Selective removal of heavy metals using novel active carbons

This item was submitted to Loughborough University’s Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/7182

Publisher: © Vladimir Strelko

Please cite the published version.
This item is held in Loughborough University’s Institutional Repository (https://dspace.lboro.ac.uk/) and was harvested from the British Library’s EThOS service (http://www.ethos.bl.uk/). It is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/
Selective Removal of Heavy Metals Using Novel Active Carbons

by

Vladimir Strelko

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

November 1999

© Vladimir Strelko 1999
Abstract

Porous carbonaceous adsorbent materials possessing weakly acidic surface functional groups have been evaluated for the selective removal of heavy metals from aqueous solutions. Active carbons derived from both agricultural products (KAU carbons) and polymeric resin (CKC carbon) have been oxidised by hot air or nitric acid to produce samples with different degrees of surface oxidation. A novel phosphorus-containing carbonaceous sorbent (PGP-P) has been prepared by pyrolysis of phosphorylated phenol-formaldehyde resin. Surface modifications have been carried out to introduce various acidic functional groups capable of selective heavy metal binding. The properties of these sorbents have been compared to those of commercially available polymeric carboxylic resin C 104 (Purolite) and oxidised Filtrasorb 400 (Chemviron).

Investigation into the physical structure of the adsorbents using microscopy and nitrogen sorption at liquid nitrogen temperatures showed that the porous structure is adversely affected by carbon oxidation. The surface area and pore volume decrease as the degree of surface oxidation increases. The low surface area and pore volume of PGP-P was attributed to the presence of phosphorus-containing functional groups which protect the surface from excessive burn-off.

The surface functionality of the sorbents was determined by FT-IR, NMR and X-ray photoelectron spectroscopy. Relatively high concentrations of different weakly acidic functional groups were detected on the surface of the materials studied.

The ion-exchange properties of the sorbents were assessed by acid-base titration techniques and electrophoretic mobility measurements. Oxidation of carbons with hot air resulted in a greater proportion of relatively weaker type surface functionality (i.e. phenolic) whereas nitric acid modification produced a higher concentration of relatively stronger carboxylic groups. Electrophoretic mobility measurements suggested that the carbon surface is negatively charged within the range of pH values studied. pH titration results demonstrated relatively greater surface acidity of active carbons compared to carboxylic resin.
Metal sorption characteristics of modified active carbons were measured in both batch and mini-column experiments (in the mg/l and µg/l range). The materials studied showed a preference towards lead and copper over nickel and cadmium. The selectivity of oxidised carbons was controlled by varying oxidation treatment conditions as well as employing different oxidising agents and carbon precursors. Improved selectivity of PGP-P towards lead was related to the formation of stable complexes with various phosphorus-containing functional groups. The selectivity of carbons towards metals was explained by the differences in the distribution of surface functional groups and soft and hard metal-ligand interactions.

The kinetics of lead sorption showed that the metal uptake rate was rapid for oxidised materials and slow for the phosphorus-containing carbon. The metal uptake rate of carbons was correlated to their pore size distribution.

Active carbons were successfully applied for the selective removal of radionuclides. The materials showed excellent decontamination factors for α-, β- and γ-emitters. This was attributed to the presence of mineral admixtures and humic acids in carbons as well as the surface functional groups.

Repeated cycles of lead sorption/elution indicated that the metal capacities of the carbon-packed mini-columns were reduced but reached a steady level after 3-4 cycles.

**Keywords:**
Heavy metals, Selectivity, Adsorption, Active carbons, Surface heteroatoms, Mini-columns.
Acknowledgements

I wish to express my sincerest gratitude to my supervisor Prof. Michael Streat for his invaluable support and encouragement throughout the period of this research project.

Grateful thanks are also due to Loughborough University and Severn-Trent Water Ltd for their financial support of this project.

I would like to thank Prof. V. Strelko, of the Institute of Sorption and Endocellology Problems, Ukraine and Dr. O. Kozyuchenko, of Mast-Carbon Ltd, UK for supplying me with adsorptive materials and with whom I had many invaluable discussions.

Special thanks go to Martin Kerry who helped me with proof-reading of my thesis and for helping me to settle down in Loughborough.

I wish to acknowledge Prof. David Sherrington from the University of Strathclyde for the elemental analysis data, researchers from the Institute of Colloid Chemistry and Chemistry of Water, Ukraine and the Institute of Physics of Metals, Ukraine for the solid state NMR and XPS measurements and AEA Technology plc for helping with radionuclide sorption experiments. Thanks also to the academic and technical staff in the Chemical Engineering Department.

Finally, I would like to thank all my friends in Loughborough for their enjoyable company and my family for their moral support and patience over the past few years.
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iii</td>
</tr>
<tr>
<td>Certificate of Originality</td>
<td>iv</td>
</tr>
<tr>
<td>List of Figures</td>
<td>ix</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xii</td>
</tr>
<tr>
<td><strong>Chapter 1: Introduction to Active Carbon</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction to Carbon</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Introduction to Activated Carbon</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Manufacture of Activated Carbons</td>
<td>3</td>
</tr>
<tr>
<td>1.3.1 Historical background</td>
<td>3</td>
</tr>
<tr>
<td>1.3.2 Activated carbon precursors</td>
<td>4</td>
</tr>
<tr>
<td>1.3.3 Manufacture of activated carbon</td>
<td>6</td>
</tr>
<tr>
<td>1.3.3.1 Physical activation</td>
<td>6</td>
</tr>
<tr>
<td>1.3.3.2 Chemical activation</td>
<td>7</td>
</tr>
<tr>
<td>1.3.3.3 Forms of activated carbon</td>
<td>9</td>
</tr>
<tr>
<td>1.3.3.4 Economic aspects</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Applications</td>
<td>10</td>
</tr>
<tr>
<td>1.4.1 Gas phase applications</td>
<td>10</td>
</tr>
<tr>
<td>1.4.2 Liquid phase applications</td>
<td>12</td>
</tr>
<tr>
<td>1.4.3 Water treatment</td>
<td>12</td>
</tr>
<tr>
<td>1.4.3.1 Potable water treatment</td>
<td>12</td>
</tr>
<tr>
<td>1.4.3.2 Industrial and municipal water treatment</td>
<td>13</td>
</tr>
<tr>
<td>1.5 Concluding Remarks and Research Objectives</td>
<td>14</td>
</tr>
<tr>
<td>1.6 References</td>
<td>15</td>
</tr>
<tr>
<td><strong>Chapter 2: Physical and Chemical Properties of Active Carbons</strong></td>
<td>17</td>
</tr>
<tr>
<td>2.1 Crystalline and Electronic Structure of Carbons</td>
<td>17</td>
</tr>
<tr>
<td>2.2 Porous Structure in Carbons</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Surface Chemistry in Carbons</td>
<td>24</td>
</tr>
<tr>
<td>2.3.1 Acidic surface groups</td>
<td>27</td>
</tr>
<tr>
<td>2.3.2 Basic surface groups</td>
<td>29</td>
</tr>
<tr>
<td>2.3.3 Other heteroatoms</td>
<td>30</td>
</tr>
<tr>
<td>2.4 Sorption of Electrolytes</td>
<td>31</td>
</tr>
<tr>
<td>2.5 Concluding Remarks</td>
<td>38</td>
</tr>
</tbody>
</table>
Chapter 3: Removal of Metals by Active Carbons

