an applied current is too small, though the oxidation time is long enough for a large number of molecules in the ACC matrix to be oxidised, the current may not be sufficient for oxidation to occur. This means that there must be an optimum constant current at which the oxidation time will be high enough to introduce the maximum amount of acidic functional groups on the ACC surface for any extent of oxidation. In order to achieve this optimum constant current, three series of experiments were performed at different extents of oxidation, e.g. 7,920 c/g, 15,840 c/g and 23,760 c/g. For each series, the ACCs were electrochemically oxidised at different currents of 0.73 A, 1.1 A, 1.47 A, 2.2 A, 4.4 A and 8.8 A, but at different oxidation time to achieve three different extents of oxidation (e.g. 7,920 c/g, 15,840 c/g and 23,760 c/g). Plots of the sodium hydroxide uptake versus applied current for the three series of experiments are shown in Figure 5.6. The three sets of results followed the same trend.

![Figure 5.6. NaOH uptake versus applied current for different extents of electrochemical oxidation.](image)

The results show that the sodium hydroxide uptake for ACCs oxidised below 1 A were low. This is attributed to the fact that applied currents below 1 A do not produce
sufficiently vigorous oxidising conditions. The sodium hydroxide uptake for ACCs oxidised above 1.47 A decreased continuously with an increase in applied current. The smallest amount of sodium hydroxide uptake was observed for the ACCs electrochemically oxidised at 8.8 A. This is attributed to the fact that though 8.8 A is the highest current, the small times of electrochemical oxidation of 15 min, 30 min and 45 min were not enough for effective oxidation of most of the cellulose molecules in the ACC matrix. The highest amount of the sodium hydroxide uptake was obtained at 1.1 A for ACCs oxidised at 7,920 c/g, 15,840 c/g and 23,7920 c/g. The sodium hydroxide uptake was 3.53 mmol/g, 4.59 mmol/g and 5.14 mmol/g for ACCs oxidised at 7,920 c/g, 15,840 c/g and 23,7920 c/g extent of oxidation respectively. Therefore, the optimum current at which the oxidation time is high enough to introduce the maximum amount of acidic functional groups on the surface of the ACC is 1.1 A. From Figures 5.2, 5.3 and 5.4, it is obvious that the electrochemical oxidation did not exceed 31,680 c/g extent of oxidation. This is because above 31,680 c/g, the ACC becomes fragile.

5.2.2. pH Titrations

It is well known that adsorption strongly depends on the nature of the adsorbent surface, porosity and surface area of the adsorbent (Dobrowolski et al., 1986). Potentiometric or pH titrations have been used to evaluate the acidic/basic properties of ion exchangers (Helfferich, 1995). Carbonaceous materials are amphoteric, which means they possess both acidic and basic surface properties. Carbons with low oxygen content have a high concentration of basic groups and adsorb anions from solutions, whereas carbons with high oxygen content have a high concentration of acidic groups and adsorb cations from solutions. Therefore, carbonaceous materials have to be titrated with acid and base to determine their surface nature. The dominance of the acidic or basic functional groups can be determined by detecting the affinity of the material for H⁺ or OH⁻ ions from the titration results. If H⁺ ions are adsorbed in excess of OH⁻ ions when adsorbent is equilibrated with acidic or basic electrolyte, the surface of the adsorbent will possess a net positive charge and the pH of the bulk solution will increase. However, if OH⁻ ions are adsorbed in excess of H⁺ ions, the surface of the adsorbent will become negatively charged and the pH of the bulk solution will decrease. So the capacity and type of surface groups can be determined from the pH titration curves. The pH titration curves are usually plotted as equilibrium solution pH

136
versus acid/alkali added or the amount of $H^+$ or $OH^-$ ion released by the adsorbent versus equilibrium solution pH. The proton binding curves, that is the plots of ion released versus equilibrium solution pH, for the unoxidised ACC (UO), the electrochemically oxidised ACC at 2.2 A for 3 h (EO 2.2 A for 3 h) and the electrochemically oxidised ACC at 1.1 A for 6 h (EO 1.1 A for 6 h) are shown in Figure 5.7. The point where the proton binding curve crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH at which the surface charge is zero at a particular ambient temperature, applied pressure and aqueous solution composition (Menendez et al., 1995; Garrison, 1998). The PZC will change depending on the type and amount of functional groups present on the adsorbent. It will be shifted to lower pH values with oxidation of the ACC due to the introduction of oxygen containing acidic functional groups, such as carboxyl, carbonyl and lactone groups onto the ACC surface (Donnet and Bansal, 1984; Chingombe et al., 2005). As shown in Figure 5.7, the PZC for unoxidised ACC is at pH 6.8 whereas it shifted to pH 2.8 for the ACC electrochemically oxidised at 1.1 A for 6 h and pH 2.7 for ACC electrochemically oxidised at 2.2 A for 3 h. It is well known that the sorption of metal ions strongly depends on the chemistry of the carbon surface (Suffet and McGuire, 1983; Bansal et al., 1988; Park and Kim, 1999a). The adsorbent surface is positively charged at solution pH values below the PZC because oxygen-containing groups are undissociated and protonated and the carbon will
remove anions from solution under these conditions. In contrast, at solution pH values higher than the PZC, the carbon surface becomes more negatively charged due to dissociation of weakly acidic oxygen-containing functional groups. Thus the carbon is able to attract and exchange cations in solution. The unoxidised ACC show a smooth curve whereas the electrochemically oxidised ones show inflection points that are typical of the behaviour of polyfunctional ion exchangers (Saha et al., 2003). Moreover, the slopes of the curves for electrochemically oxidised ACCs increased with an increase in equilibrium solution pH. This means that the concentration of hydrogen ions released increased with an increase in equilibrium solution pH, hence the cation exchange capacities of the electrochemically oxidised ACCs are expected to be higher than that of the unoxidised ACC. However, there is a distinguishing difference between the curve for electrochemically oxidised ACC at 2.2 A for 3 h and the curve for that electrochemically oxidised at 1.1 A for 6 h. The titration curve for electrochemically oxidised ACC at 2.2 A for 3 h display a lower slope which indicates less alkali neutralisation capability than the curve for electrochemically oxidised ACC at 1.1 A for 6 h above equilibrium solution pH of 4. The higher slope of the curve for the electrochemically oxidised ACC at 1.1 A for 6 h, though its PZC is slightly higher than the electrochemically oxidised ACC at 2.2 A for 3 h is attributed to the fact that sodium hydroxide titrates accessible functionalities which reside in pore walls located well below the external fibre surface (Boehm, 1966; Leon y Leon and Radovic, 1994; Pittman Jr. et al., 1997; Pittman Jr. et al., 1998; Pittman Jr. et al., 1999a). Since it had a longer oxidation time for more cellulose molecules to be oxidised, therefore, introducing more acidic functional groups, it exhibited a greater cation exchange capacity with an increase in equilibrium solution pH. This is in agreement with the sodium capacity results. It is well known that carboxyl groups on the surface of activated carbons dissociate in solution pH within the range of 2 and 6 and hydroxyl groups dissociate in solution pH above 6 (Helfferich, 1995; Rangel-Mendez and Streat, 2002a; Chingombe et al., 2005). From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the electrochemically oxidised ACCs and unoxidised ACC to produce H⁺ ions starts at equilibrium solution pH of approximately 3 and 7, respectively. Therefore, one of the types of acidic functional groups on the surfaces of electrochemically oxidised ACCs is likely to be carboxyl groups while that on the surface of unoxidised ACC is likely to be hydroxyl groups.
5.2.3. Zeta Potential Measurements

Figure 5.8 shows the zeta potential versus equilibrium solution pH plots for the unoxidised ACC, the electrochemically oxidised ACC at 1.1 A for 6 h and the electrochemically oxidised ACC at 2.2 A for 3 h. An important parameter used to characterise the electrokinetic behaviour of a solid-liquid interface is the isoelectric point (IEP). This is the equilibrium solution pH at which the zeta potential is zero. From the curves it is obvious that the IEP values of the electrochemically oxidised ACCs are not accurately measurable. This is because the proton concentration of the bulk electrolyte solution is too low and increasing the proton concentration caused further decrease of the zeta potential. Bismark et al. (1999b) had the same observation with an anodically oxidised fibre. Rangel-Mendez and Streat (2002a) also had the same observation with electrochemically oxidised granular carbon and obtained the IEP value by extrapolation. Therefore the IEP values for the electrochemically oxidised ACCs as shown in Figure 5.8 are extrapolated values. A shift in the IEP for the electrochemically oxidised ACCs to lower values when compared with the IEP for the unoxidised ACC is obvious. The IEP for unoxidised ACC is at pH 3 while that for electrochemically oxidised ACCs at 1.1 A for 6 h and 2.2 A for 3 h are at pH 1.15 and pH 0.9, respectively. This shows that the electrochemically oxidised ACCs are more acidic than the unoxidised ACC which confirms the pH titration results. The lower IEP
values for the electrochemically oxidised samples are attributed to the presence of more acidic functional groups. It is interesting to note that the zeta potential curves of electrochemically oxidised ACCs fall steeply with increasing equilibrium solution pH until about pH 4 and then start to level off to form distinct plateau areas. Dissociation of carboxylic surface groups is probably responsible for this effect since it is known that the dissociation of this group occurs at solution pH within the range of 2 and 6 (Helfferich, 1995; Rangel-Mendez and Streat, 2002a; Chingombe et al., 2005). The plateau areas of the zeta potential curves for the electrochemically oxidised ACCs are caused by complete dissociation of the carboxylic groups at about equilibrium solution pH 4 which is within the solution pH range at which this group dissociates. Therefore, there was no increase on the surface charge above solution pH 4. It is also interesting to note that there is no distinct difference between the zeta potential curves of the electrochemically oxidised ACCs at 1.1 A for 6 h and at 2.2 A for 3 h, which is opposite to the observation from the pH titration curves. This is due to the fact that, though the two ACCs were electrochemically oxidised at the same extent of oxidation, 23,760 c/g, the 6 h oxidation time allowed the oxidation of more cellulose molecules in the ACC matrix than the oxidation time of 3 h. It is well known that the IEP values are only representative of the external surface charges of carbon particles in solutions whereas the PZC varies in response to the net total of the external and internal surface charges of the carbon particles in solutions (Corapcioglu and Huang, 1987; Newcomb et al., 1993; Menendez et al., 1995). Therefore, it is expected that the IEP values and the zeta potential curves of the electrochemically oxidised ACCs are almost the same since the external surface charges of electrochemically oxidised ACCs at the same extent of oxidation are expected to be equal and this has been confirmed by the zeta potential results. However, the internal surface charges on each of the electrochemically oxidised ACCs are not equal and this has been confirmed by the pH titration and sodium capacity results. Since the IEP values are representative of external surface charges and PZC values are representative of the net total of external and internal surface charges, the difference between PZC and IEP (PZC - IEP) can be interpreted as a measure of the surface charge distribution of carbons. Greater differential values indicate more negatively charged external than internal particle surfaces and therefore more heterogeneous distribution of the surface charges. The lower differential values indicate a more homogeneous distribution of the surface charges. The electrochemical properties of the samples are summarised in Table 5.1. It
is noticeable that the value of PZC - IEP for the unoxidised ACC is higher than the values of PZC - IEP for electrochemically oxidised ACCs. Since all the ACCs are viscose rayon based and it is known (Hill and Holman, 2000; Wilks, 2001) that the double bond in the aldehyde end of the cellulose molecules consists of a σ bond and a π bond. So there is greater electron distribution over the more electronegative oxygen atom. However, the internal surface of the ACC will have a more uniform electron distribution due to bond formation between the cellulose molecules and the presence of several hydrogen and carbon atoms and so the external surface of the unoxidised ACC is more negatively charged than its internal surface. It also appears that the value of PZC - IEP for the electrochemically oxidised ACC at 2.2 A for 3 h is slightly higher than that electrochemically oxidised at 1.1 A for 6 h. This is attributed to the longer electrochemical oxidation time of 6 h that allowed the oxidation of more cellulose molecules inside the ACC matrix giving a more homogeneous distribution of the surface charges. This supports the suggestion that electrochemical oxidation is a diffusion-dependent process.

5.2.4. Elemental Analysis

Table 5.2. shows the elemental analysis results of unoxidised and electrochemically oxidised ACCs at 1.1 A for 6 h and at 2.2 A for 3 h. The unoxidised ACC has 20.03% oxygen content indicating the presence of some oxygen containing groups on the surface. This is attributed to the presence of oxygen atoms in the aldehyde end and hydroxyl end of the cellulose molecules in it. It is well known that non-carbon species are removed during carbonisation process of activated carbons (Langley, 1973; Donnet and Bansal, 1984; Reed and Matsumoto, 1993). The non-carbon species include oxygen-containing groups. However, not all the non-carbon species are removed by

<table>
<thead>
<tr>
<th>Sample</th>
<th>PZC</th>
<th>IEP</th>
<th>PZC - IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>6.8</td>
<td>3</td>
<td>3.8</td>
</tr>
<tr>
<td>EO 1.1 A for 6 h</td>
<td>2.8</td>
<td>1.15</td>
<td>1.65</td>
</tr>
<tr>
<td>EO 2.2 A for 3 h</td>
<td>2.7</td>
<td>0.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 5.1. Electrochemical properties of unoxidised and electrochemically oxidised ACCs.
Table 5.2. Elemental analysis of unoxidised and electrochemically oxidised ACCs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>76.89</td>
<td>2.03</td>
<td>1.05</td>
<td>20.03</td>
</tr>
<tr>
<td>EO 1.1 A for 6 h</td>
<td>52.33</td>
<td>2.6</td>
<td>0.84</td>
<td>44.23</td>
</tr>
<tr>
<td>EO 2.2 A for 3 h</td>
<td>52.96</td>
<td>2.87</td>
<td>1.56</td>
<td>42.61</td>
</tr>
</tbody>
</table>

carbonisation and the activated carbon surface adsorbs significant quantities of oxygen upon re-exposure to air at room temperature (Langley, 1973). The results also show a significant difference in oxygen content between the unoxidised ACC and electrochemically oxidised ACCs. The oxygen content in ACC electrochemically oxidised at 1.1 A for 6 h increased by 120.8% while the ACC electrochemically oxidised at 2.2 A for 3 h increased by 112.7%. These results follow exactly the same trend as the sodium capacity results which showed the cation exchange capacities of 1.063 mmol/g for unoxidised ACC, 4.46 mmol/g for ACC electrochemically oxidised at 2.2 A for 3 h and 4.94 mmol/g for ACC electrochemically oxidised at 1.1 A for 6 h. The increase in oxygen content in the electrochemically oxidised ACCs is attributed to introduction of weakly acidic oxygen containing functional groups during electrochemical oxidation.

5.2.5. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

It is known that the study of the chemical composition of carbon fibres by FTIR is difficult because the absorption of the fibre is very intense while the concentration of the different functional groups on its surface is relatively low. So the signal/noise ratio is often not sufficiently high even if the sample is scanned many times. Also the diameter of the fibre falls in the analytical wavelength range of infrared light, which may lead to strong interference at low wavenumbers (Gulyas et al., 2001). For these reasons the intensities of FTIR spectra of carbon fibres are not very high. FTIR spectra for unoxidised ACC (UO) and electrochemically oxidised ACC at 1.1 A for 6 h (EO) are shown in Figure 5.9 and Figure 5.10, respectively. The band assignments are
Figure 5.9. FTIR spectra for unoxidised ACC.

Figure 5.10. FTIR spectra for electrochemically oxidized ACC at 1.1 A for 6 h.
<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Band Assignment</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3435</td>
<td>- O - H Hydroxyl group</td>
<td>3412</td>
<td>- O - H Hydroxyl group</td>
</tr>
<tr>
<td>2851 and 2943</td>
<td>- CHO Aldehyde group</td>
<td>2359</td>
<td>O = C = O Carbon dioxide</td>
</tr>
<tr>
<td>2349</td>
<td>O = C = O Carbon dioxide</td>
<td>2349</td>
<td>O = C = O Carbon dioxide</td>
</tr>
<tr>
<td>1742</td>
<td>- CHO Aldehyde group</td>
<td>1725-1700</td>
<td>- COOH saturated</td>
</tr>
<tr>
<td></td>
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<td>1634</td>
<td>C = O Ketones</td>
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<td>C = O Ketones</td>
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<tr>
<td>1384</td>
<td>- CH₃ deformations</td>
<td>1383</td>
<td>- CH₃ deformations</td>
</tr>
</tbody>
</table>

Table 5.3. Band assignments for FTIR spectra of unoxidised (UO) and electrochemically oxidised (EO) ACC.

shown in Table 5.3. The distinguishing difference in the functional groups observed on the unoxidised ACC and electrochemically oxidised ACC are aldehydes and carboxylic acid, respectively. Hydroxyl groups were observed on the unoxidised and electrochemically oxidised ACCs. Since a cellulose molecule has aldehyde and hydroxyl ends it is expected that the ACCs should have aldehyde and hydroxyl functional groups on their surfaces. However, aldehyde groups were not observed on the electrochemically oxidised ACC. This is attributed to the fact that all the aldehyde groups were oxidised to produce carboxylic acid groups. Since it is known that aldehydes and alcohols are oxidised to produce carboxylic acid and that the alcohols need to be oxidised into aldehydes which are then readily oxidised into carboxylic acid (Hill and Holman, 2000; Wilks, 2001). Therefore, the aldehydes are more readily oxidised than the alcohols and so were not found on the electrochemically oxidised ACC. It is known that aldehydes and alcohols observed on the unoxidised ACC are weaker acids than carboxylic acids and start dissociating in solution pH values above 6 while the carboxylic acids dissociate in solution pH values within the range of 2 and 6 (Helfferich, 1995; Rangel-Mendez and Streat, 2002a; Chingombe et al., 2005). Therefore, the unoxidised ACC exhibits less acidic properties than the electrochemically oxidised ACCs as observed from the pH titration and zeta potential results. This is confirmed by the pH titration result which showed that the dissociation
of acidic functional groups on the unoxidised ACC starts at solution pH 7. This also explains the lower sodium capacity of unoxidised ACC since it released less H\(^+\) ions than the electrochemically oxidised ACCs as shown in the proton binding curves. This makes its surface to be less negatively charged therefore making it impossible for high sodium hydroxide uptake. The carboxylic acid groups observed on the electrochemically oxidised ACC confirms the pH titration and zeta potential results that showed that the dissociation of the acidic functional groups on the electrochemically oxidised ACCs was in the solution pH range of 2-6 where the acidic functional groups are likely to be carboxylic acids which dissociate within this solution pH range. This also explains why there was a high increase in the sodium capacity of the ACC after electrochemical oxidation in potassium chloride.

5.2.6. Reactions in Electrochemical Cell

With the confirmation that carboxylic acids are introduced onto the ACC by electrochemical oxidation and since it is known that the oxidation of aldehydes and alcohols that are in the cellulose molecules are methods of producing carboxylic acids (Hill and Holman 2000), it is possible to postulate the likely reactions that took place in the electrochemical cell. The reactions below are in agreement with reactions suggested by Horita et al. (1996), when they electrochemically oxidised carbon black.

\[
\begin{align*}
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \quad (5.1) \\
\text{KCl} & \leftrightarrow \text{K}^+ + \text{Cl}^- \quad (5.2) \\
2\text{Cl}^- - 2e^- & \leftrightarrow \text{Cl}_2(\text{g}) \quad (5.3) \\
\text{K}^+ + e^- & \leftrightarrow \text{K} \quad (5.4) \\
2\text{H}_2\text{O} & \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \quad (5.5) \\
\text{C} + 2\text{H}_2\text{O} & \leftrightarrow \text{CO}_2(\text{g}) + 4\text{H}^+ + 4e^- \quad (5.6) \\
\text{Cl}_2(\text{g}) + \text{H}_2\text{O} & \leftrightarrow \text{HOCI} + \text{H}^+ + \text{Cl}^- \quad (5.7) \\
2\text{HOCI} + 2\text{H}^+ + 2e^- & \leftrightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O} \quad (5.8)
\end{align*}
\]

It is known that in oxidising environment (e.g. in the presence of chlorine), all accessible hydroxyl groups in the cellulose \((\text{C}_6\text{H}_{10}\text{O}_5)_n\) molecules of viscose rayon based ACC are oxidised to aldehyde and ketone groups; aldehyde groups are then further oxidised to produce carboxyl groups (Hill and Holman, 2000; Wilks, 2001). Hence from the above reactions scheme it can be concluded that the oxidation of the aldehyde and hydroxyl groups within the cellulose molecules in the ACC to produce
carboxylic acid are the most likely reactions that occurred during the electrochemical oxidation of viscose rayon based ACC in the electrochemical cell.

5.2.7. Nitrogen Adsorption-Desorption Results
Nitrogen adsorption-desorption isotherms are standard tools for characterisation of porous materials, especially for characterisation of porous carbonaceous adsorbents. The nitrogen adsorption-desorption isotherms can be made to yield valuable information about the surface area and the pore structure of the adsorbents. The nitrogen adsorption-desorption isotherms obtained for unoxidised ACC and electrochemically oxidised ACCs are shown in Figures 5.11-5.17. All the isotherms except the isotherm for ACC electrochemically oxidised at 1.1 A for 6 h that is shown in Figure 5.17 are of type 1 according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985). Type 1 isotherms are characterised by a plateau that is nearly horizontal to the $p/p^0$ axis. This means that all the ACCs, except the ACC electrochemically oxidised at 1.1 A for 6 h are predominantly microporous since type 1 isotherms signify microporous solids having

![Graph](image)

Figure 5.11. Nitrogen adsorption-desorption isotherm for unoxidised ACC (UO).
**Figure 5.12.** Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 1 h (i.e. 7,920 c/g extent of oxidation).

**Figure 5.13.** Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 2 h (i.e. 15,840 c/g extent of oxidation).
Figure 5.14. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 2.2 A for 3 h (i.e. 23,760 c/g extent of oxidation).

Figure 5.15. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 2 h (i.e. 7,920 c/g extent of oxidation).
Figure 5.16. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 4 h (i.e. 15,840 c/g extent of oxidation).

Figure 5.17. Nitrogen adsorption-desorption isotherm for ACC, electrochemically oxidised at 1.1 A for 6 h (i.e. 23,760 c/g extent of oxidation).
a small external area and are characterised by an almost horizontal plateau. The sharply rising area at very low pressure \(< 0.1 \text{ p/p}^0\) is due to the filling of micropores. However, Figure 5.17 shows that nitrogen adsorption-desorption isotherm for ACC electrochemically oxidised at 1.1 A for 6 h shows a hysteresis effect, which is classified as type H4 according to IUPAC (Sing et al., 1985). The hysteresis loop in the nitrogen adsorption-desorption isotherm of ACC electrochemically oxidised at 1.1 A for 6 h indicate the existence of mesoporosity, since the type H4 hysteresis is characteristic of mesoporous substances, where capillary condensation occurs due to a bottle neck effect between micropores and mesopores. Figures 5.11-5.17 also show that the maximum nitrogen adsorption capacities of the electrochemically oxidised ACCs decreased with increase in the extent of oxidation. The maximum nitrogen adsorption capacities for ACCs electrochemically oxidised at 1.1 A were 233.39, 208.88 and 30.33 cm\(^3\)/g for 7,920, 15,840 and 23,760 c/g extents of oxidation, respectively, whilst the maximum nitrogen adsorption capacities for ACCs electrochemically oxidised at 2.2 A were 293.43, 257.19 and 173.75 cm\(^3\)/g for 7,920, 15,840 and 23,760 c/g extents of oxidation, respectively. This is attributed to blockage of more micropores of the ACCs by more carboxylic acid groups and humic substances produced with increase in extent of electrochemical oxidation. The blockage of pores by by-products from oxidation has been discussed by some other researchers (Baudu et al., 1991; Saha et al., 2001b; Saha et al., 2003). The unoxidised ACC had the highest nitrogen adsorption capacity, which was 458.49 cm\(^3\), whilst the ACC electrochemically oxidised at 1.1 A for 6 h had the lowest nitrogen adsorption capacity, which was 30.33 cm\(^3\)/g. This is expected since the ACC electrochemically oxidised at 1.1 A for 6 h had the highest sodium capacity indicating the presence of the highest quantity of carboxylic acid groups that blocked most of the micropores on it. It is also obvious that the nitrogen adsorption capacities for the ACCs electrochemically oxidised at 2.2 A are higher than the nitrogen adsorption capacities for the ACCs electrochemically oxidised at 1.1 A at the same extent of oxidation. This is due to the presence of more carboxylic acid groups on the ACCs electrochemically oxidised at 1.1 A as shown by the sodium capacity results, that blocked more micropores. Therefore, these results confirm that the decrease in surface area is not by etching but by blockage of pores by carboxylic acid groups and humic substances produced by electrochemical oxidation. The results also show that nitrogen adsorption is a function of the available surface area.
5.2.8. Surface Area Results

Figure 5.18 shows the BET surface area versus extent of oxidation plots for electrochemically oxidised ACCs at current of 1.1 A (EO 1.1 A) and electrochemically oxidised ACCs at current of 2.2 A (EO 2.2 A). The surface area specifications of

![Figure 5.18. BET surface area versus extent of oxidation for ACCs electrochemically oxidised at 1.1 A (EO 1.1 A) and at 2.2 A (EO 2.2 A).](image)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Single point surface area (m²/g) at P/P₀ 0.205</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm) (4V/A by BET)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>1395</td>
<td>1378</td>
<td>20.5</td>
</tr>
<tr>
<td>EO 1.1 A 2 h</td>
<td>763</td>
<td>752</td>
<td>19.1</td>
</tr>
<tr>
<td>EO 1.1 A 4 h</td>
<td>706</td>
<td>691</td>
<td>18.6</td>
</tr>
<tr>
<td>EO 1.1 A 6 h</td>
<td>533</td>
<td>532</td>
<td>18.7</td>
</tr>
<tr>
<td>EO 2.2 A 1 h</td>
<td>979</td>
<td>955</td>
<td>19</td>
</tr>
<tr>
<td>EO 2.2 A 2 h</td>
<td>835</td>
<td>817</td>
<td>19.3</td>
</tr>
<tr>
<td>EO 2.2 A 3 h</td>
<td>585</td>
<td>575</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 5.4. Surface area specifications of unoxidised ACC (UO) and electrochemically oxidised ACCs (EO) at different conditions.
unoxidised ACC (UO) and some selected electrochemically oxidised ACCs (EO) are shown in Table 5.4. All the ACCs analysed in this study have extensive BET surface areas that are ideal in the treatment of drinking water and wastewater. However, the BET surface area decreased with an increase in the extent of oxidation. The results showed that EO 1.1 A lost 45.4%, 49.8% and 61.3% of original BET surface area at 7,920, 15,840 and 23,760 c/g extent of oxidation, respectively while EO 2.2 A lost 30.7%, 40.7% and 58.3% of the original BET surface area at 7,920, 15,840 and 23,760 c/g extent of oxidation, respectively. However, there is a marked difference between the two plots. The BET surface areas for EO 2.2 A were higher than those for EO 1.1 A at all extent of oxidation. The difference between the BET surface area of the EO 2.2 A and EO 1.1 A gradually decreased with an increase in the extent of oxidation. This trend is attributed to the fact that at low extent of oxidation, ACC electrochemically oxidised at 2.2 A did not have enough time for most of the cellulose molecules in the viscose rayon based ACC matrix to be oxidised, so fewer pores were blocked by the acidic functional groups and humic substances. Alternatively, the ACC electrochemically oxidised at 1.1 A had more oxidation time so more of the cellulose molecules in the viscose rayon based ACC matrix were oxidised. This means that the micropore surface area is heavily oxidised therefore causing more pores to get blocked by acidic functional groups and humic substances. With an increase in the extent of oxidation at constant current, the oxidation time for the set of ACCs electrochemically oxidised at 2.2 A increased. This provided more time for the oxidation of more cellulose molecules within the matrix and hence causing more pores to be blocked. The decrease in the difference in BET surface area for EO 2.2 A and EO 1.1 A as the extent of oxidation increased is also due to the fact that even though the oxidation time for the set electrochemically oxidised at 1.1 A had longer period for the oxidation of more cellulose molecules in the ACC matrix, the available number of molecules to be oxidised are limited. This proves that at each extent of oxidation, the quantity of acidic functional groups on EO 1.1 A is higher than the quantity on EO 2.2 A. Since this is in agreement with the sodium capacity results shown in Figure 5.4, it can be concluded that the loss in BET surface area was by the blockage of pores by the acidic functional groups and humic substances. The reduction in surface area of carbonaceous materials by blockage of pores by by-products from oxidation has been discussed by some other researchers (Baudu et al., 1991; Saha et al., 2001b; Saha et al., 2003).
5.2.9. Pore Size Distribution (PSD) Results

The PSD results for different ACCs are shown in Figures 5.19-5.23. According to the

![Graph showing pore size distribution for different extents of oxidation](image)

**Figure 5.19.** Pore size distribution for unoxidised ACC (0 c/g) and electrochemically oxidised ACCs at 1.1 A at 7,920 c/g, 15,840 c/g and 23,760 c/g extents of oxidation.