3.1 Introduction

3.2 Heavy Metal Contaminants in Water

3.3 Applications of Active Carbons for Metals Removal
   3.3.1 Agricultural waste-based active carbons
   3.3.2 Coal-derived active carbons
   3.3.3 Oxidised active carbons and metals removal
   3.3.4 Removal of lead by active carbons
      3.3.4.1 Lead contamination of drinking water
      3.3.4.2 Active carbons for lead decontamination
      3.3.4.3 Sorption of low levels of lead by active carbon
   3.3.5 Removal of cadmium by active carbon
   3.3.6 Nickel removal by active carbon
   3.3.7 Copper sorption by active carbon

3.4 Reductive Sorption of Metals by Active Carbons

3.5 Humic Compounds in the Removal of Heavy Metals by Active Carbons
   3.5.1 Oxidised carbons and humic compounds

3.6 Radionuclides Removal by Active Carbons
   3.6.1 Radiation stability of resins and carbons
   3.6.2 Radionuclide removal by oxidised carbons

3.7 Concluding Remarks

3.8 References

Chapter 4: Experimental

4.1 Sorptive Materials

4.2 Preparation of Fruit Stones-Based Carbon

4.3 Preparation of Synthetic Polymer-Based Carbons
   4.3.1 Styrene/DVB copolymer-based carbon (CKC)
   4.3.2 Phenol-formaldehyde resin-based phosphorus-containing carbon
      4.3.2.1 Preparation of polycondensation phenol-formaldehyde resin
      4.3.2.2 Phosphorilation of polycondensation resin
      4.3.2.3 Carbonisation of phosphorilated resin
      4.3.2.4 Washing
      4.3.2.5 Experimental Equipment

4.4 Modification of Active Carbons
   4.4.1 Oxidation of active carbon with liquid reagents
      4.4.1.1 F 400 oxidation

References
4.4.1.2 Oxidation of KAU carbon by nitric acid

4.4.1.3 Oxidation of KAU carbon by hot air

4.4.2 Static exchange capacity

4.5 Characterisation of Sorbents

4.5.1 Elemental analysis

4.5.2 Phosphorus analysis

4.5.3 Surface area and pore size distribution

4.5.4 Boehm's titration

4.5.5 pH-titration

4.5.6 Electrophoretic mobility measurements

4.5.7 FT-IR spectroscopy

4.5.8 Scanning electron microscopy

4.5.9 Solid state nuclear magnetic resonance spectroscopy and X-ray photoelectron spectroscopy

4.6 Sorption Studies

4.6.1 Kinetic experiments

4.6.2 Batch sorption experiments

4.6.2.1 Sorption experiments at parts per million concentration range

4.6.2.2 Nomenclature

4.6.2.3 Sorption experiments at parts per billion concentration range

4.6.3 Mini-column sorption experiments

4.6.4 Sorption of radionuclides

4.6.4.1 Reference waste streams

4.6.4.2 Sorbent conditioning

4.6.4.3 Batch sorption experiments

4.7 References

Chapter 5: Physical Characterisation

5.1 Introduction

5.2 Scanning Electron Microscopy (SEM)

5.3 Nitrogen Adsorption Isotherms and Pore Size Distribution

5.4 Conclusions

5.5 References

Chapter 6: Chemical Characterisation

6.1 Introduction

6.2 Elemental Analysis

6.3 Boehm's titration

6.4 Electrophoretic mobility
### Chapter 7: Sorption Studies

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>181</td>
</tr>
<tr>
<td>7.2 Effect of Carbon Surface Oxidation</td>
<td>182</td>
</tr>
<tr>
<td>7.3 Metal Sorption from Buffered Solution</td>
<td>183</td>
</tr>
<tr>
<td>7.4 The Influence of pH on Metal Removal by Active Carbons</td>
<td>185</td>
</tr>
<tr>
<td>7.5 Metal Sorption from Aqueous Solutions</td>
<td>187</td>
</tr>
<tr>
<td>7.6 Removal of Radionuclides by Active Carbons</td>
<td>193</td>
</tr>
<tr>
<td>7.7 Kinetics of Metal Sorption</td>
<td>198</td>
</tr>
<tr>
<td>7.8 Mini-Column Experiments</td>
<td>201</td>
</tr>
<tr>
<td>7.9 Metal Recovery</td>
<td>214</td>
</tr>
<tr>
<td>7.10 General Discussion</td>
<td>218</td>
</tr>
<tr>
<td>7.11 Conclusions</td>
<td>227</td>
</tr>
<tr>
<td>7.12 References</td>
<td>228</td>
</tr>
</tbody>
</table>

### Chapter 8: Conclusions and Future Work

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Conclusions</td>
<td>232</td>
</tr>
<tr>
<td>8.2 Future Work</td>
<td>235</td>
</tr>
</tbody>
</table>