![Graph showing pore size distribution for different extents of oxidation](image)

**Figure 5.20.** Pore size distribution for unoxidised ACC (0 c/g) and electrochemically oxidised ACCs at 2.2 A at 7,920 c/g, 15,840 c/g and 23,760 c/g extents of oxidation.
Figure 5.21. Pore size distribution for electrochemically oxidised ACCs at 1.1 A and 2.2 A at 7,920 c/g extent of oxidation.

Figure 5.22. Pore size distribution for electrochemically oxidised ACCs at 1.1 A and 2.2 A at 15,840 c/g extent of oxidation.
IUPAC system (Sing et al., 1985), the pore structures are divided into three categories as follows: Micropores (width less than 20 Å)
Mesopores (width between 20 and 500 Å)
Macropores (width more than 500 Å).
Micropores are also divided into two categories as follows:
Ultra micropores (width less than 5 Å)
Super micropores (width between 10 Å and 20 Å).
It can be seen from the PSD curves in Figures 5.19 and 5.20, that unoxidised ACC exhibited bimodal pore size distributions with peaks dominant at approximately 15 Å and 28 Å. So it possesses a reasonable amount of micropores, with a small fraction of mesopores but without any macropores. All electrochemically oxidised ACCs also exhibited similar bimodal pore size distributions. However, the PSD curve of the unoxidised ACC covers a broader range of pore width than the electrochemically oxidised ACCs. This is attributed to the fixing of oxygen functional groups inside the wider mesopores which increased the nitrogen constriction to the pores, therefore, showing a reduction in pore diameter. From the PSD curves it can also be seen that there was a decrease in incremental pore volumes in all the pores for the
electrochemically oxidised ACCs which is more evident as the extent of oxidation increased. As a result of electrochemical oxidation, oxygen functional groups and humic substances were produced, causing the pores to get blocked by the oxygen functional groups which increased the nitrogen constriction to the pores, resulting in a decrease in incremental pore volume. However, it is obvious that all the ACCs in this study are predominantly microporous except the ACC electrochemically oxidised at 1.1 A for 6 h that is shown in Figure 5.23 that showed the most dominant peak at approximately 22 Å, showing that it contained more mesopores than micropores. This is confirmed by the greater decrease in BET surface area of the ACC electrochemically oxidised at 1.1 A for 6 h, since more micropores than mesopores would have given it a lower decrease in BET surface area. Saha et al. (2003), also observed that loss in microporosity results in the reduction of BET surface area. The dominant presence of the mesopores is attributed to the formation of a high quantity of oxygen containing functional groups as shown by the sodium capacity result, which blocked almost all the micropores and entered inside the mesopores. This dramatically reduced the pore width of the wider mesopores to more narrow mesopores and since almost all the micropores were blocked, the mesopores became predominant. Compared to the PSD curves of all the other ACCs, the pores are quite small. Comparing the PSD curves of ACCs electrochemically oxidised at 1.1 and 2.2 A at different extents of oxidation [e.g. 1.1 A for 2 h and 2.2 A for 1 h to give 7,920 c/g extent of oxidation (Figure 5.21), 1.1 A for 4 h and 2.2 A for 2 h to give 15,840 c/g extent of oxidation (Figure 5.22) and finally at 1.1 A for 6 h and 2.2 A for 3 h to give 23,760 c/g extent of oxidation (Figure 5.23)], showed that the PSD curves of ACCs electrochemically oxidised at 2.2 A showed higher intensities and broader curves than those electrochemically oxidised at 1.1 A. This is attributed to production of more oxygen containing functional groups by electrochemical oxidation at 1.1 A at higher oxidation time than the electrochemical oxidation at 2.2 A but at lower oxidation time. These oxygen containing functional groups blocked the micropores, therefore, reducing the incremental pore volume in the microporous range. These groups also blocked some sections of the wider mesopores, thereby reducing their pore width and so producing more narrow PSD curves. This follows the same trend with the elemental analysis and sodium capacity results which showed that the oxygen containing functional groups on ACCs electrochemically oxidised at 1.1 A were more than ACCs electrochemically oxidised at 2.2 A at the same extent of oxidation. It is interesting to
note that these results follow exactly the same trend as the BET surface area and nitrogen adsorption-desorption results. Therefore, these results support the suggestion that the reduction in the incremental pore volumes of all the electrochemically oxidised ACCs was not due to destruction of pores but was due to the blockage of pores by oxygen containing functional groups.

5.2.10. Scanning Electron Microscopy (SEM)

Scanning electron micrographs of unoxidised ACC and four most severely electrochemically oxidised ACCs in this investigation are shown in Figure 5.24. Figure 5.24 (a) is the micrograph for unoxidised (UO) ACC while (b) and (c) are the micrographs for electrochemically oxidised ACC (EO) at 1.1 A for 6 h and 8 h to give 23,760 c/g and 31,680 c/g extent of oxidation, respectively. Micrographs (d) and (e) are for ACCs electrochemically oxidised at 2.2 A for 3 h and 4 h to give 23,760 c/g and 31,680 c/g extent of oxidation, respectively. The micrographs of the ACCs electrochemically oxidised at 1.1 A are similar to that of the unoxidised ACC, therefore, no etching was observed on these ACCs. However, the micrographs of ACCs electrochemically oxidised at 2.2 A show distinguishing difference compared to that of the unoxidised ACC. Micrograph (d) shows a slightly etched surface which increased appreciably with an increase in the extent of oxidation as shown in micrograph (e). This is attributed to the fact that the higher current of 2.2 A caused much more etching than the current of 1.1 A even though more of a decrease in BET surface area and loss in porosity were observed for the ACCs electrochemically oxidised at 1.1 A. This confirms that the decrease in BET surface area and loss in microporosity were due to the blockage of the pores by weakly acidic functional groups and not etching since it has been shown that all the ACCs electrochemically oxidised at 1.1 A had higher cation exchange capacity indicating the presence of more weakly acidic functional groups than all the ACCs electrochemically oxidised at 2.2 A at the same extent of oxidation, which showed more etching.
Figure 5.24. SEM of unoxidised and selected electrochemically oxidised ACCs.
5.3. BATCH SORPTION EXPERIMENTS

Competitive and non-competitive sorption isotherms for lead and copper ions in aqueous solutions onto unoxidised ACC (UO) and electrochemically oxidised ACC (EO) are shown in Figures 5.27-5.33. The results in Figure 5.1 showed that the highest sodium capacity (4.94 mmol/g) was observed for the ACC electrochemically oxidised at 1.1 A for 6 h without etching, hence all batch experiments were conducted with this sample as EO. The speciation of metal ions in aqueous solution, sorption isotherm models, effect of electrochemical oxidation, effect of competitive sorption and the effect of solution pH on the sorption of lead and copper and the mechanisms of lead and copper sorption onto EO and UO samples are discussed in the following sections.

5.3.1. Speciation of Metal Ions in Aqueous Solution

The speciation curves for 0.0157 M copper and 0.0193 M lead in nitrate solutions are presented in Figure 5.25 and Figure 5.26, respectively. Figure 5.25 shows that at solution pH 5 (the maximum solution pH used in this study), copper exists in aqueous solution predominantly as Cu$^{2+}$ in approximate proportion of 98.3%. The concentration of the other copper species (e.g. CuNO$_3^+$, CuOH$^+$ and Cu$_2$(OH)$_3^+$) at solution pH 5 is approximately 1.7%. Figure 5.26 shows that at solution pH 5 lead
exists in aqueous solution as Pb$^{2+}$ and PbNO$_3^+$ in approximate proportions of 78.6% and 21.2%, respectively. The concentration of the other lead species at solution pH 5 (e.g. PbOH$^+$ and Pb(OH)$^{2+}$), is negligible (about 0.2%). From the speciation curves it can be seen that there is no precipitation of any of the metal species at solution pH 5. The maximum concentration of lead or copper used for the batch sorption experiments is 0.00787 M which is lower than the concentrations at which the aqueous speciation diagrams were prepared confirming that the metal removal process is purely due to sorption.

5.3.2. Sorption Isotherm Models
The analysis of the isotherm data is important to develop an equation that represents the results. Correlation of the data using empirical or theoretical equations is required in the analysis and design of adsorption processes. The most widely used isotherm equations for modelling equilibrium isotherms are the Langmuir and Freundlich equations. The experimental data for competitive and non-competitive sorption of lead and copper ions onto EO and UO samples were analysed using the Langmuir and
Freundlich isotherm models. The corresponding Freundlich and Langmuir parameters and correlation coefficients ($R^2$) are shown in Table 5.5. The correlation coefficients for the Langmuir isotherm model were higher than those for the Freundlich isotherm model for all the experimental data for sorption onto EO samples, indicating that the adsorption energy is constant over all the adsorption sites and the adsorption sites are

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mmol/g)</td>
<td>$b$</td>
</tr>
<tr>
<td>N Cu UO pH 5</td>
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</tr>
<tr>
<td>N Cu EO pH 3</td>
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<td>10.9</td>
</tr>
<tr>
<td>N Cu EO pH 4</td>
<td>1.243</td>
<td>34.7</td>
</tr>
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<td>87.8</td>
</tr>
<tr>
<td>C Cu UO pH 5</td>
<td>0.073</td>
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</tr>
<tr>
<td>C Cu EO pH 5</td>
<td>0.776</td>
<td>13.7</td>
</tr>
<tr>
<td>N Pb UO pH 5</td>
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<td>1535</td>
</tr>
<tr>
<td>N Pb EO pH 3</td>
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<td>11</td>
</tr>
<tr>
<td>N Pb EO pH 4</td>
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<td>20.5</td>
</tr>
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<td>39.8</td>
</tr>
<tr>
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<td>1.7</td>
</tr>
<tr>
<td>C Pb EO pH 5</td>
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</tr>
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</tr>
<tr>
<td>C Cu + C Pb EO</td>
<td>1.782</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 5.5. Langmuir and Freundlich isotherm constants for non-competitive (N Cu) and competitive (C Cu) copper and non-competitive (N Pb) and competitive (C Pb) lead sorption.
However, the correlation coefficients for Freundlich isotherm model were higher than those for the Langmuir isotherm model for all the experimental data for sorption onto UO samples, indicating that the adsorption energy is not constant over all the adsorption sites and the adsorption sites are not equivalent. Therefore, the correlation coefficients demonstrate that the Langmuir isotherm model fitted the experimental data for sorption onto EO samples while the Freundlich isotherm model fitted the experimental data for sorption onto UO samples. This is confirmed by the experimental and Langmuir isotherm model maximum metal ions sorbed onto EO and UO samples that are shown in Table 5.6. The Langmuir isotherm model predicted maximum metal ions sorbed were approximately the same as the experimentally

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental maximum ion sorbed (mmol/g)</th>
<th>Langmuir maximum ion sorbed (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N Cu UO pH 5</td>
<td>0.098</td>
<td>0.076</td>
</tr>
<tr>
<td>N Cu EO pH 3</td>
<td>0.634</td>
<td>0.643</td>
</tr>
<tr>
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<td>1.243</td>
</tr>
<tr>
<td>N Cu EO pH 5</td>
<td>1.693</td>
<td>1.605</td>
</tr>
<tr>
<td>C Cu UO pH 5</td>
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<tr>
<td>C Cu EO pH 5</td>
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<tr>
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<td>1.022</td>
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</table>

**Table 5.6.** Experimental and Langmuir model maximum metal ion sorbed onto EO and UO.
determined maximum metal ions sorbed onto EO samples while they differ from the experimentally determined maximum metal ions sorbed onto UO samples. This confirms that the Langmuir isotherm model fitted the experimental data for sorption onto EO samples but did not fit the experimental data for sorption onto UO samples. Therefore, all the experimental data for sorption onto EO sample were fitted with the Langmuir isotherm model (solid lines) while the experimental data for sorption onto UO sample were fitted with the Freundlich isotherm model (dashed lines) as shown in Figures 5.27-5.36. The Langmuir and Freundlich isotherm models have been used in modelling metal ions sorption isotherms by several researchers (Faur-Brasquet et al., 2002; Li et al., 2003; Xiao and Thomas, 2004; Saha et al., 2004; Chen and Wu, 2004).

5.3.3. Effect of Electrochemical Oxidation on Lead(II) and Copper(II) Sorption Equilibria

The sorption capacities of EO and UO samples were evaluated for copper and lead ions. Figure 5.27 shows the copper and lead sorption of EO and UO samples evaluated at solution pH 5 and 298 K. The electrochemical oxidation process altered the physical surface characteristics of the UO sample. Reduction in the surface area and pore volume was observed as shown in BET surface area results (Figure 5.18) and the PSD

![Graph showing sorption isotherms](image)

**Figure 5.27.** Non-competitive and competitive (Cu + Pb) sorption isotherms of copper and lead onto UO and EO at solution pH 5.
results (Figures 5.19 and 5.20). However, the changes in these surface properties did not affect the metal sorption. In contrast, a dramatic increase in the lead and copper ions uptake by EO sample for competitive and non-competitive sorption are observed and the results are shown in Figures 5.28 and 5.29. The maximum non-competitive copper and lead sorption capacities for EO sample are 1.693 and 1.867 mmol/g, respectively, while the maximum non-competitive copper and lead sorption capacities for UO sample are 0.0983 and 0.469 mmol/g, respectively. The experimental maximum non-competitive copper and lead sorption capacities for the EO sample are 17 times and 4 times greater than the experimental maximum non-competitive sorption capacities for the UO sample, respectively. The maximum competitive copper and lead sorption capacities for the EO sample are 0.7503 and 1.005 mmol/g, respectively and the maximum competitive copper and lead sorption capacities for the UO sample are 0.0853 and 0.117 mmol/g, respectively. The experimental maximum competitive copper and lead sorption capacities for the EO sample are 8.8 times and 8.6 times greater than the experimental competitive sorption capacities for the UO sample, respectively. Therefore, electrochemical oxidation of ACC dramatically increased its sorption capacity for both competitive and non-competitive sorption of.
lead and copper ions. This is directly related to the increase in more acidic oxygen containing functional groups as detected by the elemental analysis and pH titration results. This is also confirmed by the sodium capacity results which showed a much higher cation exchange capacity for the EO sample than the UO sample.

5.3.4. Competitive Lead(II) and Copper(II) Sorption Equilibria

The results of the analysis of competitive sorption of individual lead and copper ions from aqueous solutions at solution pH 5 and 298 K containing both ions together in equimolar concentrations are compared with non-competitive sorption results from the aqueous solutions containing only one (either copper or lead) ion. The competitive and non-competitive isotherms of copper and lead are shown in Figures 5.29.-5.33. Since the sorption studies included the two metal ions in the same solution at the same molar concentration, the amount of a particular metal ion sorbed by the ACC indicates its ability to compete with the other ion in solution. Sorption sites of EO and UO samples favoured lead ions more than copper ions as shown in Figures 5.27, 5.28 and 5.29. Therefore, the observed sorption preference for sorption of lead and copper ions onto EO and UO samples is Pb\(^{2+}\) > Cu\(^{2+}\). The non-competitive sorption affinity for lead is.

![Graph](image_url)

**Figure 5.29.** Competitive adsorption isotherms of copper and lead onto UO (UO competitive) and EO (EO competitive) at solution pH 5.
Figure 5.30. Non-competitive (UO Cu) and Competitive (UO Cu Competitive) adsorption isotherms of copper onto UO at solution pH 5.

Figure 5.31. Non-competitive (EO Cu) and Competitive (EO Cu Competitive) adsorption isotherms of copper onto EO at solution pH 5.
Figure 5.32. Non-competitive (UO Pb) and Competitive (UO Pb Competitive) adsorption isotherms of lead onto UO at solution pH 5.

Figure 5.33. Non-competitive (EO Pb) and Competitive (EO Pb Competitive) adsorption isotherms of lead onto EO at solution pH 5.
about 1.1 times and 4.8 times greater than that for copper for EO and UO samples, respectively. The difference of a factor of 1.1 times shows that the maximum concentration of sorption sites for copper and lead on the EO sample are approximately the same for non-competitive sorption indicating that the number of sorption sites per gram of ACC is about the same for both metals and the adsorption sites are equivalent. Table 5.6 shows that the experimentally determined maximum lead and copper ions sorbed onto EO sample are 1.866 and 1.693 mmol/g, respectively for non-competitive sorption. It is 1.005 and 0.7502 mmol/g for competitive sorption of lead and copper, respectively giving total sorption sites of 1.755 mmol/g. This confirms that the number of sorption sites per gram of EO is approximately the same for both metals for competitive and non-competitive sorption as shown in Figure 5.28. Furthermore, it can be concluded that copper and lead are sorbed on the same sites on the EO and the sorption process is by ion exchange. However, the difference of a factor of 4.8 times between lead and copper sorption onto UO sample shows that the maximum concentration of sorption sites for copper and lead on the UO sample are different for non-competitive sorption indicating that the sorption sites are not equivalent and the sorption process is not by ion exchange. The results also show that the presence of another ion reduced the sorption of the other ion present in solution. The competitive sorption resulted in maximum sorption capacity reduction of 46.16% and 55.68% for lead and copper, respectively for EO sample. It also resulted in maximum sorption capacity reduction of 75.06% and 12.96% for lead and copper, respectively for UO sample. However, the order of metal sorption capacity onto EO and UO samples follows the same trend of Pb^{2+} > Cu^{2+}, for competitive sorption. The significant reduction in the sorption of lead in the presence of copper, though it is preferred to copper, is due to weaker interaction of lead with the EO or UO samples caused by higher concentration of copper ion in the solution after the initial sorption of lead onto the EO or UO samples since both metal ions had initial equal molar concentrations. The sorption preference for EO and UO samples which is Pb^{2+} > Cu^{2+} is attributed to the fact that adsorbents prefer: the ion with the smaller hydrated ionic radius, the ion with the greater polarizability and the ion of higher valence (Helfferich, 1995; Saha et al., 2000). The crystal ionic radius for Pb^{2+} and Cu^{2+} are 1.19 Å and 0.57 Å, respectively (Lide, 2006; Dean, 1999). However, the effective hydrated ionic radius for Pb^{2+} and Cu^{2+} are 4.5 Å and 6 Å, respectively (Dean, 1999). The polarizability for lead and copper are $6.8 \times 10^{-24}$ cm$^3$ and $6.1 \times 10^{-24}$ cm$^3$, respectively.
Both ions have the same valency, therefore, lead with the smaller effective hydrated ionic radius and greater polarizability is preferred to copper. The lead ions with smaller effective hydrated radii are able to diffuse into parts of the porous structure that are not easily accessible by the larger hydrated copper ions, thereby resulting in increased sorption of lead ions. The preferred sorption of lead to copper due to smaller effective hydrated ionic radius has been reported by other researchers (Petrov et al., 1992; Budinova et al., 1994; Demirbas et al., 2005).

5.3.5. Effect of pH on Lead(II) and copper(II) sorption

The effect of pH on the removal of lead and copper was investigated by determining sorption isotherms of non-competitive copper and lead onto EO sample at solution pH values of 3, 4 and 5 at 298 K. The results are shown in Figures 5.34 and 5.35. In order to avoid precipitation of metal species, no sorption experiments were performed at solution pH greater than 5. From these figures it is clear that the sorption isotherms were affected significantly by solution pH. The maximum sorption capacity increased with an increase in solution pH. It increased by a factor of 2 times and 1.62 times for
copper and lead, respectively with an increase in solution pH from 3 to 4. With a further increase in solution pH from 4 to 5 the maximum sorption capacity increased by a factor of 1.34 times and 1.27 times for copper and lead, respectively. The effect of pH on the sorption isotherms was due to interactions between lead and copper ions in solution and the surface charge on the EO sample. It has already been pointed out in section 5.2.2 that the adsorbent surface is negatively charged at pH values higher than the PZC which is pH 2.8 for the EO sample. It becomes more negatively charged as the solution pH increases due to dissociation of weakly acidic (oxygen containing) functional groups. Hence, the amount of positively charged lead and copper that will ion exchange with the oxygenated functional groups will increase with an increase in solution pH. The reduction in the increase of the maximum sorption capacity with an increase in solution pH from 4 to 5 as compared to that with an increase in solution pH from 3 to 4 is attributed to the fact that the number of sorptive sites per gram of EO is limited. It is also noticeable from Figures 5.34 and 5.35 that the maximum sorption capacity is low for the sorption isotherm for solution pH 3. This is due to the fact that at low solution pH, the dissociation of weakly acidic functional groups is low. Also the concentration of H⁺ ions is quite high at solution pH 3 and will react with the few
negatively charged functional groups produced by the dissociation of few carboxylic functional groups on the surface of the EO sample thereby competing with Pb\(^{2+}\) or Cu\(^{2+}\) ions for the available number of binding sites.

5.3.6. Mechanism of Lead(II) and Copper(II) Sorption onto EO and UO ACCs

To elucidate the sorption mechanism of copper and lead ions onto EO and UO samples, it is necessary to understand the interactions among the metal ions in aqueous solution with the surface functional groups of the ACCs.

The PZC values for EO and UO samples are at pH 2.8 and 6.8, respectively. The highest solution pH at which batch sorption experiments were performed was pH 5. This is below the PZC of UO, so the UO surface was protonated and was positively charged. This explains why the solution pH increased during the copper and lead sorption process indicating that OH\(^-\) ions were released from the surface of the UO sample. The solution pH was adjusted by adding specific volumes of 0.1 M nitric acid to maintain the original pH. Since the ACC is viscose rayon based and the double bonds in the aldehyde ends of cellulose molecules in ACC matrix consist of σ bonds and π bonds (Hill and Holman, 2000; Wilks, 2001) therefore, there are greater electron distribution over the more electronegative oxygen atoms. This makes it possible for lead and/or copper ions to be attached to them, therefore, complex formation between the metal ions and the UO sample surface is the likely mechanism for sorption of lead and copper onto UO sample. This is confirmed by the significant difference between the experimentally determined maximum metal ion sorbed for non-competitive lead and copper onto UO as shown in Table 5.6. The maximum non-competitive lead and copper sorption capacities for UO sample are 0.469 and 0.098 mmol/g, respectively. It is also confirmed by the difference in the sorption isotherms for the UO and EO samples in Figure 5.27. Xiao and Thomas (2004) confirmed that if sorption is mainly controlled by electrostatic interactions, as in ion exchange, a similar amount of metal ions should be sorbed. They also stated that, the reason for sorption of different amounts of metal ions is surface heterogeneity. Therefore, sorption of lead and copper onto UO sample with a heterogeneous surface charge distribution is not by ion exchange but by surface complex formation with the metal ions.
The batch sorption experiments were performed at solution pH values of 3, 4 and 5, which are above the PZC of EO sample. Hence, the surface of the EO sample was negatively charged due to dissociation of the carboxylic functional groups on the EO. The EO sample therefore, behaved as a cation exchanger indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the lead and copper sorption indicating that H⁺ ions were released from the surface of the EO. The solution pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the original solution pH. Mass balances to obtain the maximum H⁺ ions released were performed using the volumes of 0.1 M sodium hydroxide added to adjust the solution pH. The experimentally determined non-competitive and competitive metal ions sorbed onto EO and H⁺ ion released from EO surface are shown in Table 5.7. It is obvious that one Pb²⁺ or Cu²⁺ ion was sorbed for approximately every two H⁺ ions released from the EO sample surface. This confirms

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum metal ion (mmol/g)</th>
<th>Maximum H⁺ ion released (mmol/g)</th>
<th>Ratio of maximum H⁺ ion released to maximum Cu²⁺ or Pb²⁺ ion sorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>N Cu EO pH 3</td>
<td>0.634</td>
<td>1.28</td>
<td>2.02</td>
</tr>
<tr>
<td>N Cu EO pH 4</td>
<td>1.267</td>
<td>2.52</td>
<td>1.99</td>
</tr>
<tr>
<td>N Cu EO pH 5</td>
<td>1.693</td>
<td>3.352</td>
<td>1.98</td>
</tr>
<tr>
<td>N Pb EO pH 3</td>
<td>0.904</td>
<td>1.8</td>
<td>1.99</td>
</tr>
<tr>
<td>N Pb EO pH 4</td>
<td>1.465</td>
<td>2.92</td>
<td>1.99</td>
</tr>
<tr>
<td>N Pb EO pH 5</td>
<td>1.867</td>
<td>3.68</td>
<td>1.97</td>
</tr>
<tr>
<td>C Cu + C Pb EO pH 5</td>
<td>1.755</td>
<td>3.4</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Table 5.7. Experimentally determined maximum non-competitive (N Cu and N Pb) and competitive (C Cu and C Pb) metal ions sorbed onto EO and H⁺ ion released from EO.
that the sorption of lead and copper onto EO sample is by ion exchange mechanism. The pH titration, zeta potential and FTIR analyses results confirmed that carboxylic acid groups (\(-\text{COOH}\)) were introduced to EO sample by electrochemical oxidation. Therefore, the ion exchange mechanism involving the interaction of the carboxylic acid sites of EO sample can be represented by the following reaction scheme:

$$2(S-\text{COOH}) + M^{2+} \leftrightarrow (S-\text{COO})_2M + 2H^+$$

where $S$ is the surface of the EO sample and $M^{2+}$ is the metal ion, i.e., Pb$^{2+}$ or Cu$^{2+}$.