### Appendix 1: List of Publications

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 1: List of Publications</td>
<td>237</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Allotropic forms of carbon</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic representation of the two methods of activation</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>The packet and fringe model of carbonaceous materials</td>
<td>18</td>
</tr>
<tr>
<td>2.2</td>
<td>The molecular tape carbon felt model</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Energy band diagram for carbon solids</td>
<td>20</td>
</tr>
<tr>
<td>2.4</td>
<td>Proposed structures of surface oxygen-containing functional groups</td>
<td>28</td>
</tr>
<tr>
<td>2.5</td>
<td>Analogous structures of surface functional groups</td>
<td>28</td>
</tr>
<tr>
<td>2.6</td>
<td>Reaction of proton with pyrone-like structure</td>
<td>29</td>
</tr>
<tr>
<td>2.7</td>
<td>Possible structures of basic surface sites on graphene layer, derived from the γ-pyrone structures</td>
<td>30</td>
</tr>
<tr>
<td>2.8</td>
<td>Surface oxides proposed by Shilov et al.</td>
<td>33</td>
</tr>
<tr>
<td>2.9</td>
<td>Schematic representation of the ion sorption by active and oxidised carbons</td>
<td>37</td>
</tr>
<tr>
<td>3.1</td>
<td>pH dependence of cation sorption by air oxidised FOU carbon</td>
<td>53</td>
</tr>
<tr>
<td>3.2</td>
<td>Effect of foreign cations on lead uptake by active carbon</td>
<td>58</td>
</tr>
<tr>
<td>3.3</td>
<td>Sorption isotherms for ammonium complexes of zinc, cadmium and nickel on platinised carbon in hydrogen and air</td>
<td>62</td>
</tr>
<tr>
<td>3.4</td>
<td>pH dependence of molybdenum(VI) removal by different active carbons</td>
<td>67</td>
</tr>
<tr>
<td>3.5</td>
<td>Relative Cr(III) and Cr(VI) uptake on conventional (M) and oxidised (MO) active carbons in the presence of humic acid (HA)</td>
<td>71</td>
</tr>
<tr>
<td>4.1</td>
<td>Chemical scheme for carbonisation of crushed fruit stones (KAU carbon)</td>
<td>90</td>
</tr>
<tr>
<td>4.2</td>
<td>Chemical scheme of styrene/DVB copolymer carbonisation</td>
<td>91</td>
</tr>
<tr>
<td>4.3</td>
<td>Chemical scheme of carbonisation of chlormethylated styrene/DVB copolymer</td>
<td>92</td>
</tr>
<tr>
<td>4.4</td>
<td>Preparation scheme of phosphorus-containing carbon</td>
<td>93</td>
</tr>
<tr>
<td>4.5</td>
<td>The apparatus for resin phosphorilation</td>
<td>94</td>
</tr>
<tr>
<td>4.6</td>
<td>Apparatus for high temperature treatment</td>
<td>96</td>
</tr>
<tr>
<td>4.7</td>
<td>Apparatus for hot air oxidation</td>
<td>101</td>
</tr>
<tr>
<td>4.8</td>
<td>Schematic diagram for metals sorption rate experiments</td>
<td>110</td>
</tr>
<tr>
<td>4.9</td>
<td>Schematic diagram of the mini-column apparatus</td>
<td>115</td>
</tr>
<tr>
<td>5.1</td>
<td>SEM of CKC</td>
<td>121</td>
</tr>
<tr>
<td>5.2</td>
<td>SEM of PGP-P</td>
<td>122</td>
</tr>
<tr>
<td>5.3</td>
<td>SEM of F 400</td>
<td>122</td>
</tr>
</tbody>
</table>
Fig. 5.4. SEM of the surface of unoxidised F 400
Fig. 5.5. SEM of the surface of oxidised F 400
Fig. 5.6. SEM of crushed F 400
Fig. 5.7. SEM of crushed CKC
Fig. 5.8. SEM of the surface of KAU-2.7
Fig. 5.9. SEM of the surface of PGP-P
Fig. 5.10. SEM of cross sectional view of CKC
Fig. 5.11. SEM of cross sectional view of styrene/DVB resin
Fig. 5.12. Overlaid nitrogen adsorption isotherms for KAU carbons
Fig. 5.13. Overlaid nitrogen adsorption isotherms for various adsorbents
Fig. 5.14. Representative nitrogen adsorption-desorption isotherm for active carbons (KAU 0.8)
Fig. 5.15. Pore size distributions for KAU carbons oxidised by nitric acid
Fig. 5.16. Pore size distributions for KAU carbons oxidised by air
Fig. 5.17. Pore size distributions for unoxidised and oxidised F 400
Fig. 5.18. Pore size distributions for miscellaneous carbons
Fig. 5.19. Surface area distribution for KAU carbons oxidised air
Fig. 5.20. Surface area distribution for KAU carbons oxidised by nitric acid
Fig. 5.21. Surface area distribution for oxidised and unoxidised F 400
Fig. 5.22. Surface area distribution for PGP-P and CKC

Fig. 6.1. Electrophoretic mobility curves for KAU carbons oxidised by air
Fig. 6.2. Electrophoretic mobility curves for KAU carbons oxidised by nitric acid
Fig. 6.3. Electrophoretic mobility curves for miscellaneous sorptive materials
Fig. 6.4. Amphoteric nature of the surfaces of carbon particles
Fig. 6.5. pH-titration curves for KAU-1.2 and blank experiment
Fig. 6.6. Proton-binding curves for KAU carbons oxidised by nitric acid
Fig. 6.7. Proton-binding curves for KAU carbons oxidised by air
Fig. 6.8. Proton-binding curves for miscellaneous sorptive materials
Fig. 6.9. FT-IR spectra of KAUini, KAU 2.7 and PGP-P
Fig. 6.10. \(^{31}\)P MAS NMR spectrum for PGP-P carbon
Fig. 6.11. P2p and Pb4f\(_{7/2}\) XPS spectra for the PGP-P carbon with and without lead