5.4. CONCLUSIONS

It has been shown that electrochemical oxidation of a viscose rayon based ACC using potassium chloride as an electrolyte under varying conditions leads to samples with different physical and chemical characteristics. Electrochemical oxidation introduced weakly acidic functional groups on the surface of the ACC as indicated by pH titration, sodium capacity measurements, zeta potential and elemental analysis results. This was also confirmed by the FTIR spectra that showed the presence of carboxylic acid groups on the electrochemically oxidised ACC. A significant increase in cation exchange capacity of ACC was obtained by electrochemical oxidation and it increased with increase in the extent of oxidation. This is due to the introduction of carboxylic acid groups. It has also been shown that the extent of electrochemical oxidation depends on both the applied current and oxidation time showing that electrochemical oxidation is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and oxidation time at any extent of oxidation used in this study to produce ACC of maximum cation exchange capacity was 1.1 A with voltage of 4.2 V and current density of 0.8 mA/m$^2$. Increase in surface acidity shifted the point of zero charge from pH of 6.8 to 2.8 and the isoelectric point from pH of 3 to 1.15 for the electrochemically oxidised ACC due to the introduction of carboxylic acid groups during electrochemical oxidation. However, a decrease in BET surface area by electrochemical oxidation was observed, which was due to blockage of pores by carboxylic acid groups. Pore size distribution was altered by electrochemical oxidation largely due to the loss in microporosity and development of mesoporosity. Maximum copper and lead ions sorption capacities of ACC increased by factors of 17 and 4 times, respectively, for non-competitive sorption for the electrochemically oxidised (EO) sample. The capacities also increased by factors of 8.8 and 8.6 times for competitive sorption of copper and lead, respectively, for
EO sample. The competitive and non-competitive sorption isotherm studies confirmed that the affinity order of lead and copper ions sorbed by the unoxidised and electrochemically oxidised ACCs is, \( \text{Pb}^{2+} > \text{Cu}^{2+} \). The solution pH plays a very important role on the sorption of lead and copper ions onto the electrochemically oxidised ACC. The uptake of lead and copper ions increased with an increase in solution pH. It is confirmed that lead and copper ions were sorbed onto EO ACC by an ion exchange mechanism. However, it is proposed that lead and copper ions were sorbed onto unoxidised (UO) ACC by complex formation with the ACC surface. The present study concludes that electrochemical oxidation of viscose rayon based ACC markedly enhanced the removal of lead and copper ions from aqueous solutions and EO ACC has a very high potential to be used as an effective adsorbent for treating aqueous solution contaminated with copper/lead in both single component and multi-component systems.
6. RESULTS AND DISCUSSIONS OF CHARACTERISATION OF ELECTROCHEMICALLY REDUCED ACTIVATED CARBON CLOTH AND ADSORPTION STUDIES

6.1. INTRODUCTION
This chapter highlights the results of various conventional techniques used to characterise the electrochemically reduced and as-received ACCs. The results from the studies of chromium(VI) sorption experiments for electrochemically reduced ACC, electrochemically oxidised ACC and as-received ACC are also described in this chapter.

6.2. CHARACTERISATION OF ACCS
This section discusses the results of the experimental procedures used to physically and chemically characterise the as-received, electrochemically oxidised and electrochemically reduced activated carbon cloth (ACC) used for adsorption of chromium(VI) from aqueous solution. The quantity and nature of the surface functional groups on the surface of the ACCs were characterised by chloride capacity, pH titration, zeta potential measurements, elemental analysis, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD), nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

6.2.1 Chloride Capacity
The total anion exchange capacity (i.e. the quantity of basic functional groups) was determined in hydrochloric acid solution. Oxygen-containing groups like carbonyl, ether, hydroxyl, phenolic and lactonic groups present on carbonaceous materials are protonated increasingly with a decrease in solution pH values (Natale et al., 2007; Jeffery, 1989; Park and Kim, 2001; Leon y Leon et al., 1992). Therefore, these surface
groups are completely protonated in solutions at low pH and are available for anion exchange. Under this condition the total anion exchange capacity can be determined. A high chloride capacity is an indication of a high content of basic surface oxygen functional groups. Preliminary experiments measuring chloride capacity indicated that the best adsorption took place using a current of 5.5 A or 6.6 A. The chloride capacity results for as-received ACC and electrochemically reduced ACCs are shown in Figure 6.1. The results in Figure 6.1 show that the chloride capacity of electrochemically reduced ACC at 5.5 A for 3 h is 3.9 times higher than that of as-received ACC. This is attributed to the introduction of basic functional groups. The extent of reduction on the carbon surface depends on the chemical composition of the electrolyte. Chlorine and hypochlorous acid (HOCI) that is formed when chlorine is present in water are strong oxidants (Chernow and Vallasi, 1993). Also from the electrochemical series of metals (Atkins and Paula, 2002) it is obvious that the potassium is a very strong reductant. Since the reduction and oxidation processes are responsible for the overall reaction in an electrolytic cell, the presence of strong oxidant and strong reductant explains why the ACC is strongly reduced when potassium chloride is used as an electrolyte. The chloride capacity data gives an

![Figure 6.1. Chloride capacity result for as-received ACC and electrochemically reduced (ER) ACC at different conditions.](image-url)
indication of the anion exchange capacity of the ACC in aqueous solution. So ACC, electrochemically reduced in potassium chloride has a high potential for toxic anion removal from aqueous solutions.

A plot of the hydrochloric acid uptake (chloride capacity) versus the extent of electrochemical reduction of ACC at a constant time of 4 h but at different currents of 0, 1.1, 2.2, 3.3 and 5.5 A is given in Figure 6.2. The extent of electrochemical reduction is defined as the product of current and electrochemical reduction time in coulomb per gram (c/g) of ACC. Figure 6.2 shows that the chloride capacity increased in direct proportion to the extent of reduction. This is attributed to an increase in the amount of basic functional groups introduced on the surface of the ACC as the reduction process increased with an increase in current. This also suggests that it is not just the total current that passed through the electrolyte to the cathode (i.e. the ACC) that is important. The chemical conditions at the cathode are very complex. As the electrolyte was potassium chloride, chlorine, oxygen and hypochlorous acid were evolved at the anode. Hydrogen and carbon dioxide were also evolved at the cathode.

Figure 6.2. HCl uptake versus extent of electrochemical reduction for 4 h at different currents.
(Horita et al., 1996). The composition of these products will depend on the current used as well as the diffusion processes at the electrodes. It would seem likely that the generation of exchangeable groups on the ACC depends on both current used for electrochemical reduction as well as the total coulombs (i.e. product of current and reduction time) passed through the solution. In order to observe the effect of reduction time, a series of electrochemical reductions of ACC were performed at a constant current of 5.5 A, but at different periods of reduction 0, 0.8, 1.2, 1.6, 2.4, 3 and 4 h to achieve different extents of reduction. The plot of hydrochloric acid uptake versus the extent of reduction at constant current is shown in Figure 6.3. It can be seen that

![Figure 6.3](image)

**Figure 6.3.** HCl uptake *versus* extent of electrochemical reduction at 5.5 A for different reduction times.

the chloride capacity increased rapidly for 31,680 c/g extent of reduction and then further increased at a rate directly proportional to the extent of reduction at constant current of reduction. This is attributed simply to the longer exposure of the ACC to the reducing condition allowing a greater reaction time for the introduction of basic groups on the ACC. The process of manufacturing viscose rayon consists of the following steps: alkalisation, shredding, preripening i.e. ageing, xanthation, dissolving, maturing and viscose fibre spinning (Wilks, 2001). At the spinning stage, the cellulose is regenerated from the viscose for the production of the viscose rayon filament.
Therefore, the ACC matrix is composed of interlinking cellulose molecules. At short periods of reduction, some of the cellulose molecules in the viscose rayon based ACC matrix will not be reduced and so the amount of basic functional groups to be introduced to the surface of the ACC will be less than the amount introduced at long periods of reduction when more of the surface molecules are reduced. The anion exchange capacity of electrochemically reduced ACC depends on both the applied current and the time of reduction, indicating that electrochemical reduction is a diffusion-dependent process.

Further experiments were performed to establish the predominant factor (applied current or reduction time) that influences the hydrochloric acid uptake of the ACC. Two sets of experiments were performed by electrochemically reducing ACCs at a specific reduction time. The first set of ACCs were electrochemically reduced at a constant current of 5.5 A for 0.8, 1.2, 1.6, 2.4, 3 and 4 h to give 15,840, 23,760, 31,680, 47,520, 59,400 and 79,200 c/g extent of reduction, respectively. The second set of ACCs were electrochemically reduced at a constant current of 6.6 A for 0.67, 1, 1.33, 2, 2.5 and 3.3 h to give the same extent of reduction as that of the first set, that is, 15,840, 23,760, 31,680, 47,520, 59,400 and 79,200 c/g extent of reduction, respectively. This was to achieve data from the two sets of experiments for the same

![Figure 6.4](image_url)  
**Figure 6.4.** HCl uptake versus extent of electrochemical reduction at 5.5 A and 6.6 A.
extent of reduction at different reduction time. Plots of hydrochloric acid uptake versus the extent of reduction for the two different sets are presented in Figure 6.4. The chloride capacity for the ACCs electrochemically reduced at 5.5 A was higher than that for the set reduced at 6.6 A at lower extent of reduction. It was 1.1 times higher at 15,840 c/g extent of reduction, i.e., 0.63 mmol/g and 0.58 mmol/g for ACCs electrochemically reduced at 5.5 A and 6.6 A, respectively. However, this trend gradually decreased with an increase in the extent of reduction up to 79,200 c/g. At this extent of reduction, the same value of 1.05 mmol/g of chloride capacity was obtained for ACC electrochemically reduced at 5.5 A and 6.6 A. The trend in chloride capacity for the two sets of electrochemically reduced ACCs is attributed to the fact that at low extent of reduction, ACC electrochemically reduced at 6.6 A did not have enough time for a large number of cellulose molecules in the ACC matrix to be reduced even though the current was higher.

When hydrochloric acid uptake was plotted against time of exposure to the reducing condition (i.e. reduction time) for the two sets of electrochemically reduced ACC at 5.5 A and 6.6 A as shown in Figure 6.5, the chloride uptake was similar for about 50% of the total improvement in chloride capacity. However, at reduction time of about

![Graph](image_url)

**Figure 6.5.** HCl uptake versus reduction time at 5.5 A and 6.6 A.
2.5 h, the production of basic functional groups that enhanced the chloride uptake slowed down at the lower current of 5.5 A. It is therefore possible that the chemical condition at the ACC surface is most significant in the early stages of reduction whilst later in the reduction process (i.e. at higher reduction time) the current becomes more significant. As the current is the driving force for reduction to occur (Atkins and Paula, 2002), the choice of current is very important. As shown in Figure 6.2, for any extent of reduction, if an applied current is too small, though the reduction time is long enough for a large number of molecules in the ACC matrix to be reduced, the current may not be sufficient for reduction to occur. This means that there must be an optimum constant current at which the reduction time will be high enough to introduce the maximum amount of basic functional groups on the ACC surface for any extent of reduction. In order to more accurately determine the optimum constant current, four series of experiments were performed at different extents of electrochemical reduction, e.g. 15,840 c/g, 23,760 c/g, 31,680 c/g and 47,520 c/g. The extent of electrochemical reduction is defined as the product of current and electrochemical reduction time in coulomb per gram (c/g) of ACC. For each series of experiment, the ACCs were electrochemically reduced at different currents of 1.1, 2.2, 3.3, 4.4, 5.5, 6.6, 7.7 and 8.8 A, but at different reduction times. Plots of the chloride capacity versus applied current for the four series of experiments are presented in Figure 6.6. The four sets of

![Figure 6.6. HCl uptake versus applied current for different extents of electrochemical reduction.](image)

181
results followed the same trend. The chloride capacities for ACCs reduced below 5.5 A were lower than that for the ACC that is reduced at 5.5 A. This is attributed to the fact that applied currents below 5.5 A do not produce sufficiently vigorous reducing conditions. The chloride capacity for reduced ACCs reached a maximum at 5.5 A and then decreased continuously with increasing applied current. The lowest chloride capacity was observed for ACCs electrochemically reduced at 8.8 A. This is attributed to the fact that though 8.8 A is the highest current, the small times of the electrochemical reduction of 30, 45, 60 and 90 min were not enough for effective reduction of most of the cellulose molecules in the ACC matrix. The optimum current was found to be 5.5 A for all electrochemical reduction times. It is to be noted that above 59,400 c/g extent of reduction, the ACCs become fragile and are not suitable for adsorption studies. The maximum chloride capacity for electrochemically reduced ACC was obtained at 5.5 A for 2.4 h (i.e. 47,520 c/g extent of reduction), which is 0.93 mmol/g and for as-received ACC (i.e. the value at 0 A), it is 0.25 mmol/g. Therefore, the chloride capacity for electrochemically reduced ACC is 3.72 times higher than that of the as-received ACC in hydrogen form. This increase is attributed to the introduction of more basic functional groups by electrochemical reduction. The highest chloride capacity without breakage of fibres was observed on electrochemically reduced ACC at 5.5 A for 3 h. For this reason electrochemical reduction of ACC at 5.5 A for 3 h was used for the remaining reduction experiments.

### 6.2.2. pH Titrations

Proton binding curve, that is the plot of ion released versus equilibrium solution pH, for as-received ACC, electrochemically reduced ACC at 5.5 A for 3 h (ER ACC) and electrochemically oxidised ACC at 1.1 A for 6 h (EO ACC) are shown in Figure 6.7. The point where the proton binding curve crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH value at which the surface charge is zero at a particular ambient temperature, applied pressure and aqueous solution composition (Garrison, 1998; Menedez et al., 1995). The PZC will be shifted to lower pH values with oxidation of the ACC due to the introduction of acidic functional groups such as carboxylic, carbonyl and lactonic groups onto the surface of the ACC (Donnet and Bansal, 1984). However, it will be shifted to higher pH values with reduction of ACC due to introduction of basic functional groups such as ether, hydroxyl and quinone groups onto the surface of the ACC (Boehm, 1994).
As shown in Figure 6.7, PZC for the as-received ACC is at pH 6.8, whereas it shifted to pH 2.8 for the EO ACC and pH 9 for ER ACC. It is well known that sorption of metal ions from aqueous solution by activated carbon strongly depends on the chemistry of carbon surface (Rangel-Mendez and Streat, 2002a; Saha et al., 2001a; Saha et al., 2003; Donnet and Bansal, 1984; Park and Kim, 1999a). The adsorbent surface is positively charged at solution pH values below the PZC because the oxygen containing groups are undissociated and are highly protonated and the carbon will remove anions from solution under these conditions. In contrast, at solution pH values higher than the PZC, the carbon surface becomes more negatively charged due to dissociation of weakly acidic oxygen containing functional groups. Thus the carbon is able to remove cations in solution. The curve for EO ACC shows the highest concentration of hydrogen ions released, hence the cation exchange capacity is expected to be higher than that of as-received ACC as shown by the sodium capacity results in Figure 5.1. The curve for ER ACC shows the highest concentration of hydroxyl ions released, hence the anion exchange capacity is expected to be higher than that of as-received ACC as shown by the chloride capacity results in Figure 6.1. It is known that carboxylic groups in activated carbons dissociate at solution pH values.

Figure 6.7. Ion released versus equilibrium solution pH for as-received ACC, ER ACC and EO ACC.
within the range of 2 and 6 and hydroxyl and ether groups dissociate at solution pH values above 6 (Helfferich, 1995; Chingombe et al., 2005). From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the as-received ACC, ER ACC and EO ACC to produce $H^+$ ions starts at equilibrium solution pH of approximately 7, 9.5 and 3, respectively. Therefore, one of the types of acidic functional groups on the surface of EO ACC is likely to be carboxylic groups while that on the surfaces of as-received ACC and ER ACC are likely to be hydroxyl groups and ether groups, respectively.

6.2.3. Zeta Potential Measurements

Figure 6.8 shows the zeta potential versus equilibrium solution pH plots for ER ACC, as-received ACC and EO ACC. An important parameter used to characterise the electrokinetic behaviour of a solid-liquid interface is the isoelectric point (IEP). This is the equilibrium solution pH at which the zeta potential is zero. From the curves it can be seen that the IEP value of the EO ACC is not accurately measurable as discussed in section 5.2.3, the proton concentration of the bulk electrolyte solution is too low and increasing the proton concentration caused further decrease of the zeta potential. Other researchers (Rangel-Mendez and Streat, 2002a; Bismark et al., 1999b) had the same
observation with electrochemically oxidised granular carbon and fibre and obtained the IEP values by extrapolation. Therefore the IEP value for the EO ACC as shown in Figure 6.8 is an extrapolated value. The IEP for as-received ACC is at pH 3 while that for EO ACC is estimated to be pH 1.15. This shows that EO ACC is more acidic than as-received ACC which confirms the pH titration results. The lower IEP value for EO ACC is attributed to the presence of more acidic functional groups. The IEP for as-received ACC is at pH 3 while that for ER ACC is at pH 3.6. This shows that the ER ACC is more basic than the as-received ACC which confirms the pH titration results. The higher IEP value for the ER ACC is attributed to the presence of more basic functional groups. Since the IEP values are representative of the external surface charges (Garrison, 1998; Menendez et al., 1995) and PZC values are representative of the net total of external and internal surface charges, the difference between PZC and IEP can be interpreted as a measure of the surface charge distribution of carbons. Greater differential values indicate more negatively charged external than internal particle surfaces and therefore more heterogeneous distribution of the surface charges. The lower differential values indicate a more homogeneous distribution of the surface charges. Electrochemical properties of as-received ACC, ER ACC and EO ACC are summarised in Table 6.1. The PZC - IEP for the ER ACC is higher than that for the as-received ACC, while that for EO ACC is lower than that for as-received ACC. Therefore the electrochemical oxidation gives a more homogeneous surface charge distribution, indicating that the oxidation reactions during electrochemical oxidation occurred both on the surface and on the internal matrix of the as-received ACC. However, the highest value of PZC - IEP for ER ACC shows that electrochemical reduction gives a more heterogeneous surface charge distribution, indicating that the reduction reactions during electrochemical reduction occurred predominantly on the

<table>
<thead>
<tr>
<th>Sample</th>
<th>PZC</th>
<th>IEP</th>
<th>PZC - IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ACC</td>
<td>6.8</td>
<td>3</td>
<td>3.8</td>
</tr>
<tr>
<td>ER ACC</td>
<td>9</td>
<td>3.6</td>
<td>5.4</td>
</tr>
<tr>
<td>EO ACC</td>
<td>2.8</td>
<td>1.15</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 6.1. Electrochemical properties of as-received ACC, electrochemically reduced ACC and electrochemically oxidised ACC.
internal matrix of the as-received ACC. This is confirmed by the very small difference in the IEP values of 0.6 between the ER ACC and the as-received ACC. The heterogeneous charge distribution for as-received ACC is attributed to the fact that the ACC is viscose rayon based and it is known that the double bond in the aldehyde end of the cellulose molecules consists of a $\sigma$ bond and a $\pi$ bond (Hill and Holman, 2000; Wilks, 2001). So there is greater electron distribution over the more electronegative oxygen atom. However, the internal surface of the as-received ACC will have a more uniform electron distribution due to bond formation between the cellulose molecules and the presence of several hydrogen and carbon atoms and so the external surface is more negatively charged than its internal surface.

### 6.2.4 Elemental Analysis

The elemental analysis results for as-received ACC, ER ACC and EO ACC are shown in Table 6.2. The as-received ACC has 20.03% oxygen content indicating the presence of some oxygen containing groups on the surface. This is attributed to the presence of oxygen atoms in the aldehyde and hydroxyl groups of the cellulose molecules of the viscose rayon based ACC (Hill and Holman, 2000; Wilks, 2001). The oxygen content in EO ACC increased by 120.8%. The increase in oxygen content in the EO ACC is attributed to the introduction of weakly acidic oxygen containing functional groups. The oxygen content in ER ACC decreased by 3.2%. This result follows the same trend as the chloride capacity results in Figure 6.1 which showed anion exchange capacity of 0.25 mmol/g for as-received ACC and 0.98 mmol/g for the ER ACC. The hydrogen content in ER ACC decreased by 13.8%. The decrease in both hydrogen content and

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ACC</td>
<td>76.89</td>
<td>2.03</td>
<td>1.05</td>
<td>20.03</td>
</tr>
<tr>
<td>ER ACC</td>
<td>77.35</td>
<td>1.75</td>
<td>1.5</td>
<td>19.4</td>
</tr>
<tr>
<td>EO ACC</td>
<td>52.33</td>
<td>2.6</td>
<td>0.84</td>
<td>44.23</td>
</tr>
</tbody>
</table>

Table 6.2. Elemental analysis of as-received ACC, electrochemically reduced ACC and electrochemically oxidised ACC.
oxygen content indicates that the likely reaction on the ACC by electrochemical reduction is dehydration of the hydroxyl functional groups. The small decrease in oxygen content in the ER ACC is attributed to the formation of weakly basic oxygen containing functional groups. It is known that the more basic oxygen containing functional groups have lower oxygen content than hydroxyl functional groups and dehydration of two molecules of hydroxyl functional groups produces one molecule of ether (Hill and Holman, 2000; Smith and March, 2001; McMurry, 2000; Denniston et al., 2004; Howarth, 1998; Vollhardt et al., 1999). Therefore one of the types of basic functional groups on the surface of ER ACC is likely to be ether groups.

6.2.5. Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

The study of the chemical composition of Carbon fibres by FTIR is difficult because the absorption of the fibre is very intense while the concentration of the different functional groups on its surface is relatively low. So the signal/noise ratio is often not sufficiently high even if the sample is scanned many times. Also the diameter of the fibre falls in the analytical wavelength range of infrared light, which may lead to strong interference at low wavenumbers (Gulyas et al., 2001). For these reasons the intensities of FTIR spectra of ACCs are not very high. FTIR spectra for the as-received ACC and ER ACC are shown in Figures 6.9 and 6.10, respectively. The band assignments are shown in Table 6.3. FTIR spectra and band assignment for the EO ACC are shown and discussed in section 5.2.5. The marked difference in the functional groups observed on as-received ACC and ER ACC as shown in Table 6.3 are the presence of aldehyde and ether groups, respectively. Since a cellulose molecule has aldehyde and hydroxyl ends, it is expected that the ACCs should have aldehyde and hydroxyl functional groups on their surfaces. However, aldehyde groups were not detected on ER ACC, because aldehyde groups readily react with hydroxyl groups to produce ether groups by dehydration (Hill and Holman, 2000; Smith and March, 2001; McMurry, 2000; Denniston et al., 2004; Howarth, 1998; Vollhardt et al., 1999). It is also known that dehydration of two molecules of hydroxyl functional groups produces one molecule of ether (Hill and Holman, 2000; Smith and March, 2001; McMurry, 2000; Denniston et al., 2004; Howarth, 1998; Vollhardt et al., 1999).
Figure 6.9. FTIR spectra for as-received ACC.

Figure 6.10. FTIR spectra for ER ACC.
Table 6.3. Band assignments for FTIR spectra of as-received ACC and ER ACC.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Band Assignment</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3435</td>
<td>- O - H Hydroxyl group</td>
<td>3434</td>
<td>- O - H Hydroxyl group</td>
</tr>
<tr>
<td>2851 and 2943</td>
<td>CHO Aldehyde group</td>
<td>2914</td>
<td>Saturated C - H and C - C</td>
</tr>
<tr>
<td>2349</td>
<td>O = C = O Carbon dioxide</td>
<td>2352</td>
<td>O = C = O Carbon dioxide</td>
</tr>
<tr>
<td>1742</td>
<td>CHO Aldehyde group</td>
<td>1600</td>
<td>C = O Ketones</td>
</tr>
<tr>
<td>1634</td>
<td>C = O Ketones</td>
<td>1383</td>
<td>- CH₃ deformations</td>
</tr>
<tr>
<td>1458</td>
<td>= C - H deformations</td>
<td>1255 and 1218</td>
<td>R - O - R' Ether</td>
</tr>
<tr>
<td>1384</td>
<td>- CH₃ deformations</td>
<td>1095</td>
<td>R - O - R' Ether</td>
</tr>
</tbody>
</table>

The ether groups observed on ER ACC confirms the pH titration and zeta potential results that showed that the ER ACC is more basic than the as-received ACC, since the negative logarithm of acidity constants (pKa) for an ether molecule produced by dehydration of two alcohol molecules is larger than the pKa value of the alcohol molecules that produced it (McMurry, 2000). It is known that a stronger base has a larger pKa value (Jeffery, 1989; Smith and March, 2001; McMurry, 2000; Lide, 2006; Dean, 1999; Skoog et al., 1997). It also confirms the elemental analysis result that showed that the likely reaction on the ACC by electrochemical reduction is dehydration of the hydroxyl functional groups. This also explains why there was an increase in the chloride capacity of the ER ACC after electrochemical reduction in potassium chloride.

6.2.6. Reactions in Electrochemical Cell

With the confirmation that ether groups are introduced onto the ACC by electrochemical reduction and since it is known that aldehydes and alcohols react to produce ethers in the presence of H⁺ by dehydration in the presence of excess alcohols, (Hill and Holman, 2000; Smith and March, 2001; McMurry, 2000; Denniston et al., 2004; Howarth, 1998; Vollhardt et al., 1999), it is possible to postulate the likely reactions that took place in the electrochemical cell. The reactions most likely to occur are as follows:-
\[2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \quad (6.1)\]
\[\text{KCl} \leftrightarrow \text{K}^+ + \text{Cl}^- \quad (6.2)\]
\[2\text{Cl}^- + 2e^- \leftrightarrow \text{Cl}_2(\text{g}) \quad (6.3)\]
\[\text{K}^+ + e^- \leftrightarrow \text{K} \quad (6.4)\]
\[2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \quad (6.5)\]
\[\text{C} + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2(\text{g}) + 4\text{H}^+ + 4e^- \quad (6.6)\]
\[\text{Cl}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{HOCI} + \text{H}^+ + \text{Cl}^- \quad (6.7)\]
\[2\text{HOCI} + 2\text{H}^+ + 2e^- \leftrightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O} \quad (6.8)\]

The above reactions are in agreement with reactions suggested by Horita et al. (1996). It has been discussed that in reducing environment (e.g. in the presence of Cl⁻), all accessible hydroxyl groups in the cellulose \((\text{C}_6\text{H}_{10}\text{O}_5)_n\) molecules of viscose rayon based ACC react with aldehyde groups to produce ether groups by dehydration. Hence from the above reactions scheme it can be concluded that the reduction of the aldehyde and hydroxyl groups within the cellulose molecules in the ACC to produce ethers are the most likely reactions that occurred during the electrochemical reduction of viscose rayon based ACC in the electrochemical cell.

6.2.7. Nitrogen adsorption-desorption results

The nitrogen adsorption-desorption isotherms obtained for as-received ACC and electrochemically reduced ACCs are shown in Figures 6.11-6.17. All the isotherms

![Nitrogen adsorption-desorption isotherm](image-url)

**Figure 6.11.** Nitrogen adsorption-desorption isotherm for as-received ACC.
Figure 6.12. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 0.8 h (i.e. 15,840 c/g extent of reduction).

Figure 6.13. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 1.2 h (i.e. 23,760 c/g extent of reduction).
Figure 6.14. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 1.6 h (i.e. 31,680 c/g extent of reduction).

Figure 6.15. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 2.4 h (i.e. 47,520 c/g extent of reduction).
Figure 6.16. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 3 h (i.e. 59,400 c/g extent of reduction).

Figure 6.17. Nitrogen adsorption-desorption isotherm for ACC, electrochemically reduced at 5.5 A for 4 h (i.e. 79,200 c/g extent of reduction).
are of type 1 according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Sing et al., 1985). Type 1 isotherms are characterised by a plateau that is nearly horizontal to the p/p⁰ axis. This means that all the ACCs are predominantly microporous, since type 1 isotherms signify microporous solids having small external area and are characterised by an almost horizontal plateau. The sharply rising area at very low pressure < 0.1 p/p⁰ is due to the filling of micropores. The adsorption process is complete at about 0.4 p/p⁰ for all the electrochemically reduced ACCs and 0.6 p/p⁰ for the as-received ACC. From Figures 6.11-6.17, it can also be seen that there was decrease in the maximum nitrogen adsorption capacities for the electrochemically reduced ACCs which increased as the extent of reduction increased up to 31,680 c/g extent of reduction. However, it was observed that the decrease in maximum nitrogen adsorption capacity, reduced for ACC electrochemically reduced at 47,520 c/g extent of reduction and remained approximately constant for further increase in extent of reduction. The maximum nitrogen adsorption capacities decreased from 458.49 cm³/g for the as-received ACC (i.e. 0 c/g) to 320.18, 348.58, 219.71, 294.75, 306.95 and 300.07 cm³/g for the electrochemically reduced ACCs at 15,840 c/g, 23,760 c/g, 31,680 c/g, 47,520 c/g, 59,400 and 79,200 c/g extent of reduction, respectively. This is attributed to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted and cross-linking by bond formation between hydroxyl and aldehyde groups that reacted to produce ether groups during the electrochemical reduction. The cross-linking reduced the maximum nitrogen adsorption capacities. However, the production of ether from hydroxyl and aldehyde also involved dehydration, which produced some micropores, thereby, reducing the decrease in the maximum nitrogen adsorption capacities. However, due to production of a smaller quantity of ethers up to 31,680 c/g extent of reduction, the dehydration was not much, therefore, fewer micropores were produced, so the lowest maximum nitrogen adsorption capacity was observed for ACC electrochemically reduced at 31,680 c/g extent of reduction. With further increase in extent of reduction, that is 47,520 c/g extent of reduction, a larger quantity of ethers were produced, which increased the dehydration that produced more micropores, thereby, increasing the maximum nitrogen adsorption capacity, that remained approximately constant with further increase in extent of reduction. Therefore, these results confirm that the decrease in surface area is not by etching but by production of ethers by
electrochemical reduction. The results also show that nitrogen adsorption is a function of the available surface area.

Figure 6.18 shows the comparison of the nitrogen adsorption isotherms of electrochemically reduced ACC with the highest anion exchange capacity but without etching, electrochemically oxidised ACC with the highest cation exchange capacity but without etching and as-received ACC. The maximum nitrogen adsorption capacity decreased from 458.49 cm$^3$/g for as-received ACC to 306.95 and 30.33 cm$^3$/g for the ER ACC and EO ACC, respectively. The smaller decrease in maximum nitrogen adsorption capacity for ER ACC is attributed to production of ether groups as discussed earlier, that enhanced the anion exchange capacity of the ER ACC, as shown by the chloride capacity results and dehydration during ether production that produced some micropores, since the production of ether from hydroxyl and aldehyde is a dehydration process (Hill and Holman, 2000; Smith and March, 2001; McMurry, 2000; Denniston et al., 2004; Howarth, 1998; Vollhardt et al., 1999), therefore the
maximum nitrogen capacity for ER ACC is much higher than the maximum nitrogen capacity for EO ACC. This is expected since electrochemical oxidation of ACC at 1.1 A for 6 h produced high quantity of oxygen containing functional groups that enhanced the cation exchange capacity of EO ACC, as shown by the sodium capacity results, which blocked almost all the micropores and entered inside the mesopores. Therefore, it can be concluded that there was no destruction of pores on the EO ACC and ER ACC used for the batch sorption experiments for chromium(VI) adsorption studies.

6.2.8. Surface area results

Figure 6.19 shows the BET surface area versus extent of reduction plot for electrochemically reduced ACCs at current of 5.5 A which is the observed optimum current, but at different times of electrochemical reduction to produce different extents of reduction. The surface area specifications of as-received ACC, selected electrochemically reduced ACCs (ER) and electrochemically oxidised ACC (EO) are shown in Table 6.4. All the ACCs analysed in this study have extensive surface areas.

![Figure 6.19](image)

**Figure 6.19**. BET surface area versus extent of reduction for ACCs electrochemically reduced at 5.5 A.
Table 6.4. Surface area specifications of as-received ACC, electrochemically oxidised ACC (EO) and electrochemically reduced ACCs (ER) at different conditions.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Single point surface area (m²/g) at P/P₀ 0.205</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm) (4V/A by BET)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ACC</td>
<td>1395</td>
<td>1378</td>
<td>20.5</td>
</tr>
<tr>
<td>ER 5.5 A 0.8 h</td>
<td>1065</td>
<td>1140</td>
<td>19.1</td>
</tr>
<tr>
<td>ER 5.5 A 1.2 h</td>
<td>1078</td>
<td>1062</td>
<td>18.6</td>
</tr>
<tr>
<td>ER 5.5 A 1.6 h</td>
<td>991</td>
<td>979</td>
<td>18.7</td>
</tr>
<tr>
<td>ER 5.5 A 2.4 h</td>
<td>960</td>
<td>938</td>
<td>19</td>
</tr>
<tr>
<td>ER 5.5 A 3 h</td>
<td>1025</td>
<td>998</td>
<td>19.3</td>
</tr>
<tr>
<td>ER 5.5 A 4 h</td>
<td>1005</td>
<td>979</td>
<td>18.5</td>
</tr>
<tr>
<td>EO 1.1 A 6 h</td>
<td>533</td>
<td>532</td>
<td>18.7</td>
</tr>
</tbody>
</table>

That are ideal in the treatment of drinking water and wastewater. Figure 6.19 shows that the BET surface area decreased slightly with an increase in the extent of reduction up to 31,680 c/g extent of reduction and remained approximately constant with further increase in extent of reduction. The results in Table 6.4 also showed that ER 5.5 A lost 17.3%, 22.9%, 29%, 31.9%, 27.6% and 29% of the original BET surface area at 15,840 c/g, 23,760 c/g, 31,680 c/g, 47,520 c/g, 59,400 c/g and 79,200 c/g extent of reduction, respectively, while EO 1.1 A lost 61.4% of the original BET surface area at 23,760 c/g extent of oxidation. The slight decrease in BET surface area for ER is attributed to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted and cross-linking by bond formation between hydroxyl and aldehyde groups that reacted to produce ether groups during the electrochemical reduction. The cross-linking reduced the number of pores within the ACC matrix, thereby reducing the BET surface area. However, the production of ether from hydroxyl and aldehyde also involved dehydration as discussed earlier, which produced some micropores, thereby, reducing the decrease in BET surface area of the electrochemically reduced ACCs. The high decrease in BET surface area for EO is attributed to the blockage of pores by acidic functional groups and humic substances produced during electrochemical oxidation.
6.2.9. Pore Size Distribution (PSD) Results

The PSD results for electrochemically reduced ACCs at 5.5 A, which is the observed optimum current but at different time of electrochemical reduction to produce different extents of reduction are compared with the PSD result of as received ACC. The results are shown in Figures 6.20-6.25. According to the International Union of Pure and Applied Chemistry (IUPAC) system (Sing et al., 1985) as discussed in section 5.2.9. It can be seen from the PSD curves that as-received ACC exhibited bimodal pore size distributions with peaks dominant at approximately 15 Å and 28 Å. So it possesses a reasonable amount of micropores, with a small fraction of mesopores but without any macropores. All electrochemically reduced ACCs also exhibited similar bimodal pore

![Figure 6.20. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 15,840 c/g extent of reduction.](image-url)
Figure 6.21. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 23,760 c/g extent of reduction.

Figure 6.22. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 31,680 c/g extent of reduction.
Figure 6.23. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 47,520 c/g extent of reduction.

Figure 6.24. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 59,400 c/g extent of reduction.
size distributions. The microporous nature of all the samples is clearly demonstrated, with the most dominant peak at approximately 15 Å, for all the samples. However, the PSD curve of the as-received ACC covers a slightly broader range of pore width than the electrochemically reduced ACCs, except the electrochemically reduced ACC at 79,200 c/g that is shown in Figure 6.25. The range of pore width decreased very slightly for electrochemically reduced ACC at 15,840 c/g and then decreased further, with increase in extent of reduction, up to 31,680 c/g and remained approximately constant with further increase in extent of reduction up to 59,400 c/g extent of reduction. The slight decrease in range of pore width for electrochemically reduced ACCs at 15,840 c/g, 23,760 c/g, 31,680 c/g, 47,520 c/g and 59,400 c/g extents of reduction is attributed to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted and cross-linking by bond formation between hydroxyl and aldehyde groups that reacted to produce ether groups during the electrochemical reduction. The cross-linking reduced the number of pores within the ACC matrix, thereby reducing the range of pore width. However, the production of ether from hydroxyl and aldehyde also involved dehydration, which produced some micropores, thereby, reducing the decrease in the range of pore width of the

*Figure 6.25. Pore size distribution for as-received ACC (0 c/g) and electrochemically reduced ACC at 5.5 A at 79, 200 c/g extent of reduction.*
electrochemically reduced ACCs. This also explains the microporous nature of all the electrochemically reduced ACCs. The PSD curve of the as-received ACC covers a much broader range of pore width than the PSD curve for electrochemically reduced ACC at 79,200 c/g. This is attributed to etching of the ACC electrochemically reduced at 5.5 A for 4 h, that was observed during the electrochemical reduction process. However, the ACC electrochemically reduced at 79,200 c/g still had microporous nature, with the most dominant peak at approximately 15 Å, showing that the etching removed the mesopores and not the micropores. This explains the small decrease of 29% in the BET surface area of the ACC electrochemically reduced at 79,200 c/g, even though etching was observed on it during electrochemical reduction. From the PSD curves it can also be seen that there was a slight decrease in incremental pore volumes in all the pores for the electrochemically reduced ACCs which increased as the extent of reduction increased up to 31,680 c/g extent of reduction and remained approximately constant for further increase in extent of reduction, except 79,200 c/g. Incremental pore volume reduced from 0.032 cm³/g for as-received ACC (i.e. 0 c/g) to 0.027, 0.025, 0.023, 0.022 and 0.023 cm³/g for electrochemically reduced ACC at 15,840 c/g, 23,760 c/g, 31,680 c/g, 47,520 c/g and 59,400 c/g extent of reduction, respectively. This follows the same trend with the nitrogen adsorption-desorption isotherm and BET surface area results. However, it reduced to 0.017 cm³/g for ACC electrochemically reduced at 79,200 c/g extent of reduction with etching. This confirms the proposal that the reduction in the incremental pore volumes of all the electrochemically reduced ACCs except the ACC that was electrochemically reduced at 79,200 c/g was not due to destruction of pores but was due to the production of ether functional groups with bond formations that increased the nitrogen constriction to the pores that resulted in decrease in incremental pore volume of electrochemically reduced ACC.

The PSD result for electrochemically reduced ACC at 5.5 A for 3 h (ER ACC), which is the ACC with the highest anion exchange capacity without etching are compared with the PSD results of as-received ACC and electrochemically oxidised ACC at 1.1 A for 6 h (EO ACC), which is the ACC with the highest cation exchange capacity without etching. The results are shown in Figure 6.26. From the PSD curves it is obvious that the as-received ACC and ER ACC are predominantly microporous, with the most dominant peak at approximately 15 Å. However, a slight reduction of
incremental pore volume was observed for ER ACC, which is due to production of ether groups that enhanced the anion exchange capacity of the ER ACC, as shown by the chloride capacity results. This confirms the suggestion that the reduction in the incremental pore volume for the ER ACC was not due to destruction of pores but was due to the production of ether functional groups with bond formations that increased the nitrogen constriction to the pores that resulted in decrease in incremental pore volume. However, EO ACC showed the most dominant peak at approximately 22 Å, showing that it contained more mesopores than micropores. This is confirmed by the greater decrease in BET surface area of the EO ACC as shown in Table 6.4. ER ACC lost 27.6% of the original BET surface area, while EO ACC lost 61.4% of the original BET surface area, since more micropores than mesopores would have given it a lower decrease in BET surface area. Saha et al. (2003), also observed that loss in microporosity results in the reduction of BET surface area. The dominant presence of mesopores is attributed to formation of high quantity of oxygen containing functional groups that enhanced the cation exchange capacity of the EO ACC, as shown by the sodium capacity results in section 5.2.1, which blocked almost all the micropores and
entered inside the mesopores. This dramatically reduced the pore width of the wider mesopores to more narrow mesopores and since almost all the micropores were blocked, the mesopores became predominant. This confirms that reduction in the incremental pore volume of the EO ACC was not due to destruction of pores but was due to the blockage of pores by oxygen containing functional groups. The maximum nitrogen capacity for ER ACC is much higher than the maximum nitrogen capacity for EO ACC. This is expected since electrochemical oxidation of ACC at 1.1 A for 6 h produced high quantity of oxygen containing functional groups that enhanced the cation exchange capacity of EO ACC, as shown by the sodium capacity results, which blocked almost all the micropores and entered inside the mesopores. Therefore, it can be concluded that there was no destruction of pores on the EO ACC and ER ACC used for the batch sorption experiments for chromium(VI) adsorption studies.

6.2.10. Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEMs) of as-received ACC, electrochemically oxidised ACC at 1.1 A for 6 h (EO ACC) and two most severely electrochemically reduced ACCs in this investigation are shown in Figure 6.27. Figure 6.27 (a) is the micrograph for as-received ACC while (b) is the micrograph for electrochemically oxidised ACC (EO) at 1.1 A for 6 h to give 23,760 c/g extent of oxidation. Micrographs (c) and (d) are for electrochemically reduced ACCs (ER) at 5.5 A for 3 h and 4 h to give 59,400 c/g and 79,200 c/g extent of reduction, respectively. The micrographs shown in Figures 6.27 (a), (b) and (c) are very similar. Therefore, no significant breakage of fibres was observed during electrochemical oxidation of ACC at 1.1 A for 6 h, and electrochemical reduction of ACC at 5.5 A for 3 h. Therefore all ACCs used in this investigation are suitable for adsorption studies. However, the micrograph of ACC electrochemically reduced at 5.5 A for 4 h show significant difference compared to that of the as-received ACC. Micrograph (d) shows a more etched surface. This is attributed to the fact that the high current of 5.5 A caused etching after 3 h of electrochemical reduction. This confirms that the decrease in BET surface areas for electrochemically oxidised ACC at 1.1 A for 6 h and electrochemically reduced ACC at 5.5 A for 3 h were not due to etching.
Figure 6.27. SEM of as-received ACC, selected electrochemically oxidised ACC and selected electrochemically reduced ACCs.
6.3. BATCH SORPTION EXPERIMENTS

The sorption isotherms for chromium(VI) ions in aqueous solutions onto as-received ACC, electrochemically reduced ACC (ER ACC) and electrochemically oxidised ACC (EO ACC) are shown in Figures 6.29–6.34. The results in Figure 5.1 showed that the highest sodium capacity (4.94 mmol/g) was observed for ACC electrochemically oxidised at 1.1 A for 6 h without etching and the results in Figure 6.1 showed that the highest chloride capacity (0.98 mmol/g) was observed for the ACC electrochemically reduced at 5.5 A for 3 h without etching hence all batch experiments were conducted with these samples as EO ACC and ER ACC, respectively. The speciation of chromium(VI) ions in aqueous solution, sorption isotherm models, effect of electrochemical reduction and electrochemical oxidation and effect of solution pH on the sorption of chromium(VI) ions and the mechanisms of chromium(VI) ions sorption onto as-received ACC, ER ACC and EO ACC samples are discussed in the following sections.

6.3.1. Speciation of Chromium(VI) Ions in Aqueous Solution

The speciation curve calculated using JCHESS and CHESS software for 0.01 M chromium(VI) in sodium dichromate solution is presented in Figure 6.28. Figure 6.28

![Figure 6.28. Speciation curve for 0.01 M chromium in sodium dichromate solution.](image-url)
shows that at solution pH 8 which is the maximum solution pH used in this study, chromium exists in aqueous solution as $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, and $\text{HCrO}_4^-$ in proportions of 98.09%, 0.016%, and 1.89%, respectively. At solution pH 6 chromium exists in aqueous solution as $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, and $\text{HCrO}_4^-$ in proportions of 29.12%, 13.67%, and 57.2%, respectively. At solution pH 4 chromium exists in aqueous solution as $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, and $\text{HCrO}_4^-$ in proportions of 0.36%, 21.58%, and 78.05%, respectively. The concentrations of the other chromium species ($\text{H}_2\text{CrO}_4$) in approximate proportions of 0.004%, 0.01%, and 0.01%, at solution pH 8, 6 and 4, respectively, are therefore negligible. It is clear from the speciation curves that there is no precipitation of any of the chromium species at solution pH 8. Therefore, at solution pH 4, 6 and 8 used for the batch sorption experiments, chromium exists predominantly in anionic species in aqueous solution. The maximum concentration of chromium(VI) used for the batch sorption experiments is 0.009616 M which is lower than the concentrations at which the aqueous speciation was calculated; therefore the batch sorption process is purely sorption and not precipitation.

6.3.2. Sorption Isotherm Models
Sorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Classical sorption models, such as Langmuir and Freundlich models have been extensively used to describe the equilibrium established between adsorbed metal ions on the adsorbent and the metal ions remaining in solution at constant temperature. The experimental data for sorption of chromium(VI) ions onto as-received ACC, ER ACC and EO ACC were analysed using the Langmuir and Freundlich isotherm models. The corresponding Freundlich and Langmuir parameters, correlation coefficients ($R^2$) and experimental values for maximum chromium(VI) ion sorbed ($q_e$) are shown in Table 6.5. The correlation coefficients for the Langmuir isotherm model were higher than those for Freundlich isotherm model for all the experimental data for sorption onto all the ACCs. Therefore, the values of correlation coefficients confirm that the Langmuir isotherm model fitted the experimental data for sorption onto as-received ACC, ER ACC and EO ACC. This is confirmed by the experimental ($q_e$) and Langmuir isotherm model ($q_{\text{max}}$) maximum chromium(VI) ions sorbed onto as-received ACC, ER ACC and EO ACC that are shown in Table 6.5. The maximum chromium(VI) ions sorbed for Langmuir isotherm model are approximately
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>qₑ (mmol/g)</th>
<th>qₑ max (mmol/g)</th>
<th>b</th>
<th>R²</th>
<th>Kᵢ</th>
<th>1/n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ACC</td>
<td>4</td>
<td>1.79</td>
<td>1.96</td>
<td>2.7</td>
<td>0.996</td>
<td>1.12</td>
<td>0.345</td>
<td>0.865</td>
</tr>
<tr>
<td>As-received ACC</td>
<td>6</td>
<td>0.78</td>
<td>0.815</td>
<td>2.8</td>
<td>0.998</td>
<td>0.51</td>
<td>0.264</td>
<td>0.851</td>
</tr>
<tr>
<td>As-received ACC</td>
<td>8</td>
<td>0.074</td>
<td>0.0799</td>
<td>1.3</td>
<td>0.987</td>
<td>0.043</td>
<td>0.297</td>
<td>0.896</td>
</tr>
<tr>
<td>ER ACC</td>
<td>4</td>
<td>3.8</td>
<td>3.949</td>
<td>5.2</td>
<td>0.999</td>
<td>2.8</td>
<td>0.302</td>
<td>0.891</td>
</tr>
<tr>
<td>ER ACC</td>
<td>6</td>
<td>1.86</td>
<td>1.914</td>
<td>3.7</td>
<td>0.981</td>
<td>1.26</td>
<td>0.259</td>
<td>0.899</td>
</tr>
<tr>
<td>ER ACC</td>
<td>8</td>
<td>0.64</td>
<td>0.679</td>
<td>2.7</td>
<td>0.997</td>
<td>0.43</td>
<td>0.248</td>
<td>0.838</td>
</tr>
<tr>
<td>EO ACC</td>
<td>4</td>
<td>0.173</td>
<td>0.208</td>
<td>0.84</td>
<td>0.993</td>
<td>0.089</td>
<td>0.366</td>
<td>0.889</td>
</tr>
<tr>
<td>EO ACC</td>
<td>6</td>
<td>0.44</td>
<td>0.448</td>
<td>2.1</td>
<td>0.977</td>
<td>0.27</td>
<td>0.277</td>
<td>0.883</td>
</tr>
<tr>
<td>EO ACC</td>
<td>8</td>
<td>0.84</td>
<td>0.83</td>
<td>6.4</td>
<td>0.99</td>
<td>0.66</td>
<td>0.131</td>
<td>0.886</td>
</tr>
</tbody>
</table>

Table 6.5. Langmuir and Freundlich isotherm constants and experimental values for maximum chromium(VI) ions sorbed (qₑ) for ACCs at solution pH 4, 6 and 8.

the same as the experimental maximum chromium(VI) ions sorbed by as-received ACC, ER ACC and EO ACC. Therefore, all the experimental data for sorption onto ACCs were fitted with the Langmuir isotherm model (solid lines) as shown in Figures 6.29–6.34. The Langmuir and Freundlich models have been used in modelling the sorption isotherms of chromium ions onto adsorbents by several researchers (Han et al., 2000; Hu et al., 2003; Garg et al., 2007; Khezami and Carpart, 2005; Natale et al., 2007; Aggarwal et al., 1999; Mohan et al., 2005; Mor et al., 2007; Saha et al., 2004; Daneshvar et al., 2002; Park et al., 2004a; Lazaridis and Charalambous, 2005; Aoyoma, 2003; Selvaraj et al., 2003).
6.3.3. Effect of Electrochemical Reduction and Electrochemical Oxidation on Chromium(VI) Sorption Equilibrium

The sorption capacities of as-received ACC, ER ACC and EO ACC were evaluated for chromium(VI) ions. Figure 6.29 shows chromium(VI) sorption of as-received ACC, ER ACC and EO ACC evaluated at solution pH 4 and 298 K. The maximum chromium(VI) sorption capacities for the as-received ACC, ER ACC and EO ACC samples are 1.79, 3.8 and 0.173 mmol/g, respectively. The experimental maximum chromium(VI) sorption capacity for ER ACC is 2.12 times higher than the experimental maximum chromium(VI) sorption capacity for as-received ACC, while the experimental maximum chromium(VI) sorption capacity for EO ACC is 10.35 times lower than the experimental maximum chromium(VI) sorption capacity for the as-received ACC.

Figure 6.29. Sorption isotherms of chromium(VI) onto as-received ACC, ER ACC and EO ACC at solution pH 4.

ER ACC and EO ACC evaluated at solution pH 4 and 298 K. The maximum chromium(VI) sorption capacities for the as-received ACC, ER ACC and EO ACC samples are 1.79, 3.8 and 0.173 mmol/g, respectively. The experimental maximum chromium(VI) sorption capacity for ER ACC is 2.12 times higher than the experimental maximum chromium(VI) sorption capacity for as-received ACC, while the experimental maximum chromium(VI) sorption capacity for EO ACC is 10.35 times lower than the experimental maximum chromium(VI) sorption capacity for the as-received ACC.
Figure 6.30 shows chromium(VI) sorption of the as-received ACC, ER ACC and EO ACC evaluated at solution pH 6 and 298 K. The maximum chromium(VI) sorption capacities for the as-received ACC, ER ACC and EO ACC samples are 0.78, 1.86 and 0.44 mmol/g, respectively. The experimental maximum chromium(VI) sorption capacity for ER ACC is 2.39 times higher than the experimental maximum chromium(VI) sorption capacity for as-received ACC, while the experimental maximum chromium(VI) sorption capacity for EO ACC is 1.77 times lower than the experimental maximum chromium(VI) sorption capacity for as-received ACC.
Figure 6.31 shows the chromium(VI) adsorption of the as-received ACC, ER ACC and EO ACC evaluated at solution pH 8 and 298 K. The maximum chromium(VI) sorption capacities for as-received ACC, ER ACC and EO ACC samples are 0.074, 0.64 and 0.84 mmol/g, respectively. The experimental maximum chromium(VI) sorption capacity for ER ACC is 8.65 times higher than the sorption capacity for as-received ACC, while the experimental maximum chromium(VI) sorption capacity for EO ACC is 11.35 times higher than the sorption capacity of as-received ACC.