Fig. 7.1. Lead sorption by unoxidised and oxidised KAU carbons
Fig. 7.2. Equilibrium solution pH vs amount of carbon introduced during metal sorption
Fig. 7.3. Effect of solution pH on the extent of metal sorption by carbons (batch mode)
Fig. 7.4. Lead uptake on oxidised carbon at different pH values (column mode)
Fig. 7.5. Equilibrium sorption of lead by air oxidised KAU carbons
Fig. 7.6. Equilibrium sorption of lead by nitric acid oxidised KAU carbons
Fig. 7.7. Equilibrium sorption of lead by miscellaneous sorbents
Fig. 7.8. Equilibrium sorption of copper by air oxidised KAU carbons 189
Fig. 7.9. Equilibrium sorption of copper by nitric acid oxidised KAU carbons 190
Fig. 7.10. Equilibrium sorption of copper by miscellaneous sorbents 190
Fig. 7.11. Lead sorption rate by different active carbons 199
Fig. 7.12. Lead sorption rate for CKC at different particle size 200
Fig. 7.13. Lead and copper normalised breakthrough curves for KAUini 203
Fig. 7.14. Lead and copper normalised breakthrough curves for KAU 0.8 203
Fig. 7.15. Lead and copper normalised breakthrough curves for KAU 1.2 204
Fig. 7.16. Lead and copper normalised breakthrough curves for KAU 1.8 204
Fig. 7.17. Lead, copper, nickel and cadmium normalised breakthrough curves for KAU 1.5 205
Fig. 7.18. Lead and copper normalised breakthrough curves for KAU 1.9 205
Fig. 7.19. Lead and copper normalised breakthrough curves for KAU 2.2 206
Fig. 7.20. Lead and copper normalised breakthrough curves for KAU 2.7 206
Fig. 7.21. Lead and copper normalised breakthrough curves for KAU 1.6 207
Fig. 7.22. Lead, copper, nickel and cadmium normalised breakthrough curves for PGP-P 207
Fig. 7.23. Lead and copper normalised breakthrough curves for Purolite C 104 208
Fig. 7.24. Lead and copper normalised breakthrough curves and effluent pH profile for F400(ox) 208
Fig. 7.25. Lead and copper normalised breakthrough curves and effluent pH profile for CKC 209
Fig. 7.26. Effect of flow rate on mini-column performance 212
Fig. 7.27. Lead and copper elution profiles for CKC 217
Fig. 7.28. Lead and copper elution profiles for F 400 (ox) 218
Fig. 7.29. Correlation of metal uptake and surface functional groups development for the oxidised carbons 220
Fig. 7.30. Postulated structure of humic compound with complexed iron 222
List of Tables

Table 1.1. Commercial activated carbon precursors 5
Table 1.2. Estimated 1990 world production capacity of activated carbon 9

Table 3.1. Typical concentration levels obtainable through chemical precipitation 45
Table 3.3. The composition of solution used for thallium separation 51
Table 3.4. Sorption (%) of lead ions on activated carbons (H-8 and M) in the presence of added cations 57
Table 3.5. Lead species in water 69
Table 3.6. Comparisons of sorption results of single ion vs. multiple ion in humic acids 70
Table 3.7. General comparison of organic and inorganic ion-exchangers 74
Table 3.8. Variation of cobalt removal efficiency with time 76
Table 3.9. The influence of γ-radiation on the ion-exchange properties of some sorbents 78

Table 4.1. List of sorptive materials used 88
Table 4.2. Structural parameters of phosphorus-containing carbon 97
Table 4.3. Conditions of oxidation and some properties of the oxidised carbons 102
Table 4.4. The metal ion content of the waste streams used in this study 116

Table 5.1. BET surface area results for the materials studied 132
Table 5.2. Surface area and pore volume results for the sorbents studied based on DFT model 139

Table 6.1. Elemental analysis of the selected sorbents 144
Table 6.2. Elemental composition of F 400 (Calgon) active carbon 145
Table 6.3. Concentration of surface functional groups of KAU carbons oxidised by nitric acid 148
Table 6.4. Concentration of surface functional groups of air oxidised KAU carbons 148
Table 6.5. Concentration of surface functional groups of various carbons 150
Table 6.6. Concentration of surface functional groups on F 400 (meq/g) 151
Table 6.7. Electrochemical properties of the sorptive materials studied 160
Table 6.8. Dissociation constants for the materials studied 164
Table 6.9. Dissociation constants for the selected aromatic acids in water 174
Table 6.10. Dissociation constants in water 175

Table 7.1. Equilibrium metal sorptive capacities of the sorbents studied (mmol/l range) 191
Table 7.2. Metal sorptive capacities of the sorbents studied (µmol/l range) 193
Table 7.3. Removal of radionuclides by F400(ox) in H⁺-form from NAEC S1 reference waste stream (γ-activity) 194
Table 7.4. Removal of radionuclides by F400(ox) in Na⁺-form from NAEC S1 reference waste stream (γ-activity) 195
Table 7.5. Removal of radionuclides by KAU 1.9 in Na⁺-form from NAEC S1 reference waste stream (γ-activity) 195
Table 7.6. Removal of radionuclides by PGP-P in H⁺-form from NAEC S1 reference waste stream (γ-activity) 196
Table 7.7. Batch contact test with selected carbons using NAEC S3 reference waste stream (α-activity). 196
Table 7.8. Batch contact test with selected carbons using NAEC S3 reference waste stream (β-activity) 196
Table 7.9. Batch contact test with selected carbons at different pH values using NAEC S5 reference waste stream (α-activity) 197
Table 7.10. Metal uptake results in mini-columns for acid oxidised KAU carbons 209
Table 7.11. Metal uptake results in mini-columns for air oxidised KAU carbons 210
Table 7.12. Metal uptake results in mini-columns for miscellaneous sorbent 210
Table 7.13. % ratio of copper and lead on adsorbent 211
Table 7.14. Results of metal recovery experiments 216
Table 7.15. Stability constants of metal-organic ligand complexes 221
Chapter 1: Introduction to Activated Carbon

1.1 Introduction to Carbon

Carbon is one of the most important elements on the planet. Its compounds are the essential part of any life forms on Earth. Carbon is the sixth element of the periodic table with an atomic mass of 12.01115 ± 0.00005. It consists of 98.89 % of the isotope $^{12}\text{C}$, 1.11 % of the isotope $^{13}\text{C}$, and several unstable isotopes with nuclide masses between 9 and 16.