The highest maximum chromium(VI) sorption capacity in all the batch sorption experiments was for ER ACC at solution pH 4 (i.e. 3.8 mmol/g). The experimental maximum chromium(VI) sorption capacity for ER ACC at solution pH 4 is 22 times higher than the maximum chromium(VI) sorption capacity for EO ACC at solution pH 4 (i.e. 0.173 mmol/g). This is directly related to the more basic oxygen containing functional ether groups as detected by the elemental analysis, pH titration and FTIR analysis and chloride capacity results. The oxygen atom in ether is more negative than...
the oxygen atom in alcohol, since it is attached to two carbon atoms (McMurry, 2000),
therefore ether functional groups are more protonated than alcohol functional groups.
This also makes ether functional groups more basic than the alcohol functional groups.
Basha et al. (2007), also observed an increase in chromium(VI) sorption capacity due
to the introduction of ether groups by chemical modification of seaweed that had
hydroxyl groups. Park et al. (1999b) also observed an increase in chromium(VI)
sorption capacity due to the introduction of ether groups by electrochemical oxidation
of activated carbon fibre in sodium hydroxide. At solution pH 4, the ER ACC is highly
protonated and so is highly positively charged, while the chromium(VI) ion exists
mostly as anions, leading to strong electrostatic attraction between ER ACC and the
chromium(VI) ions. Due to the highly positively charged surface of ER ACC, chromium(III)
ions produced by reduction of the chromium(VI) ions by hydroxyl
groups on ER ACC were repulsed and released back to the solution, therefore, higher
concentrations of chromium(III) ions were detected on the equilibrated solutions of
ER ACC than the equilibrated solutions of as-received ACC and EO ACC in all batch
sorption experiments. Adsorption of chromium(VI) onto adsorbents due to protonation
of the adsorbent surfaces has been discussed by other researchers (Bautista-Toledo et
al., 1994; Park et al., 1999b; Park and Kim, 2001; Shawabkeh, 2006; Basha et al.,
2007; Garg et al., 2007; Mor et al., 2007; Natale et al., 2007). In contrast, the
experimental maximum chromium(VI) sorption capacity that was observed for the
EO ACC (i.e. 0.84 mmol/g) at solution pH 8 is 1.3 times higher than the experimental
maximum chromium(VI) sorption capacity for ER ACC (i.e. 0.64 mmol/g) at solution
pH 8. This is directly related to the increase in more acidic oxygen containing
functional groups (carboxylic acid groups) as detected by the elemental analysis, FTIR
analysis, sodium capacity and pH titration results. Therefore, adsorption of
chromium(VI) onto EO ACC is by reduction of chromium(VI) to chromium(III) by
the hydroxyl groups on EO ACC and sorption of chromium(III) ions onto the
negatively charged surface of EO ACC due to dissociation of the carboxylic groups.
However, the maximum chromium(VI) sorption capacity for EO ACC sample at
solution pH 8 (i.e. 0.84 mmol/g) is much lower than the experimental maximum
chromium(VI) sorption capacity for ER ACC at solution pH 4 (i.e. 3.8 mmol/g). This
is attributed to the fact that, even though all the carboxylic groups on EO ACC
dissociated completely at solution pH 8, the available quantity of hydroxyl groups on
the EO ACC for reduction of chromium(VI) to chromium(III) is limited. Also, it is
known that the effective hydrated ionic radius for Cr$^{3+}$ and CrO$_4^{2-}$ are 9 Å and 4 Å, respectively (Aggarwal et al., 1999; Dean, 1999; Skoog et al., 1997). Therefore, CrO$_4^{2-}$ ions with smaller hydrated radius are able to diffuse into most of the porous structures of ER ACC. However, most of the porous structures of EO ACC are not accessible by Cr$^{3+}$ ions with larger hydrated radius which resulted in low sorption of Cr$^{3+}$ ions produced by reduction of chromium(VI) by hydroxyl groups on EO ACC.

6.3.4. Effect of pH on Chromium(VI) Sorption

The effect of pH on the removal of chromium(VI) was investigated by determining sorption isotherms of chromium(VI) onto as-received ACC, ER ACC and EO ACC at solution pH values of 4, 6 and 8 at 298 K. The results for as-received ACC are shown in Figure 6.32. The maximum chromium(VI) sorption capacities for as-received ACC, at solution pH 4, 6 and 8 are 1.79, 0.78 and 0.074 mmol/g, respectively. The maximum chromium(VI) sorption capacity decreased with an increase in solution pH. It decreased by a factor of 2.3 times with an increase in solution pH from 4 to 6. With a further increase in solution pH from 6 to 8, the maximum chromium(VI) sorption
capacity decreased by a factor of 10.5 times. The effect of pH on the sorption isotherms was due to interactions between chromium(VI) ions in solution and the surface charge on the as-received ACC. The PZC for as-received ACC is at pH 6.8. Therefore at solution pH 4 the surface is positively charged due to protonation of hydroxyl groups which results in high chromium(VI) sorption capacity. As pH of the solution increased to pH 6 the as-received ACC undergoes deprotonation and the chromium(VI) sorption capacity decreases. As pH of the solution increased to pH 8 which is above the PZC of the as-received ACC, it becomes negatively charged due to dissociation of hydroxyl functional groups and can only adsorb the chromium(III) ions produced by reduction of chromium(VI). However, the dissociation of the hydroxyl groups is small since the difference between pH 8 and the PZC is small, therefore the chromium(VI) sorption capacity for as-received ACC at solution pH 8 is very low.

The results for ER ACC are shown in Figure 6.33. The maximum chromium(VI) adsorption capacities observed for ER ACC at solution pH 4, 6 and 8 are 3.8, 1.86 and

![Figure 6.33. Sorption isotherms of chromium(VI) onto ER ACC at solution pH 4, 6 and 8.](image-url)
0.64 mmol/g, respectively. The maximum chromium(VI) sorption capacity decreased with an increase in solution pH. It decreased by a factor of 2.04 times with an increase in solution pH from 4 to 6. With a further increase in solution pH from 6 to 8 the maximum sorption capacity decreased by a factor of 2.91 times. The effect of pH on the sorption isotherms was due to interactions between chromium(VI) ions in solution and the surface charge on the ER ACC. The PZC for ER ACC is at pH 9. Therefore at solution pH 4, 6 and 8 the ER ACC was positively charged due to protonation of ether groups and adsorbed the chromium(VI) in anionic form. At solution pH 4 the ER ACC surface is highly positively charged which results in high chromium(VI) sorption capacity. As pH of the solution increased to pH 6, the ER ACC undergoes deprotonation and the chromium(VI) sorption capacity decreases. As pH of the solution increased to pH 8, ER ACC undergoes more deprotonation. Also, competition between CrO$_4^{2-}$ and OH$^-$ ions in the solution for the active sites on ER ACC exists at solution pH 8 which results in further decrease in chromium(VI) sorption capacity.

The results for EO ACC are shown in Figure 6.34. The maximum chromium(VI) sorption capacities observed for EO ACC at solution pH 4, 6 and 8 are 0.173, 0.44 and

![Figure 6.34. Sorption isotherms of chromium(VI) onto EO ACC at solution pH 4, 6 and 8](image-url)
0.84 mmol/g, respectively. The maximum chromium(VI) sorption capacity increased with an increase in solution pH. It increased by a factor of 2.54 times with an increase in solution pH from 4 to 6. With a further increase in solution pH from 6 to 8, the maximum sorption capacity increased by a factor of 1.91 times. The effect of pH on the sorption isotherms was due to interactions between chromium(VI) ions in solution and the surface charge on the EO ACC. The PZC for EO ACC is at pH 2.8. Therefore at solution pH 4, 6 and 8 the EO ACC was negatively charged due to dissociation of carboxylic groups and adsorbed the chromium(III) produced by the reduction of chromium(VI) by the hydroxyl groups on EO ACC. It becomes more negatively charged as the solution pH increases due to increase in dissociation of the carboxylic functional groups. Hence, the amount of positively charged chromium(III) that will ion exchange with the oxygenated functional groups will increase with an increase in solution pH. The reduction in the increase of the maximum chromium(VI) sorption capacity with an increase in solution pH from 6 to 8 as compared to that with an increase in solution pH from 4 to 6 is attributed to the fact that the number of hydroxyl groups on EO ACC for reduction of chromium(VI) to chromium(III) is limited. It is also noticeable from Figure 6.34 that the maximum chromium(VI) sorption capacity is low for the sorption isotherm for solution pH 4. This is due to the fact that at solution pH 4, the dissociation of carboxylic functional groups is low. Also the concentration of H⁺ ions is high and will react with the few anionic functional groups on the surface of the EO ACC thereby restricting the number of binding sites for chromium(III) ions.

6.3.5. Mechanism of Chromium(VI) Sorption onto as-received ACC, ER ACC and EO ACC

To elucidate the sorption mechanism of chromium(VI) onto as-received ACC, ER ACC and EO ACC, it is necessary to understand the interactions among the metal ions in aqueous solution with the surface functional groups on the ACCs. PZC for as-received ACC, ER ACC and EO ACC are at pH 6.8, 9 and 2.8, respectively.

At solution pH 4 and 6, which are below the PZC for as-received ACC, the surface of the as-received ACC was positively charged due to protonation of hydroxyl groups, therefore, it behaved as an anion exchanger indicating that the sorption process was ion exchange. During the chromium(VI) sorption process, cleavage occurs on the protonated surface of as-received ACC to release OH⁻ ions into the solution. This
explains why the solution pH increased during the sorption process and so was adjusted by adding specific volumes of 0.1 M nitric acid to maintain solution pH at 4 and 6. However at solution pH 8, which is above the PZC, the as-received ACC surface was positively charged due to the dissociation of hydroxyl groups, therefore, it behaved as a cation exchanger and could only adsorb chromium(III) that is in cationic form indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the sorption process indicating that H⁺ ions were released from the surface of the as-received ACC. The solution pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the solution pH at 8.

Mass balances to obtain the maximum H⁺ or OH⁻ ions released were performed using the volumes of 0.1 M sodium hydroxide or nitric acid added to adjust the solution pH. The experimentally determined chromium ions sorbed onto as-received ACC and H⁺ or OH⁻ ions released from its surface are shown in Table 6.6. At solution pH 4 one

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Maximum chromium(VI) ion sorbed (mmol/g)</th>
<th>Maximum H⁺ ion released (mmol/g)</th>
<th>Maximum OH⁻ ion released (mmol/g)</th>
<th>Ratio of maximum H⁺ or OH⁻ ion released to maximum chromium(VI) ion sorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received ACC</td>
<td>4</td>
<td>1.79</td>
<td>0</td>
<td>1.826</td>
<td>1.02</td>
</tr>
<tr>
<td>As-received ACC</td>
<td>6</td>
<td>0.78</td>
<td>0</td>
<td>1.178</td>
<td>1.51</td>
</tr>
<tr>
<td>As-received ACC</td>
<td>8</td>
<td>0.074</td>
<td>0.237</td>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td>ER ACC</td>
<td>4</td>
<td>3.8</td>
<td>0</td>
<td>3.784</td>
<td>0.995</td>
</tr>
<tr>
<td>ER ACC</td>
<td>6</td>
<td>1.86</td>
<td>0</td>
<td>2.796</td>
<td>1.5</td>
</tr>
<tr>
<td>ER ACC</td>
<td>8</td>
<td>0.64</td>
<td>0</td>
<td>1.285</td>
<td>2.01</td>
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<tr>
<td>EO ACC</td>
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<td>0.529</td>
<td>0</td>
<td>3.06</td>
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<tr>
<td>EO ACC</td>
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<td>0.44</td>
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<td>0</td>
<td>3.07</td>
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<td>EO ACC</td>
<td>8</td>
<td>0.84</td>
<td>2.425</td>
<td>0</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Table 6.6. Experimental values for maximum Cr(VI) ions sorbed onto ACCs and H⁺ or OH⁻ ions released from ACCs.
chromium(VI) ion was sorbed for approximately every one OH\(^-\) ion released from the surface of the as-received ACC. This confirms that sorption of chromium(VI) onto the as-received ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at solution pH 4 chromium exists as HCrO\(_4^-\) in proportion of 78.05%. Therefore, it is expected that for every chromium ion sorbed, one OH\(^-\) ion will be released from the surface of as-received ACC. At solution pH 6, two chromium(VI) ions were sorbed for approximately every three OH\(^-\) ions released from the surface of the as-received ACC. This confirms that the sorption of chromium(VI) onto as-received ACC is mainly governed by an ion exchange mechanism, since the speciation curves show that at solution pH 6, chromium exists as HCrO\(_4^-\) in proportion of 57.2% and as CrO\(_4^{2-}\) and Cr\(_2\)O\(_7^{2-}\) in proportion of 43%. Therefore, it is expected that for two chromium ions sorbed, three OH\(^-\) ions will be released from the as-received ACC surface. At solution pH 8, one Cr\(^{3+}\) ion was sorbed for approximately every three H\(^+\) ions released from the as-received ACC surface. This confirms that the sorption of chromium(III) onto as-received ACC is mainly governed by an ion exchange mechanism. The sorption sites on the as-received ACC are mainly hydroxyl functional groups. Therefore, the ion exchange mechanism involving the interaction of the hydroxyl sites of as-received ACC with chromium(VI) ions in aqueous solution can be represented by the following reaction schemes:

At solution pH 4 the reactions are:

\[
\begin{align*}
S-OH + H_2O &\rightarrow S-O^+(H_2) + OH^- \quad (6.9) \\
S-O^+(H_2) + HCrO_4^- &\rightarrow SHCrO_4 + H_2O \quad (6.10)
\end{align*}
\]

Where S is the surface of the as-received ACC. Combining equations (6.9) and (6.10) gives:

\[
S-OH + HCrO_4^- \rightarrow SHCrO_4 + OH^- \quad (6.11)
\]

At solution pH 6 the reactions are: equation (6.11) and

\[
\begin{align*}
2S-OH + 2H_2O &\rightarrow 2S-O^+(H_2) + 2OH^- \quad (6.12) \\
2S-O^+(H_2) + Cr_2O_7^{2-} &\rightarrow SCr_2O_7S + 2H_2O \quad (6.13)
\end{align*}
\]

Combining equations (6.12) and (6.13) gives:

\[
2S-OH + Cr_2O_7^{2-} \rightarrow SCr_2O_7S + 2OH^- \quad (6.14)
\]
At solution pH 8 the reactions are:
Reduction of chromium(VI) by hydroxyl groups:

\[
\text{ACC} + \text{CrO}_4^{2-} \rightarrow \text{Cr}^{3+} + \text{H}_2\text{O} + \text{ACC (oxidised)} \quad (6.15)
\]

Adsorption of Cr\(^{3+}\):

\[
3\text{S-OH} + \text{Cr}^{3+} \rightarrow (\text{S-O})_3\text{Cr} + 3\text{H}^+ \quad (6.16)
\]

The solution pH at which the batch sorption experiments were performed i.e. pH 4, 6 and 8 are below the PZC of ER ACC. Hence, the surface of the ER ACC surface was positively charged due to protonation of ether groups therefore, it behaved as an anion exchanger indicating that the sorption process was ion exchange. During the chromium(VI) sorption, cleavage occurs on the protonated surface of ER ACC to release OH\(^-\) ions into the solution. This explains why the solution pH increased during the sorption process and so was adjusted by adding specific volumes of 0.1 M nitric acid to maintain the solution pH at 4, 6 and 8. Mass balances to obtain the maximum OH\(^-\) ions released were performed using the volumes of 0.1 M nitric acid added to adjust the solution pH. The experimentally determined chromium(VI) ions sorbed onto ER ACC and OH\(^-\) ion released from ER ACC surface at solution pH 4, 6 and 8 are shown in Table 6.6. At solution pH 4, one chromium(VI) ion was sorbed for approximately every one OH\(^-\) ion released from the ER ACC surface. This confirms that the sorption of chromium(VI) onto ER ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at solution pH 4 chromium exists as HCrO\(_4\)^\(\cdot\) in proportion of 78.05%. Therefore, it is expected that for every chromium ion sorbed, one OH\(^-\) ion will be released from the ER ACC. At solution pH 6, two chromium(VI) ions were sorbed for approximately every three OH\(^-\) ions released from the ER ACC surface. This confirms that the sorption of chromium(VI) onto ER ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at solution pH 6 chromium exists as HCrO\(_4\)^\(\cdot\) in proportion of 57.2% and as CrO\(_4\)^\(-2\) and Cr\(_2\)O\(_7\)^\(-2\) in proportion of 43%. Therefore, it is expected that for every two chromium ions sorbed, three OH\(^-\) ions will be released from the ER ACC. At solution pH 8 one chromium(VI) ion was sorbed for approximately every two OH\(^-\) ions released from the ER ACC surface. This confirms that the sorption of chromium(VI) onto ER ACC is mainly governed by ion exchange mechanism, since the speciation curves show that at solution pH 8 chromium exists as CrO\(_4\)^\(-2\) in proportion of 98.09%. Therefore, it is expected that for every one chromium ion sorbed, two OH\(^-\) ions will be released from
the ER ACC. The sorption sites on ER ACC are mainly ether functional groups. Therefore, the ion exchange mechanism involving the interaction of the ether sites of ER ACC with chromium(VI) ions in aqueous solution can be represented by the following reaction schemes:

At solution pH 4 the reactions are:

\[
\begin{align*}
S'-O-S' + H_2O & \rightarrow S'-O^+(H)-S' + OH^- \\
S'-O^+(H)-S' + HCrO_4^- & \rightarrow S'-OH + S'HCrO_4
\end{align*}
\]

(6.17)  
(6.18)

Where \( S' \) is the surface of ER ACC. Combining equations (6.17) and (6.18) gives:

\[
S'-O-S' + H_2O + HCrO_4^- \rightarrow S'-OH + S'HCrO_4 + OH^- 
\]

(6.19)

At solution pH 6 the reactions are: equation (6.19) and

\[
\begin{align*}
2S'-O-S' + 2H_2O & \rightarrow 2S'-O^+(H)-S' + 2OH^- \\
2S'^-O^+(H)-S' + Cr_2O_7^{2-} & \rightarrow 2S'^-OH + S'Cr_2O_7S'
\end{align*}
\]

(6.20)  
(6.21)

Combining equations (6.20) and (6.21) gives:

\[
2S'^-O-S' + 2H_2O + Cr_2O_7^{2-} \rightarrow 2S'^-OH + S'Cr_2O_7S' + 2OH^- 
\]

(6.22)

At solution pH 8 the reactions are: equation (6.20) and

\[
\begin{align*}
2S'^-O^+(H)-S' + CrO_4^{2-} & \rightarrow 2S'^-OH + S'CrO_4S'
\end{align*}
\]

(6.23)

Combining equations (6.20) and (6.23) gives:

\[
2S'^-O-S' + 2H_2O + CrO_4^{2-} \rightarrow 2S'^-OH + S'CrO_4S' + 2OH^- 
\]

(6.24)

The solution pH at which the batch sorption experiments were performed i.e. pH 4, 6 and 8 are above the PZC of EO ACC. Hence, the surface of the EO ACC was negatively charged due to dissociation of carboxylic groups. Therefore, EO ACC behaved as a cation exchanger in all the batch sorption experiments and could only adsorb chromium(III) that is in cationic form indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the sorption process indicating that \( H^+ \) ions were released from the surface of the EO ACC. The solution pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the initial solution pH. Mass balances to obtain the maximum \( H^+ \) ions released were performed using the volumes of 0.1 M sodium hydroxide added to adjust the solution pH. The experimentally determined chromium ions sorbed onto the EO ACC and \( H^+ \) ion released from the surface of the EO ACC are shown in Table 6.6.
At solution pH 4, 6 and 8, one Cr\(^{3+}\) ion was sorbed for approximately every three H\(^+\) ions released from the EO ACC surface. This confirms that the sorption of chromium(III) onto EO ACC is mainly governed by ion exchange mechanism. The sorption sites on the EO ACC are mainly carboxylic functional groups. Therefore, the ion exchange mechanism involving the interaction of the carboxylic sites of EO ACC with chromium(VI) ions in aqueous solution can be represented by the following reaction schemes:

At solution pH 4, 6 and 8 the reactions are:
Reduction of chromium(VI) by hydroxyl groups:
\[
\text{ACC} + \text{CrO}_4^{2-} \rightarrow \text{Cr}^{3+} + \text{H}_2\text{O} + \text{ACC (oxidised)} \quad (6.15)
\]
Adsorption of \text{Cr}^{3+}:
\[
3(\text{S}^- - \text{COOH}) + \text{Cr}^{3+} \leftrightarrow (\text{S}^- - \text{COO})_3\text{Cr} + 3\text{H}^+ \quad (6.26)
\]
Where S\(^-\) is the surface of EO ACC.

6.4. CONCLUSIONS
It has been shown that electrochemical reduction of a viscose rayon based ACC using potassium chloride as an electrolyte under varying conditions leads to samples with different physical and chemical characteristics. Electrochemical reduction introduced weakly basic functional groups on the surface of the ACC as indicated by pH titration, chloride capacity measurements, zeta potential and elemental analyses results. This was also confirmed by the FTIR spectra that showed the presence of ether groups on the electrochemically reduced ACC. A significant increase in anion exchange capacity for ACC was obtained by electrochemical reduction and it increased with increase in the extent of reduction. This is due to the introduction of ether groups onto the ACC. It has also been shown that the extent of electrochemical reduction depends on both the applied current and reduction time showing that electrochemical reduction is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and reduction time at any extent of reduction used in this study to produce ACC of maximum anion exchange capacity was 5.5 A with voltage of 9.8 V and current density of 6.4 mA/m\(^2\). Increase in surface basicity shifted the point of zero charge from pH of 6.8 to 9 and the isoelectric point from pH of 3 to 3.6 for the electrochemically reduced ACC due to the introduction of ether groups during electrochemical reduction. However, a small decrease in BET surface
area by electrochemical reduction was observed, which was due to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted with other hydroxyl groups and aldehyde groups to produce ether groups during the electrochemical reduction. However, the production of ether from hydroxyl and aldehyde also involved dehydration, which produced some micropores, thereby, reducing the decrease in the BET surface area. Pore size distribution was not altered by electrochemical reduction. Therefore, this work demonstrates that electrochemically reduced ACC can be used as an effective sorbent for treating acidic aqueous solution contaminated with chromium(VI) and electrochemically oxidised ACC can be used as an effective sorbent for treating basic or neutral aqueous solutions contaminated with chromium(VI). The maximum chromium(VI) sorption capacity for ACC increased by a factor of 2.12 times at solution pH 4 for electrochemically reduced ACC while it increased by a factor of 11.35 times at solution pH 8 for electrochemically oxidised ACC. The highest maximum chromium(VI) sorption capacity in all the batch sorption experiments was found to be for electrochemically reduced ACC at solution pH 4 (i.e. 3.8 mmol/g). It was 4.52 times higher than the maximum chromium(VI) sorption capacity of electrochemically oxidised ACC at solution pH 8 (i.e. 0.84 mmol/g). Most of the industrial wastewaters contaminated with chromium(VI) are highly acidic, therefore, electrochemical reduction of ACC is an efficient way of enhancing chromium(VI) sorptive capacity for wastewater treatment. The solution pH plays a very important role on the sorption of chromium(VI) ions onto the electrochemically reduced and electrochemically oxidised ACCs. The uptake of chromium(VI) ions decreased with an increase in solution pH for electrochemically reduced ACC, while it increased with an increase in solution pH for electrochemically oxidised ACC. It is confirmed that chromium(VI) ions were sorbed onto all the ACCs by ion exchange mechanisms. However, chromium(VI) was sorbed onto electrochemically reduced ACC in anionic form while it was sorbed onto electrochemically oxidised ACC in cationic form due to reduction of chromium(VI) ions to chromium(III) ions by hydroxyl functional groups on the ACCs. The present study concludes that electrochemical reduction of viscose rayon based ACC markedly enhanced the removal of chromium(VI) ions from aqueous solutions.
7. CONCLUSIONS AND FUTURE WORK

7.1. GENERAL CONCLUSIONS

The objectives of this research were:

- Electrochemical oxidation of a viscose rayon based activated carbon cloth (ACC) to alter the surface functional groups on the ACC to improve its cation sorption ability.
- Determination of optimum conditions for electrochemical oxidation of the viscose rayon based ACC.
- Electrochemical reduction of a viscose rayon based ACC to alter the surface functional groups on the ACC to improve its anion sorption ability.
- Determination of optimum conditions for electrochemical reduction of the viscose rayon based ACC.
- Physical and chemical characterisation of as-received and modified ACCs to elucidate the relationship between the physical and chemical properties of the ACCs and their sorption behaviour.
- Evaluation of as-received and electrochemically oxidised ACCs for noncompetitive and competitive removal of copper(II) and lead(II) ions from aqueous solutions.
- Evaluation of as-received, electrochemically reduced and electrochemically oxidised ACCs for the removal of chromium(VI) ions from aqueous solution.
- Correlation of equilibrium data by conventional theoretical models.
- Postulation of possible sorption mechanism of copper(II) and lead(II) ions onto the as-received and electrochemically oxidised ACCs.
- Postulation of possible sorption mechanism of chromium(VI) ions onto the as-received, electrochemically oxidised and electrochemically reduced ACCs.