Carbon is the thirteenth most frequently occurring element. The Earth's crust including the lithosphere, hydrosphere and atmosphere contains $2.9 \times 10^{16}$ t of carbon which equals 0.087 wt % or 0.152 atmospheric % mostly as compounds and only a small portion in elementary form.

Carbon exists in several allotropic forms presented in Figure 1.1. Carbon atoms in these forms are uniform by valent modifications (sp$^3$, sp$^2$, and sp-hybridisation of valent electrons). However the majority of carbon materials i.e. carbonised derivatives of organic compounds, coals, active carbons, carbon fibres, glassy carbons, etc., generally contain carbon atoms in different valent modifications.

It should be emphasised that the diversity of properties of the mentioned materials are due to the following reasons:

- carbon relatively easily forms from its compounds,
- carbon crystallises with great difficulty because of the high melting point of graphite,
- carbon products contain impurities of other elements which can only be removed with special methods of treatment.

Amongst all carbon materials, active carbons occupy a very important place due to a unique combination of sorptive and other properties. First of all, they are the oldest adsorbents known to mankind. The use of active carbon in the form of carbonised wood (charcoal) is described as early as 1550 BC in an ancient Egyptian papyrus.
Adsorptive properties of active carbons with respect to gases and dissolved compounds were discovered in 18th century as a result of the research of Scheele and Lowitz.

Figure 1.1. Allotropic forms of carbon.

Taking into account a great amount of research work published to date, dedicated to preparation, characterisation, properties and applications of active carbons, this chapter will contain modern views on methods of their manufacture, an overview of the current activated carbon market situation and highlight the most important areas of activated carbon products application with particular emphasis on water treatment.
1.2 Introduction to Activated Carbon

The term 'activated carbon' defines a group of materials with highly developed internal surface area and porosity and hence a large capacity for adsorbing chemicals from gases or liquids. Activated carbon is an exceptionally versatile sorbent because the size and distribution of the pores within the carbon matrix can be controlled to meet the needs of current and emerging applications. Engineering requirements of specific applications are satisfied by producing activated carbons in the form of powders, granules, and shaped products. The strong market position held by activated carbon adsorbents relates to their unique properties and low cost compared with that of possible competitive adsorbents.

Through the choice of precursor, method of activation and control of processing conditions, the adsorptive properties of activated carbon can be specially designed for many diverse applications, such as purification of potable water and adsorption of emissions from motor vehicles.

1.3 Manufacture of activated carbons

1.3.1 Historical background

The technology of activated carbon synthesis dates back many centuries. The first recorded production and application of charcoal for medicinal purposes was cited in Egyptian papyri. The basis for industrial production and utilisation of active carbon was established in the late 18th century. An English sugar refinery successfully used wood charcoal for the decolorisation of sugar syrups. Methods of producing decolorising charcoals from plant materials were first set out in British patents between 1856 and 1863. In 1901 R. Von Ostrejko set the basis for the commercial development of activated carbons. The process involved the incorporation of metallic chlorides with carbonaceous material before carbonisation and the mild oxidation of...
charred materials with carbon dioxide or steam at raised temperatures\(^9\). Marketing of the first industrially produced activated carbon 'Eponit' was started in 1911 by Fanto Works, Austria. They adopted Von Ostrejko's gasification approach in the manufacture of 'Eponit' from wood. It was marketed as a decoloriser for the sugar-refining industry\(^8\). The introduction of poisonous gases into the battlefields of the First World War gave great impulse to the development of large scale production methods for adsorbent carbons suitable for use in military gas masks. Granulated carbons, with adequate adsorptive properties and providing low resistance to air flow through the gas mask canister, were developed by activating wood chips with zinc chloride. These were the first manufactured carbons with reliably controlled adsorptive and physical properties. A group studying under Chaney in the USA examined a wide range of precursors intended to produce adsorbents for gas mask canisters. They determined that coconut shell yielded the best combination of the required characteristics in the resulting carbon\(^10\). The advances made in the manufacture of granulated activated carbons during the First World War found a number of post-war applications in the purification of gases or in extraction of vapours from gas streams. The process was applied to the recovery of liquid petroleum from natural gas, extraction of benzene from manufactured coal-gas and the recovery of volatile solvent vapours from various industrial processes.

Since these early days, industry has developed a much wider range of active carbons for both liquid-phase and vapour-phase applications. Over the last two decades there has also been a developing interest in other carbon forms (e.g. activated carbon fibres and microbeads) and applications continue to be developed in response to growing demands for environmental protection and for emerging technologies, such as the catalytic reduction of NO\(_x\) and natural gas storage\(^6\).

1.3.2 Activated carbon precursors

Almost all carbon-containing materials can be used for the manufacture of activated carbon; e.g. wood, bones, nut shells, fruit stones, peat, charcoal, brown coal, lignite, bituminous coal and mineral oil products.

However, for economical reasons, lignite, coal, bones, wood, peat and lignin are most often used for the manufacture of liquid-phase carbons. Coconut shells, coal and
petroleum residues are used for manufacture of gas adsorbent carbons. The properties of the final product will depend on the nature of the raw material, the nature of the activating agent and the conditions of the activation process. Thus, high bulk density and volatile matter content are important parameters of the raw material. The bulk density contributes towards enhanced strength of the resulting carbon whereas the volatile matter may not only save energy in the production step but also will allow a better control over the yield. Low density materials like wood, which are also high in volatile content, produce activated carbons with large pore volume and low bulk density. On the other hand, coconut shells, fruit pits and similar materials, which possess high bulk density and volatile content, produce hard, granular carbons with large pore volume and are suitable for many applications.

There is also some evidence in the literature that organic polymers can also be used as raw materials. The resulting products are used as adsorbents with very large specific surface areas (e.g. active carbons of the Saran type 11). Synthetic polymeric materials such as phenol-formaldehyde resins, rayon, polyacrylonitrile, PVC-vinylidene copolymer, etc. have also been considered as raw materials for the production of speciality active carbons 12,13,14,15.

Selection of the raw material is based mainly on the following criteria:

- likelihood of yielding a good activated carbon,
- low in inorganic matter,
- availability and cost of the starting material,
- low degradation upon storing,
- ease of activation.

The principal commercial carbon sources and the proportions in which they are used are summarised in Table 1.1.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Use (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>35</td>
</tr>
<tr>
<td>Coal</td>
<td>28</td>
</tr>
<tr>
<td>Lignite</td>
<td>14</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>10</td>
</tr>
<tr>
<td>Peat</td>
<td>10</td>
</tr>
<tr>
<td>Other</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1.1. Commercial activated carbon precursors 16.
1.3.3 Manufacture of activated carbon

There are two main processes used by industry to manufacture activated carbon: physical (or thermal) and chemical activation. A schematic representation of activated carbon production by physical and chemical activation is shown in Figure 1.2. The main differences between these two methods may be summarised as follows:

- Physical activation implies a two stage process, usually at high temperature. The yield of activated carbon is low.
- Chemical activation is carried out in only one stage at lower temperature. The yield of activated carbon is higher compared to physical activation.

![Figure 1.2. Schematic representation of the two methods of activation.](image)

1.3.3.1 Physical activation

The production of activated carbon by this method is divided into two main stages: the carbonisation of the raw material and the activation of the carbonised product. Carbonisation, i.e. pyrolysis of the carbon-containing material up to 600 - 650°C in the absence of oxidising gases, involves the removal of non-carbon species and production of fixed carbon (char) with a primary porous structure. During this process most organic solids undergo reactions leading to the loss of hydrogen and the formation of free radicals which condense to form a rigid cross-linked solid char. At high carbonisation temperatures graphite-like microcrystallites are formed within the
structure which include impurities, tetrahedrally bonded carbon atoms and heterocyclic groups. At low carbonisation temperatures impurities such as tar may be left in the pores without decomposition. This results in a carbonised material with low surface area and limited surface activity. The resulting material may be enhanced by activation via partial gasification with steam, carbon dioxide or a mixture of both. These gases behave as mild oxidising agents at 800 - 1000°C. Several reactions between carbon and oxidising gases during the activation process are possible:

\[
\begin{align*}
C + \frac{1}{2}O_2 & \rightarrow CO \quad \Delta H = -285 \text{ kJ/mol} \\
C + H_2O & \rightarrow CO + H_2 \quad \Delta H = +117 \text{ kJ/mol} \\
C + 2H_2O & \rightarrow CO_2 + 2H_2 \quad \Delta H = +75 \text{ kJ/mol} \\
C + CO_2 & \rightarrow 2CO \quad \Delta H = +159 \text{ kJ/mol}
\end{align*}
\]

Since these reactions are endothermic, the carbon particles must have a good contact with the activating gas. This gas has to be at a higher temperature than required by the reaction. Below 800°C the reaction rate is low and, consequently, it is convenient to supply extra heat by burning the product gases (carbon monoxide and hydrogen):

\[
\begin{align*}
CO + \frac{1}{2} O_2 & \rightarrow CO_2 \quad \Delta H = -285 \text{ kJ/mol} \\
H_2 + \frac{1}{2} O_2 & \rightarrow H_2O \quad \Delta H = -238 \text{ kJ/mol}
\end{align*}
\]

In the case of activation with air or oxygen, the reactions between carbon and the activating agent are exothermic. Consequently, there is excessive burning and the reaction is difficult to control. As the reaction is very aggressive, burning is not just restricted to pores but also occurs on the surface of the product grains, causing excessive weight loss. Hence the method is rarely used.

Physically processed carbons are generally microporous if activated with carbon dioxide whereas steam produces a wider pore size distribution with greater development of meso- and macroporosity.

1.3.3.2 Chemical activation

A second commercial route to producing activated carbons involves the reaction of a carbon precursor with reagent, and is known as chemical activation. Porosity is
developed concurrently with the transformations which occur during heat treatment to
temperatures in the range 350 to 900°C. Although the reactant mixture may be heat
treated in stages, usually a single kiln is required, compared to two kilns which are
normally used for carbonisation and activation in physical activation process. The
viability of the chemical activation process depends on efficiency of reagent recovery
for recycle. This necessitates a subsequent leaching stage followed by a further
operation to dry the washed carbon. The reagents which have been most used
industrially are zinc chloride and phosphoric acid. The preferred precursors are
lignocellulosic materials, wood being the most common 16, 17. The zinc chloride
process was the principal method of chemical activation up to about 1970 18.
However, low recovery efficiencies, corrosion problems, the presence of residual zinc
in the carbon and the need for stringent control of plant emissions have contributed to
its replacement by phosphoric acid. Smaller volume chemical activation processes
utilise the action of such Lewis acids as aluminium chloride, ferric chloride,
potassium sulphide, potassium thiocyanate hydroxides and carbonates of alkali metals,
and chlorides of calcium and magnesium 18, 19. Processes have also been developed
involving the reaction of potassium or sodium hydroxides. Activated carbons of
exceptionally high surface area (> 3000 m²/g) have been produced. However, to date,
only limited quantities of activated carbon have been produced using these activating
agents 20.

Due to the nature of the chemical activation process:

- Only non-mineral precursors can be applied successfully. To date only wood
  (both soft and hard) and olive stones are being used on a commercial scale.
- Products generally exhibit a significant volatile content and, consequently, a low
  ignition temperature. Unlike products of physical activation, the carbon matrix is
  by no means graphitic and contains fair amount of heteroatoms (including residual
  phosphates and zinc).
- In contrast to products of the physical process, the content of water extractable
  species is generally low, because of the inherent washing process which is
  necessary for recovering the chemical agent 21.
1.3.3.3 *Forms of activated carbon products*

In order to meet the engineering requirements of specific applications, activated carbons are produced and classified as granular, powdered, or shaped products. Granular activated carbons are produced directly from granular precursors, such as sawdust and crushed and sized coconut char or coal. The granular product is screened and sized for specific applications. Powdered activated carbons are obtained by grinding granular products. Shaped activated carbon products are generally produced as cylindrical pellets by extrusion of the precursor, with suitable binder, before activation\textsuperscript{15,21}.