It has been shown that electrochemical oxidation of a viscose rayon based ACC using potassium chloride as an electrolyte introduced weakly acidic functional groups on the surface of the ACC as indicated by pH titration, sodium capacity measurements, zeta potential and elemental analysis results. This was also confirmed by the FTIR spectra that showed the presence of carboxylic acid groups on the electrochemically oxidised ACC. A significant increase in cation exchange capacity for ACC was obtained by
electrochemical oxidation and it increased with an increase in the extent of oxidation. This is due to the introduction of carboxylic acid groups. It has also been shown that the extent of electrochemical oxidation depends on both the applied current and oxidation time showing that electrochemical oxidation is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and oxidation time at any extent of oxidation used in this study to produce ACC of maximum cation exchange capacity was 1.1 A, with voltage of 4.2 V and current density of 0.8 mA/m². The PZC and IEP shifted to lower pH values for the electrochemically oxidised ACCs due to the introduction of carboxylic acid groups during electrochemical oxidation. However, a decrease in BET surface area by electrochemical oxidation was observed, which was due to blockage of pores by carboxylic acid groups. Pore size distribution was altered by electrochemical oxidation largely due to the loss in microporosity and development of mesoporosity. Copper and lead ions sorption capacities of ACC increased by factors of 17 and 4 times, respectively for non-competitive sorption for electrochemically oxidised (EO) samples. The sorption capacities also increased by factors of 8.8 and 8.6 times for competitive sorption of copper and lead, respectively for EO samples. The competitive and non-competitive sorption isotherm studies confirmed that the affinity order of lead and copper ions adsorbed by the unoxidised and electrochemically oxidised ACCs is, Pb²⁺ > Cu²⁺. The solution pH plays a very important role on the sorption of lead and copper ions onto the electrochemically oxidised ACC. The uptake of lead and copper ions increased with an increase in solution pH. It is confirmed that lead and copper ions were sorbed onto EO ACC by an ion exchange mechanism. However, it is proposed that lead and copper ions were sorbed onto unoxidised (UO) ACC by complex formation with the ACC surface.

It has also been shown that electrochemical reduction of a viscose rayon based ACC using potassium chloride as an electrolyte introduced weakly basic functional groups on the surface of the ACC as indicated by pH titration, chloride capacity measurements, zeta potential and elemental analyses results. This was also confirmed by the FTIR spectra that showed the presence of ether groups on the electrochemically reduced ACC. A significant increase in anion exchange capacity for ACC was obtained by electrochemical reduction and it increased with an increase in the extent of reduction. This is due to the introduction of ether groups onto the ACC. It has also
been shown that the extent of electrochemical reduction depends on both the applied current and reduction time showing that electrochemical reduction is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and reduction time at any extent of reduction used in this study to produce ACC of maximum anion exchange capacity was 5.5 A with voltage of 9.8 V and current density of 6.4 mA/m². The PZC and IEP shifted to higher pH values for the electrochemically reduced ACC due to the introduction of ether groups during electrochemical reduction. However, a small decrease in BET surface area by electrochemical reduction was observed, which was due to the cross-linking by bond formation between hydroxyl groups within the ACC matrix that reacted with other hydroxyl groups and aldehyde groups to produce ether groups during the electrochemical reduction. However, the production of ether from hydroxyl and aldehyde also involved dehydration, which produced some micropores, thereby, reducing the decrease in the BET surface area. Pore size distribution was not altered by electrochemical reduction. Chromium(VI) sorption capacity for ACC increased by a factor of 2.12 times at solution pH 4 for electrochemically reduced ACC while it increased by a factor of 11.35 times at solution pH 8 for electrochemically oxidised ACC. The highest chromium(VI) sorption capacity in all the batch sorption experiments was found to be for the electrochemically reduced ACC at solution pH 4 (i.e. 3.8 mmol/g). It was 4.52 times higher than the highest chromium(VI) sorption capacity at solution pH 8, which was found to be for the electrochemically oxidised ACC (i.e. 0.84 mmol/g). Therefore, this work demonstrates that electrochemically reduced ACC can be used as an effective sorbent for treating acidic aqueous solution contaminated with chromium(VI) and electrochemically oxidised ACC can be used as an effective sorbent for treating basic or neutral aqueous solutions contaminated with chromium(VI). Most of the industrial wastewaters contaminated with chromium(VI) are highly acidic, therefore, electrochemical reduction of ACC is an efficient way of enhancing chromium(VI) sorptive capacity for wastewater treatment. The solution pH plays a very important role on the sorption of chromium(VI) ions onto the electrochemically reduced and electrochemically oxidised ACCs. The uptake of chromium(VI) ions decreased with an increase in solution pH for electrochemically reduced ACC, while it increased with an increase in solution pH for electrochemically oxidised ACC. It is confirmed that chromium(VI) ions were sorbed onto all the ACCs by ion exchange mechanisms. However, chromium(VI) was sorbed onto
electrochemically reduced ACC in anionic form while it was sorbed onto
electrochemically oxidised ACC in cationic form due to reduction of chromium(VI)
ions to chromium(III) ions by hydroxyl functional groups on the ACCs. These
conclusions from the results show that, the objectives of this research have been
achieved.

7.1.1. Comparative Study

Table 7.1 shows comparison of maximum sorption capacities of adsorbents for target
pollutants of study at different solution pH values from recently published journals,

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Target pollutant</th>
<th>Maximum metal ion sorbed (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosin-tripolyphosphate resin</td>
<td>5</td>
<td>Cu(II)</td>
<td>3.15</td>
<td>Lee et al. (2001)</td>
</tr>
<tr>
<td>Activated sawdust</td>
<td>5</td>
<td>Cu(II)</td>
<td>0.212</td>
<td>Arcar and Eren (2006)</td>
</tr>
<tr>
<td>Cross-linked starch/acrylonitril</td>
<td>5</td>
<td>Cu(II)</td>
<td>1.53</td>
<td>Zhang et al. (2007)</td>
</tr>
<tr>
<td>Electrochemically oxidised ACC</td>
<td>5</td>
<td>Cu(II)</td>
<td>1.693</td>
<td>This research.</td>
</tr>
<tr>
<td>Biomass plant-based GAC</td>
<td>5</td>
<td>Pb(II)</td>
<td>1.16</td>
<td>Gercel and Gercel (2007)</td>
</tr>
<tr>
<td>Electrochemically oxidised ACC</td>
<td>5</td>
<td>Pb(II)</td>
<td>1.867</td>
<td>This research.</td>
</tr>
<tr>
<td>Bacterial strain</td>
<td>5</td>
<td>CPb(II)</td>
<td>0.18</td>
<td>Tunali et al. (2006)</td>
</tr>
<tr>
<td>Dried biomass (P. Putida)</td>
<td>5</td>
<td>CPb(II)</td>
<td>0.147</td>
<td>Uslu and Tanyol (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCu(II)</td>
<td>0.329</td>
<td></td>
</tr>
<tr>
<td>Electrochemically oxidised ACC</td>
<td>5</td>
<td>CPb(II)</td>
<td>0.75</td>
<td>This research.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCu(II)</td>
<td>1.005</td>
<td></td>
</tr>
<tr>
<td>Activated carbo-aluminosilicate</td>
<td>4</td>
<td>Cr(VI)</td>
<td>1.58</td>
<td>Shawabkeh et al. (2006)</td>
</tr>
<tr>
<td>Green alga-based GAC</td>
<td>1</td>
<td>Cr(VI)</td>
<td>2.16</td>
<td>Elsikaily et al. (2007)</td>
</tr>
<tr>
<td>Electrochemically reduced ACC</td>
<td>4</td>
<td>Cr(VI)</td>
<td>3.8</td>
<td>This research.</td>
</tr>
<tr>
<td>Coal-based GAC</td>
<td>8</td>
<td>Cr(VI)</td>
<td>0.135</td>
<td>Natale et al. (2007)</td>
</tr>
<tr>
<td>Electrochemically oxidised ACC</td>
<td>8</td>
<td>Cr(VI)</td>
<td>0.84</td>
<td>This research.</td>
</tr>
</tbody>
</table>

Table 7.1. Comparison of maximum sorption capacities of adsorbents for target
pollutants of study at different solution pH values (CCPb and CCu are competitive
lead and copper from multicomponent solutions of copper and lead)
the adsorbents with the highest maximum adsorption capacities in sections 2.2, 2.3, 2.4 and 2.5 and the maximum adsorption capacities obtained from this research work. The solution pH was chosen because metal sorption capacities of adsorbents are affected significantly by solution pH. From Table 7.1 it is obvious that electrochemically oxidised ACC has the highest noncompetitive sorption capacity for lead, highest competitive sorption capacity for lead and copper, therefore electrochemically oxidised ACC is the most effective adsorbent for treatment of wastewater contaminated with these target pollutants, especially in industrial wastewater as ACC is technically easy in column processes. It is also obvious that electrochemically reduced ACC has the highest sorption capacity for chromium(VI) at solution pH 4 and electrochemically oxidised ACC has the highest sorption capacity for chromium(VI) at solution pH 8, therefore electrochemically reduced ACC in this study is a very effective sorbent for treating acidic aqueous solutions contaminated with chromium(VI) and electrochemically oxidised ACC is an effective sorbent for treating basic or neutral aqueous solutions contaminated with chromium(VI). Most of the industrial wastewaters contaminated with chromium(VI) are highly acidic, therefore, electrochemical reduction of ACC is an efficient way of enhancing chromium(VI) sorptive capacity for industrial wastewater treatment.

However, from Table 7.1, the highest maximum adsorption capacity of 3.15 mmol/g for noncompetitive copper at solution pH 5 was observed for a very expensive adsorbent, Chitosin-tripolyphosphate resin, which is not economically favourable for industrial applications. Therefore, it is better to use more than one column with electrochemically oxidised ACC that is economically favourable, the cost of electrochemically oxidised ACC is 1.25 pound/g for industrial applications. Therefore, electrochemically oxidised ACC and electrochemically reduced ACC are the most economically favourable adsorbents for industrial wastewater treatments. The cost of electrochemically oxidised ACC and electrochemically reduced ACC were obtained as follows:

For 1 g of electrochemically oxidised ACC:

- Cost of potassium chloride used oxidation is 1.22 pound.
• Cost of electricity is 0.27 pound per kwh (from British gas website), therefore, for 1.1 A for 6 h at voltage of 4.2 V, the cost of electricity is approximately 0.01 pound.

• Current cost of ACC is about 17 pound/Kg, therefore, cost of 1 g ACC is 0.017

• Therefore, cost of electrochemically oxidised ACC is 1.25 pounds/g.

For 1 g of electrochemically reduced ACC:

• Cost of potassium chloride used oxidation is 1.22 pounds.

• Cost of electricity is 0.27 pound per kwh (from British gas website), therefore, for 5.5 A for 3 h at voltage of 11 V, the cost of electricity is approximately 0.5 pound.

• Current cost of ACC is about 17 pound/Kg, therefore, cost of 1 g ACC is 0.017

• Therefore, cost of electrochemically reduced ACC is 1.74 pounds/g.

For industrial application, 1 kg of ACC can be used for several column applications, maybe 20 columns with high column length and high column volume of ACC and the cost of 1 kg of electrochemically oxidised ACC is 1250 pounds and the cost of 1 kg of electrochemically reduced ACC is 1750 pounds. With the fact that these 20 columns could be used for several years, electrochemically oxidised ACC and electrochemically reduced ACC are more economically favourable than commercial resins.

7.2. FUTURE WORK

Since the present study has shown that electrochemical oxidation of a viscose rayon based ACC in potassium chloride markedly enhanced the cation exchange capacity of the ACC and that electrochemical reduction of the viscose rayon based ACC in potassium chloride markedly enhanced the anion exchange capacity of the ACC, the following recommendations are suggested for future work:

• Electrochemical oxidation of activated carbon fibres (ACF) based on different precursors to alter the surface functional groups on the ACFs to improve the cation sorption abilities of the ACFs.
• Electrochemical reduction of activated carbon fibres (ACF) based on different precursors to alter the surface functional groups on the ACFs to improve the anion sorption ability.

• Physical and chemical characterisation of as-received and modified ACFs to analyse the relationship between the physical and chemical properties of the ACFs and their sorption behaviour.

• Evaluation of as-received and electrochemically oxidised ACFs for noncompetitive and competitive removal of some other toxic cations (e.g. arsenic, beryllium, mercury, nickel and zinc) from aqueous solutions.

• Evaluation of as-received and electrochemically reduced ACFs for the removal of other toxic anions (e.g. molybdenum, perchlorate, arsenate and cyanide) from aqueous solution.

• Evaluation of as-received and electrochemically reduced ACFs for the removal of highly toxic organic compounds, pesticides and herbicides that are often predominant in wastewaters (e.g. atrazine, benazolin and 2,4-dichlorophenoxyacetic acid).

• Application of electrochemically oxidised ACC and electrochemically reduced ACC for adsorption of toxic metals from aqueous solutions in column systems, since most of the industrial wastewater treatments are performed in columns.
7. REFERENCES


235


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9. APPENDICES

8.1. RESEARCH PUBLICATIONS

JOURNAL PAPERS


CONFERENCE PROCEEDINGS

COPIES OF REFERED JOURNAL PAPER PUBLICATIONS
Surface properties of electrochemically oxidised viscose rayon based carbon fibres

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Abstract

A viscose rayon based activated carbon cloth (ACC) was subjected to electrochemical oxidation under a wide variety of current conditions to modify the surface properties. The changes in the surface properties were physically and chemically characterised. The cation exchange capacity of ACC increased with an increase in the extent of oxidation. The electrochemically oxidised ACC at 1.1 A for 6 h showed highest cation exchange capacity without any change in surface morphology. A loss of 49% BET surface area and a significant loss in microporosity were observed and attributed to blockage of pores through formation of carboxylic acidic groups and humic substances. However, the cation exchange capacity and oxygen content increased by about 365% and 121%, respectively. Increase in surface acidity shifted the point of zero charge from pH of 6.8 to 2.8 and the isoelectric point from pH of 3 to 1.15. The optimum constant current for electrochemical oxidation was found to be 1.1 A.

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Introduction

Activated carbon fibres are produced in the form of cloth (ACC) and felt (ACF). Carbon fibres can be prepared from synthetic and natural precursors and they possess surface area between 1000 and 2100 m² g⁻¹, which is relatively higher than the surface area of granular activated carbons. They are robust and compact and easier to handle and therefore offer opportunities for the design of intensified water treatment [1–4]. The materials are highly microporous, approximately 90% of the total pore volume is attributed to micropores. These micropores are directly accessible, thereby increasing intraparticle diffusion so that the overall sorption rate is faster than granular activated carbons that possess a combination of micropores, mesopores and macropores [1,2].

The adsorption onto activated carbon fibres depends on many factors, such as raw materials, activation process, pore structure and surface functionalities [2–4]. The adsorption behaviour of activated carbon fibres is not determined only by their specific surface area or pore size distribution but also by their surface functional groups [4]. Electrochemical oxidation of activated carbon fibres in different electrolytes and chemical oxidation by reagents such as nitric acid, air, phosphoric acid, hydrogen peroxide and ozone introduces weakly acidic surface groups such as carboxylic, carbonyl, phenolic and lactone [2,4,5]. Therefore, detailed characterisation of oxidised carbon fibre surfaces is essential to understand the modifications that occur during electrochemical oxidation. In the present investigation, a viscose rayon based ACC was electrochemically oxidised at different extent of oxidation, from 0 to 31,680 c/g (coulomb/g). The amount and nature of the surface functional groups were characterised by sodium ion uptake, pH titration, zeta potential measurements, elemental analysis, Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) surface area, pore size distribution (PSD) and scanning electron microscopy (SEM).

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2. Experimental

A viscose rayon based ACC, ZORFLEX® FM 10 (supplied by Charcoal Cloth International) was used as a starting material for this investigation. Before use, the ACC was converted to hydrogen form by passing 2 L of 5% (w/w) hydrochloric acid very slowly (for 48 h) through a column containing 20 g of the ACC [6-8]. After conversion, the ACC was washed with 30 L of deionised water and the conductivity of the washed water was measured. Washing was continued until the conductivity of the washed water was the same as that of deionised water. After washing, the ACC was dried in an oven at 383 K for 24 h. It was then put in a desiccator overnight and weighed. All chemicals used for this work were of analytical grade and obtained from Fisher Scientific, UK.

Viscose rayon based activated carbon cloth, ZORFLEX® FM 10 in hydrogen form was modified electrochemically using 0.5 M potassium chloride as an electrolyte. The choice of potassium chloride was based on the studies of electrochemical oxidation in several electrolytes [2-9] that showed that activated carbon oxidised in potassium chloride had the highest cation exchange capacity. The electrochemical cell was immersed in a thermostatically controlled water bath regulated at 303 K. One gram of ACC was wrapped round the anode (platinised titanium) and immersed in 0.5 M potassium chloride for 1 h prior to the electrochemical oxidation process. Two cathodes (platinised titanium) were used as counter electrodes. The electrodes were placed at equal distance from the anode to achieve uniform surface oxidation of the ACC [8]. The electrochemical oxidation was carried out at currents ranging from 0.55 to 2.2 A at different oxidation times (e.g. 0.25, 0.5, 0.75, 1, 2, 3, 4 and 6 h). For each oxidation, the chosen current was kept constant by adjusting the voltage throughout the chosen oxidation time and using fresh electrolyte each time. After oxidation, the oxidised ACC was washed with deionised water until the conductivity of the washed water reached the same value as the conductivity of deionised water. The oxidised ACC was dried in an oven at 383 K for 24 h and was kept in a desiccator overnight and then weighed.

The details of the experimental procedures for sodium capacity determination, pH titration, zeta potential measurement, elemental analysis, surface area and pore size distribution have been reported by Harry et al. [8]. The surface chemistry of the ACCs was characterised by Fourier transform infra red (FTIR) spectroscopy analysis. The spectra were recorded on a Mattson 3000 FT-IR spectrometer at a resolution of 4 cm⁻¹ at 64 scans. The surface morphology of each ACC was observed using scanning electron microscopy (SEM). The SEM of the ACCs were taken on a Carl Zeiss 1530 microscope at 298 K. The bath normal electron mode was used at an accelerating voltage of 5 kV. All the analyses have been replicated three times and the average values have been reported (except SEM analysis).

3. Results and discussion

3.1. Sodium capacity

The total cation exchange capacity (i.e. the quantity of acidic functional groups) was determined in sodium hydroxide solution. Since sodium hydroxide neutralisation is presumed to probe chemically and physically accessible acidic sites such as carboxylic, lactonic and phenolic functional groups [12-18], it follows that sodium hydroxide titrates accessible functionalities which may reside in pore walls located well below the external fibre surface. Oxygen-containing groups like carbonyl, carboxyl, phenolic and lactonic groups present on carbonaceous materials dissociate increasingly with an increase in solution pH values [15]. Therefore, these surface groups are completely dissociated in solutions at high pH and are available for ion exchange. The sodium capacity results for modified and as-received ACC are shown in Fig. 1. The results in Fig. 1 show that the sodium capacity of electrochemically oxidised ACC at 1.1 A for 6 h is 4.7 times higher than that of unoxidised ACC. This increase is attributed to the introduction of weakly acidic functional groups. The extent of oxidation on the carbon surface depends on the chemical composition of the electrolyte [9]. The chloride ion (Cl⁻) and hypochlorous acid (HOCI) that are formed when chlorine is present in water act as strong oxidants [19]. Also from the electrochemical series of metals [20], it is obvious that the potassium ion (K⁺) that is formed when a potassium salt is present in water is a very strong reductant. Since the reduction and oxidation processes are responsible for the overall reaction in an electrolytic cell, the presence of strong oxidant and strong reductant explains why the ACC is strongly oxidised when potassium chloride is used as an electrolyte.

A plot of sodium capacity versus the extent of electrochemical oxidation of ACC at a constant time of 4 h but at different currents of 0, 0.55, 1.1, 1.47, and 2.2 A is given in Fig. 2. The extent of electrochemical oxidation is defined as the product of current and electrochemical oxidation time in coulomb per gram (c/g) of ACC. However, it was observed that at 0.55 A the sodium capacity did not improve
significantly. This is shown in Fig. 2 for the 7920 c/g extent of oxidation. Above 7920 c/g, the sodium capacity increased with extent of oxidation. This is attributed to an increase in the amount of weakly acidic functional groups introduced on the surface of the ACC, as oxidation proceeded with increase in current. The chemical conditions at the anode are very complex. As the electrolyte was potassium chloride, chlorine, oxygen and hypochlorous acid were evolved at the anode [21]. The composition of these products will depend on the current used as well as the diffusion processes at the electrodes. It would seem likely that the generation of exchangeable groups on the ACC depends on both current used and the total coulombs passed through the solution.

In order to observe the effect of oxidation time, a series of electrochemical oxidations of ACC were performed at a constant current of 1.1 A, but for different oxidation times (0–8 h). The plot of sodium capacity versus the extent of oxidation at constant current is shown in Fig. 3. It can be seen that the sodium capacity increased rapidly for 7920 c/g extent of oxidation and continued to increase with oxidation time. This is attributed simply to the longer exposure of the ACC to the oxidising condition allowing a greater reaction time for the introduction of weakly acidic groups. The process of manufacturing viscose rayon consists of the following steps: alkalisation, shredding, preripening i.e. aging, santhation, dissolving, maturing and viscose fibre spinning [22]. At the spinning stage, the cellulose is regenerated into viscose for the production of the viscose rayon filament. Therefore, the ACC matrix is composed of interlinking cellulose molecules. At shorter periods of oxidation, less of the cellulose molecules in the viscose rayon based ACC matrix will be oxidised to form surface acidic functional groups. The cation exchange capacity of electrochemically oxidised ACC depends on both the applied current and the time of oxidation, indicating that electrochemical oxidation is a diffusion-dependent process.

In order to achieve the optimum constant current, three series of experiments were performed at different extents of oxidation, e.g. 7920 c/g, 15,840 c/g and 23,760 c/g. For each series of experiment, the ACCs were electrochemically oxidised at different currents of 0.73, 1.1, 1.47, 2.2, 4.4 and 8.8 A. Plots of the sodium capacity versus applied current for the three series of experiments are presented in Fig. 4. The three sets of results followed the same trend. The results show that sodium capacity for ACCs oxidised below 1 A were low. This is attributed to the fact that applied currents below 1 A do not produce sufficiently vigorous oxidising conditions. The sodium capacity for ACCs oxidised above 1.47 A decreased continuously with an increase in applied current. The lowest sodium capacity was observed for ACCs electrochemically oxidised at 8.8 A and the highest sodium capacity was obtained at 1.1 A for ACCs oxidised at 7920, 15,840 and 23,760 c/g. Therefore, the optimum current was found to be 1.1 A for all oxidation times. It is to be noted that above 31,680 c/g extent of oxidation, the ACCs become fragile and are not suitable for adsorption studies.

Pittman Jr. et al. [16] reported sodium capacity of 2.5 mmol/g at 10,600 c/g extent of oxidation using 1% (w/w) potassium nitrate as an electrolyte for a polyacrylonitrile (PAN) based ACC. Park et al. [23] reported sodium capacity of 0.812 mmol/g at 0.45 A/m² current density using 35% (w/w) of sodium hydroxide as an electrolyte for a phenol based ACC. Waseem et al. [24] reported sodium capacity of 1.048 mmol/g at 4112 c/g extent of oxidation using potassium nitrate as an electrolyte for a PAN based ACC. Rangel-Mendez and Streat [2] reported sodium capacity of 6.4 mmol/g at 62,640 c/g extent of oxidation using 0.5 M potassium chloride as an electrolyte for a PAN based ACC. The highest sodium capacity of 6.31 mmol/g was obtained in this study at 31,680 c/g extent of oxidation.

### 3.2. pH titration

The proton binding curves, i.e. the plots of ion released versus equilibrium solution pH, for unoxidised ACC (UO), the electrochemically oxidised ACC at 2.2 A for 3 h (EO 2.2 A for 3 h) and the electrochemically oxidised ACC at 1.1 A for 6 h (EO 1.1 A for 6 h) are shown in Fig. 5. The point where the proton binding curve crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH value at which the
surface charge is zero at particular ambient temperature, applied pressure and aqueous solution composition \cite{25,26}. The PZC will change depending on the type and amount of functional groups present on the adsorbent. It will be shifted to lower pH values with oxidation of the ACC due to the introduction of acidic functional groups, such as carboxylic, phenolic, carbonyl and lactonic groups onto the surface of the ACC \cite{27-29}. As shown in Fig. 5, the PZC for unoxidised ACC is at pH 6.8, whereas it shifted to pH 2.8 for ACC electrochemically oxidised at 1.1 A for 6 h and pH 2.7 for ACC electrochemically oxidised at 2.2 A for 3 h. It can be seen from Fig. 5 that the unoxidised ACC show a smooth curve whereas the electrochemically oxidised ACCs show inflection points that are typical of the behaviour of polyfunctional ion exchangers \cite{12}. Moreover, the slopes of the curves for electrochemically oxidised ACCs increased with an increase in equilibrium pH. Also, there is a marked difference between the curve for electrochemically oxidised ACC at 2.2 A for 3 h and the curve for that oxidised at 1.1 A for 6 h. The titration curve for electrochemically oxidised ACC at 2.2 A for 3 h displays a lower slope indicating less alkali neutralisation capability than the curve for electrochemically oxidised ACC at 1.1 A for 6 h above equilibrium pH of 4. These results are in agreement with the sodium capacity results of these samples. It is well known that carboxylic groups in activated carbons dissociate at pH values within the range of 2 and 6 and hydroxyl groups dissociate at pH values above 6 \cite{2,28}. From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the electrochemically oxidised ACCs and unoxidised ACC to produce H⁺ ions starts at equilibrium solution pH of approximately 3 and 6.8, respectively. Therefore, one of the types of acidic functional groups on the surfaces of electrochemically oxidised ACCs is likely to be carboxylic, while that on the surface of unoxidised ACC is likely to be hydroxyl groups. This is expected since the cellulose molecules of the viscose rayon based ACC contain hydroxyl groups in its matrix.

3.3. Zeta potential measurements

Fig. 6 shows the zeta potential versus equilibrium solution pH plots for unoxidised ACC and electrochemically oxidised ACCs at 1.1 A for 6 h and 2.2 A for 3 h. An important parameter used to characterise the electrokinetic behaviour of a solid-liquid interface is the isoelectric point (IEP). This is the equilibrium solution pH at which the zeta potential is zero. From the curves it is obvious that the IEP values of the electrochemically oxidised ACCs are not accurately measurable. This is because the proton concentration of the bulk electrolyte solution is too low and increasing the proton concentration caused further decrease of the zeta potential. Bismark et al. \cite{10} made the same observation with an anodically oxidised fibre. Rangel-Mendez and Streat \cite{9} also observed this with electrochemically oxidised granular carbon and obtained the IEP values by extrapolation. As shown in Fig. 6, the IEP value for unoxidised ACC is 3, while the extrapolated IEP values for electrochemically oxidised ACCs at 1.1 A for 6 h and 2.2 A for 3 h are 1.15 and 0.9, respectively. This shows that the electrochemically oxidised ACCs are more acidic than the unoxidised ACC, which also confirms the pH titration results. The lower IEP values for the electrochemically oxidised samples is attributed to the presence of more acidic functional groups. It is interesting to note that the zeta potential curves of electrochemically oxidised ACCs fall steeply with increasing equilibrium solution pH until about pH 4 and then start to level off to form a distinct plateau. Dissociation of carboxylic surface groups is responsible for this effect since it is well known that the dissociation of this group occurs at pH values within the range of 2 and 6 \cite{2,28}. The wider plateau for the electrochemically oxidised ACCs is caused by complete dissociation of carboxylic groups at about equilibrium solution pH of 4. Therefore, there was no increase on the surface charge above pH 4. It is also interesting to note that there is no distinct difference between the zeta potential curves of the electrochemically oxidised ACCs at 1.1 A for 6 h and at 2.2 A for 3 h, in contrast to the observation from the pH titration curves.