1.3.3.4 *Economic aspects*

The world's production capacity of activated carbon, excluding China and Eastern European countries, was estimated to be $375 \times 10^3$ metric tons in 1990\textsuperscript{22}. In 1991, the price of most granular activated carbon products was 1.65 to 6.60 US$/kg, but some speciality carbons were more expensive\textsuperscript{23}. The price of powdered products was substantially less, ranging from 0.55 to 1.75 US$/kg. The breakdown of world production capacity in 1990 is shown in Table 1.2.

<table>
<thead>
<tr>
<th>Country</th>
<th>Metric ton ($ \times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>146</td>
</tr>
<tr>
<td>Western Europe</td>
<td>108</td>
</tr>
<tr>
<td>Japan</td>
<td>72</td>
</tr>
<tr>
<td>Pacific Rim, Other</td>
<td>49</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>375</strong></td>
</tr>
</tbody>
</table>

*Table 1.2. Estimated 1990 world production capacity of activated carbon (excluding Eastern Europe and China).*

Production capacity was almost equally split between powdered and non-powdered activated carbon products. Worldwide production capacity in 1990 for granular and shaped products was split, with about 70% for liquid phase and 30% for gas phase applications\textsuperscript{23}. The demand for activated carbon in 1990 was estimated at 94% of
production capacity. Consumption is increasing at a reported rate of approximately 4-5% per year\textsuperscript{22,23}. Increasingly stringent environmental regulations, particularly in the United States and Western Europe, are largely responsible for the increased demand for activated carbon products.

Activated carbon is a recyclable material which can be regenerated. Thus the economics, especially market growth, of activated carbon, particularly granular and shaped products, is affected by regeneration and industry regeneration capacity. The decision to regenerate an activated carbon product depends on the cost, size of the carbon system, type of adsorbate and environmental issues involved. Large carbon systems, such as those used in potable and waste water processing, generally require a high temperature treatment. During regeneration carbon losses of 1 to 15% typically occur from the treatment and movement of the carbon. However, material loss is compensated for by the addition of new carbon to the adsorber system. Regeneration of spent carbon is considerably less expensive than the purchase of virgin activated carbon. Similarly, landfill disposal of powdered carbon is becoming more restrictive environmentally and more costly. Large consumers of powdered activated carbon now find that regeneration is an attractive alternative.

1.4 Applications

Several examples are given in this section of activated carbon applications for gas phase and liquid phase sorption. This section is intended to highlight important areas of activated carbon use with particular emphasis on water treatment. A detailed account of activated carbon applications can be found elsewhere in the literature\textsuperscript{19,15,24}.

1.4.1 Gas phase applications

Gas phase applications of activated carbon include separation, gas storage and catalysis. Gas phase activated carbon products are generally more expensive than liquid phase carbons. Most of the activated carbon used in gas phase applications is granular or shaped, although the use of powdered activated carbon, especially in
dioxin and mercury removal from incinerator flue gases, is emerging. Separation processes comprise the major gas phase applications of activated carbon. These usually exploit the differences in the adsorptive behaviour of gases and vapours by activated carbon on the basis of molecular weight and size. A specific feature of this business is that product specifications are generally dictated by the manufacturer of the equipment or devices in which activated carbon is used.

Relevant application areas include:

- Solvent recovery and other in-situ regeneration operations (like styrene and vinyl chloride monomer),
- Gas separation (pressure swing adsorption),
- Gas masks (both industrial and military purposes),
- Air conditioning (ozone, odour etc.)

More specific applications include:

- Adsorption of radioactive iodine in accidental leakages, krypton and xenon from reactor core or heat exchanger systems at nuclear power plants,
- Flue gas cleaning,
- Sewage gas deodorisation.

Despite many research efforts, it is not commercially viable to store methane or hydrogen by means of activated carbon.

The high surface area and surface activity of activated carbons make them candidates for use as catalysts, despite the low activated carbon market volume (only 5%). To date only a limited number of applications have reached a relevant commercial status. These include:

- Dry primary cell batteries,
- Catalyst carrier for precious metals (hydrogenation),
- Catalysis for vinylacetate/-chloride, cyanuric chloride and phosgene production,
- Desulphurisation,
- Demercurisation.

Due to the character of the product, more general industrial applications like selective catalytic reduction of NOx are likely to emerge in the future.
1.4.2 Liquid phase applications

Activated carbons for use in liquid phase applications differ from gas phase carbons primarily in pore size distribution. Liquid phase carbons have significantly more pore volume in the macropore range. This allows liquids to penetrate more rapidly into mesopores and micropores. The larger pores also promote greater adsorption of large molecules, either impurities or products, in many liquid phase applications. Both powdered activated carbons (on a once through basis) and granulated activated carbons (on a regeneration basis) are being used. Selection between the two is generally based on the chosen method and overall process economics.\(^{21}\)

Invariably in-process purification is the main objective for these applications. Relevant areas of application include:

- Sweetener decolorisation (corn syrups, starch, cane sugar, beet sugar),
- Antibiotics, vitamins and other pharmaceuticals,
- Food, beverages and edible oils (improving colour, taste and odour),
- Chemicals (like organic and inorganic acids, dye stuffs, agricultural chemicals, glycerine, waxes, etc.)\(^ {27}\).

More specific applications in this area include immobilisation, gold recovery, purification of electroplating solutions from organics, removal of toxins from the bloodstream and the treatment of ailments of the digestive system in humans. In all cases adsorption-desorption processes occur in the liquid phase.\(^ {6}\)

1.4.3 Water treatment

1.4.3.1 Potable water treatment

The production of clean potable water supplied to the public has a great importance. Unpurified natural water used for drinking has often been a cause of outbreaks of intestinal diseases. Only water from some underground sources can be directly used for drinking. However these sources of clean water are not substantial enough to satisfy growing public demand. Surface water is mainly used for such needs in most developed countries. Obviously this water requires thorough purification to remove toxic compounds and microbiological contamination.
With ever increasing levels of pollution, the water-supplying industry requires modern and effective technologies for water treatment. In order to obtain high quality potable water, several stages of purification are needed. Adsorption of micropollutants by activated carbons is normally one of these stages and is widely used in today's water industry. This accounts for approximately 24% of the worldwide usage of both powdered and granulated activated carbon products. Powdered activated carbon has been used for many years to treat public water supplies in order to improve taste and odour. In recent years granulated carbon products have also been used for this generally dual-purpose option (both adsorption and filtration) since they can be regenerated and reused.