It is well known that the IEP values are only representatives of the external surface charges of carbon particles in solutions whereas the PZC varies in response to the net total of the external and internal surface charges of the
The electrochemical properties of unoxidised and electrochemically oxidised ACCs are shown in Table 1. It is noticeable that the value of PZC-IEP for the unoxidised ACC is higher than those for the electrochemically oxidised ACCs. It is also clear that the PZC-IEP value for electrochemically oxidised ACC at 2.2 A for 3 h is higher than that electrochemically oxidised at 1.1 A for 6 h. This is attributed to a change in the distribution of surface charge and suggests that electrochemical oxidation is a diffusion-dependent process.

### 3.5. Fourier transform infra red (FTIR) spectroscopy analysis

It is well known that the study of the chemical composition of carbon fibres by FTIR is difficult because the absorption of the fibre is very intense while the concentration of the different functional groups on its surface is relatively low. So the signal/noise ratio is often not sufficiently high even if the sample is scanned many times. Also, the diameter of the fibre falls in the analytical wavelength range of infrared light, which may lead to strong interference at low wavenumbers [31]. For these reasons the intensities of FTIR spectra of carbon fibres are not very high. The FTIR spectra for unoxidised ACC (UO) and electrochemically oxidised ACC at 1.1 A for 6 h (EO) are shown in Figs. 7 and 8, respectively. The band assignments are shown in Table 3. The marked difference in the functional groups observed on the unoxidised ACC and electrochemically oxidised ACC are the presence of aldehyde and carboxylic acid groups, respectively. Since a cellulose molecule has...
aldehyde and hydroxyl ends, it is expected that the ACCs should have aldehyde and hydroxyl functional groups on their surfaces. However, aldehyde groups were not detected on the electrochemically oxidised ACC. This is attributed to the fact that all the aldehyde groups were oxidised to carboxylic acid groups on the electrochemically oxidised ACC. This is because aldehyde groups are readily oxidised to produce carboxylic acid groups while the alcohol groups need to be oxidised to aldehyde groups, which are further oxidised to carboxylic acid groups \[22,30\]. As the aldehyde groups are more readily oxidised than the alcohols, they were not found on the electrochemically oxidised ACC.

The carboxylic acid groups observed on the electrochemically oxidised ACC also confirms the pH titration and zeta potential results that showed that the dissociation of the acidic functional groups occurs at the pH range of 2–6.

### 3.6. Reactions in electrochemical cell

With the confirmation that carboxylic acid groups are introduced onto the ACC by electrochemical oxidation and since the oxidation of aldehyde and alcohol groups present in the cellulose molecules of the viscose rayon based ACC are methods of producing carboxylic acids \[30\], it is possible to postulate the likely reactions that took place in the electrochemical cell. The reactions most likely to occur are as follows:

\[
\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \\
\text{KCl} & \leftrightarrow \text{K}^+ + \text{Cl}^- \\
2\text{Cl}^- - 2\text{e}^- & \rightarrow \text{Cl}_{2(\text{g})} \\
\text{K}^+ + \text{e}^- & \leftrightarrow \text{K} \\
2\text{H}_2\text{O} & \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \\
\text{C} + 2\text{H}_2\text{O} & \leftrightarrow \text{CO}_{2(\text{g})} + 4\text{H}^+ + 4\text{e}^- \\
\text{Cl}_{2(\text{g})} + \text{H}_2\text{O} & \leftrightarrow \text{HOCI} + \text{H}^+ + \text{Cl}^- \\
2\text{HOCI} + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{Cl}_{2(\text{g})} + 2\text{H}_2\text{O}
\end{align*}
\]

The above reactions are in agreement with the reactions suggested by Horita et al. \[21\] when they electrochemically oxidised carbon black. From the above reactions scheme it can be concluded that the oxidation of the aldehyde and hydroxyl groups within the cellulose molecules in the ACC to produce carboxylic acid groups are the most likely reactions that occurred during the electrochemical oxidation of a viscose rayon based ACC.

### 3.7. BET surface area and pore size distribution (PSD)

Surface area of the unoxidised and electrochemically oxidised samples was measured by nitrogen adsorption/desorption method and the porosity distributions were calculated using the Density Functional Theory (DFT) model. The DFT model is a widely used and recognised powerful tool for calculating the porosity of materials.
ool for calculating the PSD of adsorbents in inhomogeneous fluids [28,32–38]. Fig. 9 shows the BET surface area versus extent of oxidation plots for electrochemically oxidised ACCs at current of 1.1 A (EO 1.1 A) and 2.2 A (EO 2.2 A). All the ACCs analysed in this study have extensive BET surface areas that are ideal in the treatment of drinking and waste water. However, the BET surface area decreased with an increase in the extent of oxidation. The results showed that EO 1.1 A lost 45.3%, 49.4% and 61.9% of the original BET surface area at 7920 c/g, 15,840 c/g and 23,760 c/g extent of oxidation, respectively while EO 2.2 A lost 29.8%, 40.2% and 58.1% of the BET surface area at 7920 c/g, 15,840 c/g and 23,760 c/g extent of oxidation, respectively. This is attributed to the blockage of pores by acidic functional groups and formation of humic substances during electrochemical oxidation. BET surface areas for EO 2.2 A were higher than those for EO 1.1 A at all extent of oxidation but this gradually decreased with greater extent of oxidation. This suggests that at each extent of oxidation, the quantity of acidic functional groups on EO 1.1 A is

Fig. 11. SEM of unoxidised and some selected oxidised ACCs: (a) UO, (b) EO 1.1 A 6 h, (c) EO 1.1 A 8 h, (d) EO 2.2 A 3 h and (e) EO 2.2 A 4 h.
higher than the quantity on EO 2.2 A. Since this is in agreement with the sodium capacity results in Fig. 1, it can be concluded that the loss in BET surface area was by the blockage of pores by the acidic functional groups and humic substances. Reduction in surface area of carbonaceous materials by by-products formation after oxidation has been discussed by other researchers [12,28,29].

Fig. 10 shows the pore size distribution (PSD) curves of unoxidised ACC and electrochemically oxidised ACCs at 1.1 A at different extents of oxidation. PSD curves of unoxidised ACC and electrochemically oxidised ACCs at 2.2 A at different extents of oxidation showed the same trend as those in Fig. 10 which shows that unoxidised ACC exhibited bimodal pore size distributions with predominant peaks at approximately 15 Å and 28 Å. So it possesses a reasonable amount of micropores, with a small fraction of mesopores but without any macropores. All electrochemically oxidised ACCs also exhibited similar bimodal pore size distributions. The PSD curve of the unoxidised ACC covers a broader range of pore width than the electrochemically oxidised ACCs.

This is attributed to the fixation of oxygen-containing functional groups. From the PSD curves it can also be seen that there was a decrease in incremental pore volume in all pore diameters for the electrochemically oxidised ACCs, which is more evident as the extent of oxidation increased. As a result of electrochemical oxidation, oxygen-containing functional groups and humic substances were produced, causing the pores to shrink and/or get blocked by the oxygen functional groups. All the ACCs in this study are predominantly microporous except the ACC that was electrochemically oxidised at 1.1 A for 6 h (i.e. 23,760 c/g in Fig. 10). It has the most dominant peak at approximately 22 Å, indicating that it contained more mesopores than micropores. This is confirmed by the greater reduction in BET surface area of the electrochemically oxidised ACC at 1.1 A for 6 h. Saha et al. [12,29] also observed that loss in microporosity results in the reduction of BET surface area.

3.8. Scanning electron microscopy (SEM)

Scanning electron micrographs (SEMs) of unoxidised ACC and two most severely oxidised ACCs in this investigation are shown in Fig. 11. Fig. 11a is the micrograph for unoxidised ACC (UO) while 11b and 11c are the micrographs for electrochemically oxidised ACC (EO) at 1.1 A for 6 h and 8 h to give 23,760 c/g and 31,680 c/g extent of oxidation, respectively. Micrographs 11d and 11e are for ACCs electrochemically oxidised at 2.2 A for 3 h and 4 h to give 23,760 c/g and 31,680 c/g extent of oxidation, respectively. The micrographs of the ACCs electrochemically oxidised at 1.1 A i.e. 11b and 11c are very similar to that of the unoxidised ACC i.e. 11a. Therefore, no significant breakage of fibres was observed during electrochemical oxidation of these ACCs. However, the micrographs of electrochemically oxidised ACCs at 2.2 A i.e. 11d and 11e show some differences compared to the unoxidised ACC. Micrograph 11e appears to show that fibres are breaking and are probably becoming more fragile after severe oxidation.

4. Conclusions

Electrochemical oxidation of a viscose rayon based ACC introduced weakly acidic functional groups on the surface of the ACC as indicated by pH titration, sodium capacity, zeta potential and elemental analysis results. This was also confirmed by the FTIR spectra that showed the presence of carboxylic acid groups on the electrochemically oxidised ACC. A significant increase in cation exchange capacity of ACC was obtained by electrochemical oxidation and it increased with the extent of oxidation. The extent of electrochemical oxidation depends on both the applied current and oxidation time showing that electrochemical oxidation is both a diffusion-dependent and current-dependent process. The optimum constant current at which a combination of applied current and oxidation time at any extent of oxidation used in this study to produce the ACC of maximum cation exchange capacity was 1.1 A. The PZC and IEP shifted to lower pH values for the electrochemically oxidised ACCs due to the introduction of weakly acidic carboxylic functional groups during the oxidation process. However, a decrease in BET surface area by electrochemical oxidation was observed, which was attributed to blockage of pores by carboxylic acid groups. Pore size distribution was altered by electrochemical oxidation largely due to the loss in microporosity and development of mesoporosity. The results indicate considerable potential for electrochemically oxidised activated carbon cloth for the removal of trace toxic metal pollutants from water at neutral or near neutral pH values.

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References


Effect of electrochemical oxidation of activated carbon fiber on competitive and noncompetitive sorption of trace toxic metal ions from aqueous solution

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Abstract

A viscose-rayon-based activated carbon cloth (ACC) was electrochemically oxidized to enhance its cation sorption capacity for comparison with as-received ACC. The ACCs were characterized by sodium capacity measurement, pH titration, zeta potential measurement, elemental analysis, Brunauer-Emmet-Teller surface area, and pore size distribution. Batch sorption experiments showed that electrochemically oxidized ACC (EO) is more effective for the removal of lead and copper ions compared to unoxidized ACC (UO) for both competitive and noncompetitive sorption. For electrochemically oxidized fibers the copper and lead sorption capacities of ACC increased 17 and 4 times, respectively, for noncompetitive sorption and 8.8 and 8.6 times, respectively, for competitive sorption. However, reduction in the sorption capacities for both metals was observed for the competitive sorption. The sorption of lead and copper onto EO was by ion exchange, while that onto UO was likely to be due to surface complex formation. The affinity order of the two metal ions sorbed by UO and EO is Pb2+ > Cu2+. The effect of pH on sorption isotherms indicated that metal uptake increased with an increase in solution pH.

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Keywords: Viscose-rayon-based activated carbon cloth; Lead; Copper; Sorption isotherms; Electrochemical oxidation; Competitive and noncompetitive sorption; Characterization

1. Introduction

There have been increasing concerns and more stringent regulation standards pertaining to the discharge of heavy metals to the aquatic environment, due to their toxicity and detriment to living species, including humans. The European Community (EC) Council Directive 98/78/EC has highlighted the most toxic heavy metals in residual water, namely arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. The maximum permissible concentrations in drinking water for lead and copper have been set by the EC Council Directive at 0.01 and 2 mg/L, respectively [1]. Unlike most organic pollutants, heavy metals are nondegradable and can accumulate in living tissues. Acute lead poisoning can seriously affect the gastrointestinal track and the nervous system. The relatively immediate effects of acute lead poisoning are nausea, abdominal pains, anorexia, insomnia, irritability, and coordination loss. In severe situations neurological effects such as restlessness, hyperactivity, confusion and impairment of memory, coma, and death can occur [2]. Copper is a very important trace metal that is predominantly found in the nuclei and mitochondria of the living cell. It is an essential element required for the activity of several biological enzymes [3]. However, ingestion of high quantities of copper may cause gastrointestinal bleeding, hypotension, convulsions, and significant DNA damage [4].

Many treatment processes such as chemical precipitation, ultrafiltration, biological processes, electrodialysis, adsorption, and reverse osmosis are currently used to remove heavy metal pollutants from water. Among these methods, adsorption onto activated carbon is a widely applied method. Due to their wide range of applications and low cost compared with possible competitive adsorbents, several forms of activated carbons with special characteristics have been produced. Activated carbon now exists in granular (GAC), powder (PAC), and fiber forms. The carbon fibers are produced in the forms of cloth (ACC) and felt
The porous structure of ACC is composed mainly of micropores, while GAC and PAC contain complex porous networks of macropores, mesopores, and micropores. In ACC the access to the micropores is directly from the external surface; however, in the GAC and PAC, the macropores are open to the particle external surface and they branch into mesopores and finally into micropores. Most of the sorption in all the activated carbon forms takes place in the micropores; thus sorption area in ACC can be accessed more easily than in other forms [5].

ACC has some advantages over the traditional forms. Generally, intraparticle diffusion in GAC is very slow and this makes the overall rate of sorption in GAC very low [6]. For PAC processes, the overall rate of sorption is very high, but PAC presents the disadvantage of complicated handling. The overall rate of sorption in ACC is as fast as in PAC, but it does not have the handling problems existing in PAC.

The selectivity and sorption capacity of conventional activated carbons toward heavy metals is rather low. However, metal sorption onto activated carbon can be enhanced considerably by the introduction of weakly acidic functional groups such as carboxylic, carbonyl, phenolic, and lactonic through electrochemical oxidation of activated carbons in different electrolytes and chemical oxidation by reagents such as nitric acid, air, phosphoric acid, hydrogen peroxide, and ozone [6–8].

While much research has been carried out on the uptake of single species of metal ions, the problem of competition between different metal ions has received less attention. Consequently, in this work a viscose-rayon-based ACC was electrochemically oxidized to enhance its cation sorption capacity. The cation sorption capacity was compared with that of the as-received ACC. In order to characterize the electrochemically oxidized and unoxidized ACCs, techniques such as sodium uptake, pH titration, zeta potential measurements, elemental analysis, Brunauer–Emmett–Teller (BET) surface area, and pore size distribution (PSD) were used. Competitive and noncompetitive lead and copper sorption experiments for the electrochemically oxidized and unoxidized ACCs were studied. Metal concentration and pH effects on the sorption isotherms were investigated.

1. Experimental

1.1. Materials

A viscose-rayon-based activated carbon cloth (ACC), ZORPLEX FM 10 (supplied by Charcoal Cloth International), was used as a starting material for this investigation. Before use the ACC was converted to hydrogen form by passing 2 L of 5% (w/w) hydrochloric acid very slowly (for 48 h) through a column containing 20 g of the ACC. After conversion, the ACC was washed with 50 L of deionized water and the conductivity of the washed water was measured. Washing was continued until the conductivity of the washed water was the same as that of deionized water. After washing, the ACC was dried in an oven at 383 K for 24 h. It was then put into a desiccator overnight and weighed. All converted samples were kept in sealed plastic bags to avoid any contamination. All chemicals used were of analytical grade and obtained from Fisher Scientific, UK.

2.2. Electrochemical oxidation

Viscose-rayon-based activated carbon cloth, ZORPLEX FM 10, in hydrogen form was modified electrochemically using 0.5 M potassium chloride as an electrolyte. The choice of potassium chloride was based on the fact that studies of electrochemical oxidation in several electrolytes [9–11] showed that activated carbon oxidized in potassium chloride had the highest cation exchange capacity. The electrochemical cell was immersed in a thermostatically controlled water bath regulated at 303 K. A 1-g piece of ACC was wrapped round the anode (platinized titanium) and immersed in 0.5 M potassium chloride solution for 1 h prior to the electrochemical oxidation process. The schematic of the electrochemical cell used for oxidation is shown in Fig. 1. Two cathodes (platinized titanium) were used as counterelectrodes. As shown in Fig. 1, the cathodes were placed at equal distances from the anode to achieve uniform surface oxidation of the ACC. The electrochemical oxidation was carried out at currents of 1.1 and 2.2 A at different oxidation times of 2, 4, and 6 h and 1, 2, and 3 h, respectively. For each oxidation the chosen current was kept constant by adjusting the voltage throughout the chosen oxidation time and using fresh electrolyte each time. After oxidation, the oxidized ACC was washed with deionized water until the conductivity of the washed water reached the same value as the conductivity of deionized water. The oxidized ACC was dried in an oven at 383 K for 24 h, kept in a desiccator overnight, and then weighed.

2.3. Sodium capacity determination

Sodium sorption capacity was determined in order to compare the cation exchange capacity of modified and as-received ACC in aqueous solution. The sodium sorption capacity gives an indication of the cation exchange capacity of adsorbents in aqueous solution, which is related to the quantity of acidic functional groups generated upon electrochemical oxidation [9,
2.4. pH titrations

This technique determines the acidic and basic properties of ion exchangers and the nature of their surface functional groups [9,12,13]. A 25-mg piece of oxidized or unoxidized ACC was weighed using a Sartorius BP 210 D balance (±0.0005 g accuracy) and placed in a 50-ml conical flask. A predetermined volume (0–2 ml) of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain a titration curve over a pH range of 2–12. The pH of the solution in each flask, prior to the addition of the adsorbent, was measured using a Mettler-Toledo 340 digital pH meter. The flasks were sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 48 h. Blank experiments without any adsorbent were also performed under otherwise identical conditions. The solutions with the adsorbent were filtered after 48 h. The pH of the supernatant solutions and the solutions of the blank experiments were measured and then back-titrated with a volumetric standard of 0.01 M hydrochloric acid or 0.1 M sodium hydroxide using phenolphthalein as an indicator to obtain the amount of H⁺ or OH⁻ released by the adsorbent.

2.5. Zeta potential measurements

Zeta potential measurements were performed on a Malvern Zetamaster 3000HS_A. The oxidized and unoxidized ACCs were cut to small pieces, finely ground, and sieved to obtain particle size <45 μm. Samples of 25 mg of the finely ground ACCs were weighed using a Sartorius BP 210 D balance (±0.0005 g accuracy) and placed in 50-ml conical flasks. A volume of 20 ml of 0.1 M sodium chloride was added to each flask. A predetermined volume (0–20 ml) of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide was added to each flask to obtain the zeta potential over a pH range of 1–12. The flasks were sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 298 K and 150 rpm for 48 h. Aliquots of 5 ml of adsorbent suspensions were injected directly into the electrophoretic quartz cell with a plastic Luer syringe. Each sample was measured three times to provide an average reading. The cell was rinsed after each measurement with 40 ml of deionized water.

2.6. Elemental analysis

The samples were analyzed in the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK on a Perkin–Elmer Series II 2400 elemental analyzer. Each sample was accurately weighed (1–2 mg) and wrapped in tin foil prior to analysis. The combustion of the sample was done in the combustion tube at 2073 K in a controlled environment in the presence of pure oxygen after the system was purged with helium carrier gas. The gaseous combustion products were further decomposed in the presence of a series of catalysts. A thermal conductivity detector quantified the percentages of carbon, hydrogen, and nitrogen. The oxygen content was determined by difference.

2.7. Surface area and pore size distribution

Brunauer–Emmet–Teller (BET) surface area and pore size distribution (PSD) measurements of ACCs were done by a nitrogen adsorption and desorption method using a Micromeritics ASAP (accelerated surface area and porosimetry) 2010 surface analyzer. The samples were weighed and then outgassed at 393 K under a vacuum of less than 10 mm Hg on the degas ports of the analyzer for a minimum period of 24 h. The adsorption isotherms were generated by dosing 99.99% pure nitrogen onto the samples within a bath of liquid nitrogen at a temperature of 77 K. The mass of the degassed sample was determined by subtracting the weight of the degassed empty tube from the nitrogen backfilled sample-containing tube. The density functional theory (DFT) model was used to determine the pore size distribution [13].

2.8. Speciation of metal ions in aqueous solution

Knowledge of the relationship between the adsorbent surface chemistry and metal speciation helps to explain the sorption mechanisms [9,14]. To verify that there was no precipitation of metal species in the pH range in which this investigation was done, aqueous speciation of lead and copper as a function of pH was studied using JCHESS and CHESS software at concentrations of 0.0193 and 0.0157 M (higher than the maximum operating metal concentrations used) for lead (II) nitrate and copper (II) nitrate solutions, respectively.

2.9. Batch sorption experiments

Competitive and noncompetitive sorption of copper (II) and lead (II) from nitrate solutions were studied in batch experiments to obtain isotherms at pH values of 3, 4, and 5. For noncompetitive sorption experiments, 20 ml of copper (II) nitrate or lead (II) nitrate solutions at several initial concentrations (0.03–7.87 mM) were added to 50-ml conical flasks with 0.025 g of electrochemically oxidized or unoxidized ACC in each flask. For competitive sorption experiments, 20 ml of equimolar copper–lead nitrate solutions at several initial concentrations (0.03–7.87 mM) were added to several 50-ml conical flasks with 0.025 g of electrochemically oxidized or unoxidized ACC in each flask. The pH of the solutions was measured...
sing a Mettler-Toledo 340 digital pH meter and were adjusted to the required value by the addition of 0.1 M sodium hydroxide or 0.1 M nitric acid. The flasks were then sealed with parafilm and agitated in a Brunswick C25 series incubator shaker at 98 K and 150 rpm. The original pH values were maintained at a regular interval by adding 0.1 M sodium hydroxide or 0.1 M nitric acid to the solutions. The added volume of sodium hydroxide or nitric acid was recorded each time. This was continued until equilibrium was achieved, i.e., when there was no significant change in solution pH for 48 h; this was about 5 days for unoxidized ACC and 8 days for electrochemically oxidized ACC. To investigate the effect of pH on the sorption capacity of electrochemically oxidized ACC, a series of noncompetitive batch sorption experiments were conducted at pH values of 3, 4, 5, and 6. All other batch sorption experiments were conducted at pH 5.

The equilibrated solutions were filtered to remove ACC particles and the concentrations of the supernatant solutions were determined using a Varian AA 200 atomic absorption spectrophotometer (AAS) in acetylene–air flame emission mode.

4. Results and discussion

4.1. Sodium capacity

The total cation exchange capacity (i.e., the quantity of acidic functional groups) was determined in sodium hydroxide solution. Since sodium hydroxide neutralization is presumed to probe chemically and physically accessible acidic sites such as carboxylic, lactonic, and phenolic functional groups [15–19], it follows that sodium hydroxide titrates accessible functionalities that may reside in pore walls located well below the external surface. Oxygen-containing groups such as carbonyl, carboxyl, phenolic, and lactonic groups present on carbonaceous materials dissociate increasingly with an increase in solution pH values [16]. Therefore, these surface groups are completely dissociated in solutions at high pH and are available for ion exchange. Under this condition, the total cation exchange capacity can be determined. A high sodium capacity is an indication of high content of surface oxygen functional groups.

The sodium capacity results for modified and as-received ACC are shown in Fig. 2. The results in Fig. 2 show that the sodium capacity of electrochemically oxidized ACC at 1.1 A for 6 h is 4.7 times higher than that of unoxidized ACC. This increase is attributed to the introduction of more acidic functional groups. The extent of oxidation on the carbon surface depends on the chemical composition of the electrolyte [9]. The chlorine ion (Cl⁻) and hypochlorous acid (HOCI) that are formed when chlorine is present in water are strong oxidants [20]. Also, from the electrochemical series of metals [21], it is obvious that the potassium ion (K⁺) that is formed when potassium is present in water is a very strong reductant. Since the reduction and oxidation processes are responsible for the overall reaction in an electrolys cell, the presence of a strong oxidant and a strong reductant explains why the ACC is strongly oxidized when potassium chloride is used as an electrolyte. The sodium capacity data give an indication of the cation exchange capacity of the ACC in aqueous solution. So ACC electrochemically oxidized in potassium chloride has a high potential for trace metal removal from aqueous solutions. The results in Fig. 2 also show that the highest sodium capacity (4.94 mmol/g) was observed for the ACC electrochemically oxidized at 1.1 A for 6 h, and hence all subsequent experiments were conducted with this sample.

3.2. pH titrations

The pH titration curves are usually plotted as equilibrium solution pH vs acid/alkali added or the amount of H⁺ or OH⁻ ion released by the adsorbent vs equilibrium solution pH. The proton binding curves, that is, the plots of ions released vs equilibrium solution pH, for unoxidized ACC (UO) and electrochemically oxidized ACC (EO) are shown in Fig. 3. The point where the proton binding curve crosses the pH axis has crucial significance. It is called the point of zero charge (PZC). This has been defined as the pH value at which the surface charge is zero at a particular ambient temperature, applied pressure, and aqueous solution composition [22,23]. The PZC will change depending on the type and number of functional groups present on the adsorbent. It will be shifted to lower pH values with oxidation of the ACC due to the introduction of acidic functional groups such as carboxylic, phenolic, carbonyl, and lactonic groups onto the surface of the ACC [24]. As shown in Fig. 3, the PZC for the UO sample is at pH 6.8, whereas it is shifted to pH 2.8.

![Fig. 2. Sodium capacity result for unoxidized ACC (UO) and electrochemically oxidized ACC (EO) under different conditions.](image1)

![Fig. 3. Ion released vs equilibrium solution pH for UO and EO.](image2)
for the EO sample. It is well known that sorption of metal ions strongly depends on the chemistry of the carbon surface [25,26]. The adsorbed surface is positively charged at pH values below the PZC because the oxygen-containing groups are undissociated and the ACC sample will remove anions from solution under these conditions. In contrast, at solution pH values higher than the PZC, the ACC surface becomes more negatively charged due to dissociation of weakly acidic oxygen-containing functional groups. Thus the ACC sample is able to attract and exchange cations in solution. The shapes of the proton binding curves of the UO and EO ACC samples are different. UO ACC shows a smooth curve whereas EO ACC shows inflection points that are typical of the behavior of polyfunctional ion exchangers [13]. Moreover, the slope of the curve for EO ACC increased with an increase in equilibrium pH. This means that the concentration of hydrogen ions released increased with an increase in equilibrium pH; hence the cation exchange capacity is expected to be higher than that of UO ACC, as shown by the sodium capacity results. It is well known that carboxylic groups in ACC dissociate at pH values within the range from 2 to 6 and hydroxyl groups dissociate at pH values above 6 [27,28]. From the pH titration curves it can be seen that the dissociation of the acidic functional groups on the EO and UO ACC samples to produce H⁺ ions starts at an equilibrium solution pH of approximately 3 and 7, respectively. Therefore, one of the types of acidic functional groups on the surface of the EO sample is likely to be carboxylic groups, while that on the surface of the UO sample is likely to be hydroxyl groups.

The process of manufacturing viscose rayon consists of the following steps: alkalization, shredding, preripening, i.e., aging, xanthation, dissolving, maturing, and viscose fiber spinning [29]. At the spinning stage, the cellulose is regenerated from the viscose for the production of the viscose rayon filament. Therefore, the ACC matrix is composed of interlinking cellulose molecules and so it is expected that the UO ACC will have hydroxyl groups on its surface, since the cellulose molecules contain hydroxyl groups [3,29].

3.3. Zeta potential measurements

Fig. 4 shows the zeta potential vs equilibrium solution pH plots for UO and EO samples. An important parameter used to characterize the electrokinetic behavior of a solid–liquid interface is the isoelectric point (IEP). This is the equilibrium solution pH at which the zeta potential is zero. From the curves it is obvious that the IEP value of the EO sample is not accurately measurable. This is because the proton concentration of the bulk electrolyte solution is very low and increasing the proton concentration caused further decrease of the zeta potential. Bismark et al. [10] had the same observation with an anodically oxidized fiber. Rangel-Mendez and Streat [9] also had the same observation with electrochemically oxidized granular carbon and obtained the IEP values by extrapolation. Therefore, the IEP value for the EO sample as shown in Fig. 4 is an extrapolated value. A shift in the IEP of the EO sample to a lower value when compared with the IEP of the UO sample is obvious. The IEP for UO sample is 3, while that for EO sample is 1.15. This shows that the EO sample is more acidic than the UO sample, which confirms the pH titration results. The lower IEP value for the EO sample is attributed to the presence of more acidic functional groups. It is interesting to note that the zeta potential curve of the EO sample falls steeply with increasing equilibrium solution pH until about pH 4 and then starts to level off to form a distinct plateau area. Dissociation of carboxylic surface groups is probably responsible for this effect, since it is well known that dissociation of this group occurs at pH values in the range from 2 to 6 [27,28]. The plateau area of the zeta potential curve for the EO sample is caused by complete dissociation of carboxylic groups at about an equilibrium solution pH of 4, which is within the pH range at which this group dissociates. Therefore, there was no increase in the surface charge above pH 4. Since the IEP values are representative of external surface charges [23,28] and the PZC values are representative of the net total of external and internal surface charges, the difference between PZC and IEP can be interpreted as a measure of the surface charge distribution of carbons. Greater differential value indicates more negatively charged external than internal particle surfaces and therefore a more heterogeneous distribution of the surface charges. A lower differential value indicate a more homogeneous distribution of the surface charges. The electrochemical properties of EO and UO samples are summarized in Table 1. It is noticeable that the value of PZC – IEP for the UO sample is higher than that for the EO sample. It was 3.8 for the UO sample and 1.65 for the EO sample; therefore the electrochemically oxidized ACC has a more homogeneous surface charge distribution. This is attributed to the fact that all the ACCs are viscose-rayon-based and it is well known that the double bond at the aldehyde end of the cellulose molecules consists of a α bond and a γ bond [3,29]. So there is greater electron distribution over the more electronegative oxygen atom. However, the internal surface of the ACC will have a more uniform electron distribution due to bond formation between the cellulose molecules and the presence of several hydrogen and

<table>
<thead>
<tr>
<th>Sample</th>
<th>PZC</th>
<th>IEP</th>
<th>PZC – IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>6.8</td>
<td>3</td>
<td>3.8</td>
</tr>
<tr>
<td>EO</td>
<td>2.8</td>
<td>1.15</td>
<td>1.65</td>
</tr>
</tbody>
</table>
carbon atoms and so the external surface of the UO sample is more negatively charged than its internal surface.

3.4. Elemental analysis

Table 2 shows the elemental analysis results of UO and EO samples. The UO sample has 20.03% oxygen content, indicating the presence of some oxygen-containing groups on the surface. This is attributed to the presence of oxygen atoms at the aldehyde end and hydroxylic end of the cellulose molecules. It is well known that noncarbon species are removed during the carbonization of activated carbons [24,30,31]. The noncarbon species also include some oxygen-containing groups. However, not all the noncarbon species are removed, and the activated carbon surface adsorbs significant quantities of oxygen upon exposure to air at room temperature [31]. The results also show a significant difference in oxygen content between the UO and EO samples. This is directly related to the increase in oxygen-containing groups. The oxygen content in the EO sample increased by 120.8%. These results follow the same trend as the sodium capacity results for the UO and EO samples, which are 1.06 and 4.94 mmol/g, respectively. The increase in oxygen content in the EO sample is attributed to the introduction of more acidic oxygen-containing functional groups during electrochemical oxidation.

3.5. Surface area and pore size distribution

Physical characteristics of porous materials, such as surface area and pore structure, are extremely important when applied in catalytic and sorption processes. The surface area is the reactive zone where chemisorption and/or physisorption occur. Alternatively, pore size and shape will define the process performance, since kinetics are directly related to adsorbate intraparticle diffusion. The BET surface areas for the UO and EO samples are 1395 and 532 m²/g, respectively. All the ACCs analyzed in this study have extensive BET surface areas that are ideal in the treatment of drinking and waste water. However, the BET surface area decreased with electrochemical oxidation. The results show that the EO sample lost 61.9% of the original BET surface area. This is attributed to the blockage of pores by oxygen-containing functional groups and humic substances produced during electrochemical oxidation. The reduction in the surface area of carbonaceous materials by by-products from oxidation has been discussed by other researchers [12,13].

The pore size distribution (PSD) curves for EO and UO samples are shown in Fig. 5. It can be seen from the PSD curves that the UO sample exhibited bimodal pore size distributions with peaks dominant at approximately 15 and 28 Å. So it possesses a reasonable number of micropores with a small fraction of mesopores but without any macropores. The EO sample also exhibited similar bimodal pore size distributions. However, the PSD curve of the UO sample covers a broader range of pore width than the EO sample. This is attributed to the fixing of oxygen functional groups inside the wider mesopores, which increased the nitrogen constriction to the pores, therefore showing a reduction in pore diameter. From the PSD curves it can also be seen that there was a decrease in incremental pore volume in the pore diameters for the EO sample. As a result of electrochemical oxidation, more acidic oxygen functional groups and humic substances were produced, causing the pores to shrink and/or get blocked by the more acidic oxygen functional groups, which increased the nitrogen constriction to the pores, resulting in a decrease in incremental pore volume. However, it is obvious that the UO sample is predominantly microporous, while the EO sample showed the most dominant peak at approximately 22 Å, showing that it contained more mesopores than micropores. This is confirmed by the decrease in BET surface area of the EO sample, since more micropores than mesopores would have given it a higher BET surface area. Saha et al. [13] also observed that loss in microporosity results in the reduction of BET surface area. The dominant presence of the mesopores is attributed to the formation of a high quantity of oxygen functional groups, as shown by the sodium capacity results, which blocked almost all the micropores and entered inside the mesopores. This dramatically reduced the pore width of the wider mesopores to more narrow mesopores and since almost all the micropores were blocked, the mesopores became predominant.

3.6. Speciation of metal ions in aqueous solution

The speciation curves calculated using JCHESS and CHESS software for 0.0157 M copper and 0.0193 M lead in nitrate solutions are presented in Figs. 6a and 6b, respectively. Fig. 6a shows that at pH 5 (the maximum pH used in this study), copper exists in aqueous solution predominantly as Cu²⁺ in an approximate proportion of 98.3%. The concentration of other copper species (e.g., CuNO₃⁺, CuOH⁺, and Cu₂(OH)₂⁺) at pH 5 is approximately 1.7%.
Fig. 6. Speciation curves for (a) 0.0157 M copper and (b) 0.0193 M lead in nitrate solution.

Fig. 6b shows that at pH 5 lead exists in aqueous solution as Pb$^{2+}$ and PbNO$_3^-$ in approximate proportions of 78.6 and 21.2%, respectively. The concentrations of other lead species (e.g., PbOH$^+$ and Pb(OH)$_3^+$) at pH 5 is negligible (about 0.2%). From the speciation curves it can be seen that there is no precipitation of any of the metal species at pH 5. The maximum concentration of lead or copper used for the batch sorption experiments is 0.00787 M, which is lower than the concentrations at which the aqueous speciation diagrams were prepared, confirming that the metal removal process is purely due to sorption.

3.7. Batch sorption experiments

Competitive and noncompetitive isotherms for sorption of lead and copper ions in aqueous solutions onto unoxidized ACC (UO) and electrochemically oxidized ACC (EO) are shown in Figs. 7-14. The sorption isotherm models, effect of electrochemical oxidation, effect of competitive sorption, and effect of pH on the sorption of lead and copper and the likely mechanism of lead and copper sorption onto EO and UO samples are discussed in the following sections.

3.7.1. Sorption isotherm models

The analysis of the isotherm data is important to develop an equation that represents the results. Correlation of the data using empirical or theoretical equations is required in the analy-
sis and design of adsorption processes. The most widely used
isorbent equations for modeling equilibrium isotherms are the
Langmuir and Freundlich equations. The Langmuir isotherm is
expressed as
\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \]  
(1)
where \( q_e \) is the amount of adsorbate adsorbed per unit mass of
adsorbent (mmol/g), \( C_e \) is the equilibrium concentration of the
adsorbate (mmol/L), and \( q_{\text{max}} \) and \( b \) are empirical constants;
\( q_{\text{max}} \) is the maximum value of \( q_e \) obtainable with an increase in
\( C_e \) and \( b \) gives an indication of the strength of bonding between
the adsorbate and the adsorbent. The Freundlich isotherm is ex-
pressed as
\[ q_e = K_f C_e^{1/n} \]  
(2)
where \( q_e \) is the amount of adsorbate adsorbed per unit mass of
adsorbent (mmol/g), \( C_e \) is the equilibrium concentration of the
adsorbate (mmol/L), and \( K_f \) is an approximate indicator of ad-
sorption capacity, while \( 1/n \) is a function of strength of adsorp-
tion. The experimental data for competitive and noncompetitive
isorption of lead and copper ions onto EO and UO samples were
alyzed using the Langmuir and Freundlich isotherm models. The corresponding Freundlich and Langmuir parameters
and correlation coefficients (\( R^2 \)) are shown in Table 3. The
relation coefficients for the Langmuir isotherm model were
higher than those for the Freundlich isotherm model for all
the experimental data for sorption onto the EO sample. How-
ever, the correlation coefficients for Freundlich isotherm model
were higher than those for the Langmuir isotherm model for all
the experimental data for sorption onto the EO sample. There-
fore, the correlation coefficients demonstrate that the Langmuir
isorbent model fitted the experimental data for sorption onto

![Fig. 10. Isotherms of noncompetitive (EO Cu) and competitive (EO Cu com-
petitive) of sorption copper onto EO at pH 5.](image)

![Fig. 11. Isotherms of noncompetitive (UO Pb) and competitive (UO Pb com-
petitive) sorption of lead onto UO at pH 5.](image)

![Fig. 12. Isotherms of noncompetitive (EO Pb) and competitive (EO Pb competi-
tive) sorption of lead onto EO at pH 5.](image)

![Fig. 13. Isotherms of noncompetitive sorption of copper onto EO at pH 3, 4,
and 5.](image)

![Fig. 14. Isotherms of noncompetitive sorption of lead onto EO at pH 3, 4,
and 5.](image)
Table 3
Langmuir and Freundtich isotherm constants for noncompetitive (N Cu) and competitive (C Cu) copper and noncompetitive (N Pb) and competitive (C Pb) lead sorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir isotherm constants</th>
<th>Freundtich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mmol/g)</td>
<td>( b )</td>
</tr>
<tr>
<td>N Cu UO pH 5</td>
<td>0.076</td>
<td>13.067</td>
</tr>
<tr>
<td>N Cu EO pH 3</td>
<td>0.643</td>
<td>10.884</td>
</tr>
<tr>
<td>N Cu EO pH 4</td>
<td>1.243</td>
<td>34.669</td>
</tr>
<tr>
<td>N Cu EO pH 5</td>
<td>1.605</td>
<td>87.76</td>
</tr>
<tr>
<td>C Cu UO pH 5</td>
<td>0.073</td>
<td>11.591</td>
</tr>
<tr>
<td>C Cu EO pH 5</td>
<td>0.776</td>
<td>13.658</td>
</tr>
<tr>
<td>N Pb UO pH 5</td>
<td>0.383</td>
<td>18.348</td>
</tr>
<tr>
<td>N Pb EO pH 3</td>
<td>0.193</td>
<td>10.971</td>
</tr>
<tr>
<td>N Pb EO pH 4</td>
<td>1.472</td>
<td>20.528</td>
</tr>
<tr>
<td>N Pb EO pH 5</td>
<td>1.861</td>
<td>39.801</td>
</tr>
<tr>
<td>C Pb UO pH 5</td>
<td>0.104</td>
<td>1.683</td>
</tr>
<tr>
<td>C Pb EO pH 5</td>
<td>1.022</td>
<td>6.112</td>
</tr>
<tr>
<td>C Cu + C Pb UO</td>
<td>0.177</td>
<td>6.676</td>
</tr>
<tr>
<td>C Cu + C Pb EO</td>
<td>1.782</td>
<td>4.576</td>
</tr>
</tbody>
</table>

Table 4
Experimental and Langmuir model maximum metal ion sorbed onto EO and UO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental maximum ions sorbed (mmol/g)</th>
<th>Langmuir maximum ions sorbed (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N Cu UO pH 5</td>
<td>0.098</td>
<td>0.076</td>
</tr>
<tr>
<td>N Cu EO pH 3</td>
<td>0.63</td>
<td>0.64</td>
</tr>
<tr>
<td>N Cu EO pH 4</td>
<td>1.27</td>
<td>1.24</td>
</tr>
<tr>
<td>N Cu EO pH 5</td>
<td>1.69</td>
<td>1.61</td>
</tr>
<tr>
<td>C Cu UO pH 5</td>
<td>0.085</td>
<td>0.073</td>
</tr>
<tr>
<td>C Cu EO pH 5</td>
<td>0.75</td>
<td>0.78</td>
</tr>
<tr>
<td>N Pb UO pH 5</td>
<td>0.47</td>
<td>0.38</td>
</tr>
<tr>
<td>N Pb EO pH 3</td>
<td>0.90</td>
<td>0.91</td>
</tr>
<tr>
<td>N Pb EO pH 4</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td>N Pb EO pH 5</td>
<td>1.87</td>
<td>1.86</td>
</tr>
<tr>
<td>C Pb UO pH 5</td>
<td>0.12</td>
<td>0.104</td>
</tr>
<tr>
<td>C Pb EO pH 5</td>
<td>1.01</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The electrochemical oxidation process altered the physical surface characteristics of the UO sample. A reduction in surface area and pore volume was observed, as shown in the surface area results and the PSD curves in Fig. 5. However, the change in these surface properties does not seem to affect the metal sorption. In contrast, a dramatic increase in the lead and copper ion uptake by the EO sample for competitive and noncompetitive sorption is observed and the results are shown in Figs. 7 and 8. The maximum noncompetitive copper and lead sorption capacities of the EO sample are 1.69 and 1.87 mmol/g, respectively, while the maximum noncompetitive copper and lead sorption capacities of UO sample are 0.098 and 0.47 mmol/g, respectively. The noncompetitive copper and lead sorption capacities of the EO sample are approximately 17 times and 4 times greater than the noncompetitive sorption capacities of the UO sample, respectively. The maximum competitive copper and lead sorption capacities of the EO sample are 0.75 and 1.005 mmol/g, respectively, and the maximum competitive copper and lead sorption capacities of the UO sample are 0.085 and 0.117 mmol/g, respectively. The competitive copper and lead sorption capacities of the EO sample are approximately 8.8 and 8.6 times greater than the competitive sorption capacities of the UO sample, respectively. Therefore, electrochemical oxidation of ACC dramatically increased its sorption capacity for both competitive and noncompetitive sorption of lead and copper ions. This is directly related to the increase in acidic oxygen-containing functional groups as detected by the elemental analysis and pH titration results. This is also confirmed by the sodium capacity results, which showed a much higher cation exchange capacity for the EO sample than the UO sample.

3.7.2. Effect of electrochemical oxidation on lead and copper sorption equilibrium

The sorption capacities of EO and UO samples were evaluated for copper and lead ions. Fig. 7 shows the copper and lead sorption of EO and UO samples evaluated at pH 5 and 298 K...
on. The competitive and noncompetitive isotherms of copper and lead are shown in Figs. 8–12.

Since the sorption studies included the two metal ions in the same solution at the same molar concentration, the amount of a particular metal ion sorbed by the ACC indicates its ability to compete with the other ion in solution. Sorption sites of EO and UO samples favored lead ions, more than copper ions, as shown in Figs. 7 and 8. Therefore, the observed sorption preference for EO and UO samples is Pb\(^{2+}\) > Cu\(^{2+}\). The noncompetitive sorption affinity for lead is about 1.1 times and 4.8 times greater than that for copper for EO and UO samples, respectively. The difference of a factor of 1.1 times shows that the maximum concentration of sorption sites for copper and lead on the EO sample are approximately the same for noncompetitive sorption, indicating that the number of sorption sites per gram of ACC is about the same for both metals. Table 4 shows that the experimentally determined maximum lead and copper ions sorbed onto EO sample are 1.87 and 1.69 mmol/g, respectively, for noncompetitive sorption. It is 1.01 and 0.75 mmol/g for competitive sorption of lead and copper, respectively, giving total sorption sites of 1.76 mmol/g. This confirms that the number of sorption sites per gram of EO is approximately the same for both metals for both competitive and noncompetitive sorption, as shown in Fig. 7. Furthermore, it can be assumed that copper and lead are sorbed onto the same sites on the EO, and the sorption process is likely to be by ion exchange. However, the difference of a factor of 4.8 times between lead and copper sorption onto the EO sample show that the maximum concentrations of sorption sites for copper and lead on the UO sample are different for noncompetitive sorption, indicating that the sorption process is likely not to be by ion exchange. The results also show that the presence of another ion reduced the sorption of the other ion present in solution. The competitive sorption resulted in maximum sorption reduction of 46 and 56% for lead and copper, respectively, for the EO sample. It also resulted in maximum sorption reduction of 75 and 13% for lead and copper, respectively, for the UO sample. However, the order of metal sorption capacity onto EO and UO samples follows the same trend, Pb\(^{2+}\) > Cu\(^{2+}\), for competitive sorption. The significant reduction in the sorption of lead in the presence of copper (though it is preferred to copper) is due to weaker interaction of lead with the EO or UO samples caused by higher concentration of copper ion in the solution after the initial sorption of lead onto the EO or UO samples, since both metal ions had initial equal molar concentrations. The sorption preference for EO and UO samples, which is Pb\(^{2+}\) > Cu\(^{2+}\), is attributed to the fact that adsorbers prefer the ion with the smaller hydrated ionic radius, the ion with the greater polarizability, and the ion of higher valence [27,36]. The crystal ionic radii for Pb\(^{2+}\) and Cu\(^{2+}\) are 1.19 and 0.57 Å, respectively [37,38]. However, the effective hydrated ionic radii for Pb\(^{2+}\) and Cu\(^{2+}\) are 4.5 and 6 Å, respectively [38], and the polarizability for lead and copper atoms are 6.8 \times 10^{-24} and 6.1 \times 10^{-24} cm\(^3\), respectively [37]. Both ions have the same valency; therefore, lead with the smaller effective hydrated ionic radius and greater polarizability is preferred to copper. The lead ions with smaller effective hydrated radii are able to diffuse into parts of the porous structure that are not easily accessible by the larger hydrated copper ions, thereby resulting in increased sorption of lead ions. The preferred sorption of lead to copper due to smaller effective hydrated ionic radius has been reported by other researchers [39,40].

3.7.4. Effect of pH on lead and copper sorption

The effect of pH on the removal of lead and copper was investigated by determining sorption isotherms of noncompetitive lead and copper onto EO sample at solution pH values of 3, 4, and 5. The results are shown in Figs. 13 and 14. In order to avoid precipitation of metal species, no sorption experiments were performed at a pH greater than 5. From these figures it is clear that the sorption isotherms were affected significantly by solution pH. The maximum sorption capacity increased with an increase in solution pH. It increased about 2 times and 1.6 times for copper and lead, respectively, with an increase in solution pH from 3 to 4. With a further increase in solution pH from 4 to 5 the maximum sorption capacity increased by a factor of 1.34 and 1.27 times for copper and lead, respectively. The effect of pH on the sorption isotherms was due to interactions between lead and copper ions in solution and the surface charge on the EO sample. It has already been pointed out that the adsorbent surface is negatively charged at pH values higher than the PZC, which is pH 2.8 for the EO sample. It becomes more negatively charged as the pH increases due to dissociation of weakly acidic (oxygen-containing) functional groups. Hence, the amount of positively charged lead and copper that will ion-exchange with the oxygenated functional groups will increase with an increase in pH. The reduction in the increase of the maximum sorption capacity with an increase in pH from 4 to 5 as compared to that with an increase in pH from 3 to 4 is attributed to the fact that the number of sorptive sites per gram of ACC is limited. It is also noticeable from Figs. 13 and 14 that the maximum sorption capacity is low for the sorption isotherm for pH 3. This is due to the fact that at low pH, the dissociation of weakly acidic functional groups is low. Also, the concentration of H\(^+\) ions is high and will react with the few anionic functional groups on the surface of the EO sample, thereby restricting the number of binding sites for metal ions.

3.7.5. Mechanism of lead and copper sorption onto EO and UO ACC

To elucidate the mechanism of sorption of copper and lead ions onto EO and UO samples, it is necessary to understand the interactions between the metal ions in aqueous solution and the surface functional groups of the ACCs.

The PZC for EO and UO samples is at pH 2.8 and 6.8, respectively. The highest pH at which the batch sorption experiments were performed was pH 5. This is below the PZC of UO, so the ACC surface was positively charged. This explains why the solution pH increased during the copper and lead sorption process and so was adjusted by adding specific volumes of 0.1 M nitric acid to maintain the original pH. However, the greater electron distribution over the more electronegative oxygen atoms makes it possible for lead and/or copper ions to be attached to them; therefore, complex formation between the metal ions and the UO sample surface is the likely mechanism...
for sorption of lead and copper onto the UO sample. This is confirmed by the significant difference between the experimentally determined maximum metal ion sorbed for noncompetitive lead and copper onto UO, as shown in Table 4. It is also confirmed by the difference in the sorption isotherms for the UO and EO samples in Fig. 7. Xiao and Thomas [32] confirmed that if sorption is mainly controlled by electrostatic interactions, as in ion exchange, a similar amount of metal ions should be sorbed. They also stated that the reason for sorption of different amounts of metal ions is surface heterogeneity. Therefore, sorption of lead and copper onto a UO sample with a heterogeneous surface charge distribution is not by ion exchange but by surface complex formation with the metal ions.

The batch sorption experiments were performed at solution pH values of 3, 4, and 5, which are above the PZC of the EO sample. Hence, the surface of the EO sample was negatively charged. The EO sample therefore behaved as a cation exchanger, indicating that the sorption process was ion exchange. This explains why the solution pH decreased during the lead and copper sorption, indicating that H\(^+\) ions were released from the surface of the EO sample. The pH was adjusted by adding specific volumes of 0.1 M sodium hydroxide to maintain the original pH. Mass balance to obtain the maximum H\(^+\) ions released was performed using the volume of 0.1 M sodium hydroxide added to adjust the solution pH. The experimentally determined noncompetitive and competitive metal ions sorbed onto the EO sample and H\(^+\) ions released from the EO sample are shown in Table 5. It is obvious that one Pb\(^{2+}\) or Cu\(^{2+}\) ion was sorbed for approximately every two H\(^+\) ions released from the EO sample surface. This confirms that the sorption of lead and copper onto EO sample is mainly governed by an ion-exchange mechanism. The pH titration and zeta potential results indicated that carboxylic acids were introduced to the EO sample by electrochemical oxidation. As it is well known that the aldehyde and alcohol groups present in the cellulose molecules of the UO viscose rayon sample are converted to carboxylic acids by oxidation [3], the sorption sites on the EO sample are therefore mainly carboxylic functional groups.

### 4. Conclusions

This work demonstrates that electrochemically oxidized ACC can be used as an effective sorbent for treating aqueous solutions contaminated with copper and/or lead in both single and multicomponent systems. Copper and lead ion sorption capacities of ACC increased by factors of 17 and 4 times, respectively, for noncompetitive sorption for the electrochemically oxidized (EO) sample. The capacities also increased by factors of 8.8 and 8.6 times for competitive sorption of copper and lead, respectively, for the EO sample. The competitive and noncompetitive sorption studies also showed that the affinity order of the two metal ions sorbed by unoxidized and electrochemically oxidized ACCs is Pb\(^{2+}\) > Cu\(^{2+}\). The solution pH plays a very important role in the sorption of lead and copper ions onto the electrochemically oxidized ACC. The uptake of lead and copper ions increased with an increase in solution pH.

It is confirmed that lead and copper ions were sorbed onto EO ACC mainly by an ion-exchange mechanism. However, it is proposed that lead and copper ions were sorbed onto unoxidized (UO) ACC by complex formation with the ACC surface. The present study concludes that electrochemical oxidation of viscose-rayon-based ACC markedly enhanced the removal of lead and copper ions from aqueous solutions.

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### References