According to the EPA, over 700 pollutants have been identified in municipal and well water supplies. These most often include detergents, dyes, aromatic hydrocarbons, esters and pesticides as well as heavy metals. Normal water disinfection and filtration processing steps remove or destroy the bulk of these contaminants. However, treatment by activated carbon is an important treatment step to remove residual contaminants for reasons of safety and palatability. For pesticides and non-volatile aromatics in particular, granulated activated carbon has received the best available technology status.

Important properties of a granular activated carbon for water treatment are:

- Adsorptive capacity and selectivity,
- Ability to withstand thermal reactivation,
- Resistance to attrition losses during transport and handling.

1.4.3.2 Industrial and municipal water treatment

Contamination of urban drinking water supplies with liquid waste is a particularly serious issue. Liquid industrial wastes and municipal sewage may contain suspended solids, hazardous microorganisms and toxic organic and inorganic compounds. Effective purification of water contaminated in this way becomes problematic. Biological, physical and chemical methods of water treatment are in most cases insufficient to enable safe waste discharge or the use of the industrial water in closed cycles. Adsorption by activated carbon products can be used to remove residual
toxins and other organic compounds after primary filtration and secondary biological treatment 21.

1.5 Concluding Remarks and Research Objectives

This chapter summarises the methods of activated carbon manufacture, gives an overview of the current activated carbon market situation and highlights the most important areas of activated carbon products application with particular emphasis on water treatment. Activated carbon has proved to be one of the most versatile products to be used in separation and purification processes. It is widely utilised nowadays by industry to remove organic contaminants from potable and waste water.

The separation of heavy metal pollutants from aqueous solutions is of particular interest to the water and waste water industry. A limited amount of work has been published to date regarding the use of activated carbon as a potential sorbent for heavy metals removal in water treatment, but no systematic studies have been performed as yet.

The specific objectives of this research are:

- To review the sorption study of metal ions on various active carbons,
- To study systematically the synthesis and the properties of modified active carbons derived from natural as well as from polymeric materials,
- To investigate the physical and chemical surface characteristics of the carbon materials by several techniques in order to understand the process and mechanism of metal ions sorption,
- To carry out the sorption of heavy metals in an attempt to assess the sorptive capacity and the kinetics of the carbons under investigation,
- To evaluate the sorption of such heavy metal species as lead(II), copper(II), nickel(II) and cadmium(II) from multi-component aqueous solutions.
1.6 References

5. Lowitz, T. Crell's Chemische Annalen. 1786, 1, p.211.
22. The Economics of Activated Carbon. 3rd Ed., Roskill Information Services Ltd.,


26. Radovic, L.R. Carbon as a catalyst support. In Science and Technology of

27. Baker, F.S. Activated carbon: Markets and regeneration. In Science and

28. EPA publications in the Internet.
Chapter 2: Physical and Chemical Properties of Active Carbons

2.1 Crystalline and Electronic Structure of Carbons

Carbonaceous materials were originally classified into two groups. Active carbon was included in the group known as "amorphous carbon" \(^1\), together with carbon blacks and unactivated products of the pyrolysis of organic compounds, such as cokes, chars, wood charcoal, etc. The other group, called "crystalline carbon", included graphite and diamond. This classification appeared to be unsatisfactory, because active carbons, carbon blacks and other carbonaceous materials are not entirely amorphous. X-ray diffraction investigations \(^2\) showed that carbonaceous materials may exist in a form which is intermediate between the amorphous and the crystalline states. Thus, X-ray patterns for carbon blacks consist of two types of reflections – crystalline type reflections and diffuse two-dimensional lattice reflections. The former reflections are usually attributed to the presence of small crystallites of graphite. These crystallites are analogous to graphite in two dimensions, as they are composed of parallel layers of hexagonally ordered carbon atoms. However, the structure is different from graphite in that the parallel planes are not perfectly orientated with respect to their common perpendicular axis. The angular displacement of one layer with respect to another is random and the layers overlap one another irregularly. For this arrangement Biscoe and Warren \(^3\) proposed the term "turbostratic structure". It was assumed that carbon atoms have a strong tendency towards two-dimensional condensation to give aromatic molecules (graphitisation). It was claimed \(^4\) that the presence of graphitic reflections is direct evidence of the formation of blocks (clusters, packets) of two-dimensional layers of aromatic molecules. On this evidence, the presence of crystallites (graphite-like particles or micelles) with fairly sharp boundaries and embedded at random orientations in the amorphous matrix was postulated. This resulted in the packet and fringe model of the carbon structure and is presented in Figure 2.1. However, investigation using high resolution (~ 0.3 nm) electron
microscopy and interference microscopy (to reveal the periodicity of atomic layers) were unsuccessful in the search for discrete crystallite particles\textsuperscript{5,6,7}. Therefore, along with the packet and fringe model, the molecular tape carbon felt model was proposed\textsuperscript{5,6}. According to this model any carbonaceous substance (from vitreous carbon to carbon fibre) is held to consist of a uniform molecular-tape felt without any discreet supermolecular formations. Graphic representation of this model is shown in Figure 2.2.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{packet_and_fringe_model.png}
\caption{The packet and fringe model of carbonaceous materials.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{molecular_tape_model.png}
\caption{The molecular tape carbon felt model.}
\end{figure}
The structural models of carbon materials described do not contradict but complement each other. They also suggest that the carbons are turbostratic in nature and explain the formation of local non-uniformities such as defects of structure, microcavities, etc. Consequently, active carbons belong to the microcrystalline range of carbons. The amorphous phase content in carbons can be as high as 35%.

Electrophysical properties of carbons (electroconductivity, paramagnetism, etc.) are attributed to their electronic structure. These properties were under investigation for nearly one hundred years resulting in a large amount of published work. It was shown that thermoelectric power, electrical resistivity and other important characteristics are dependent on the precursor of carbon, conditions of thermal treatment and other factors influencing the structural transformations of carbonaceous materials. Thus, the electrical resistivity drops by a factor $2 \times 10^9$ for cokes thermally treated between 500 and 1000°C. This is related to the significant structural changes of carbonaceous materials under heat treatment. It is generally accepted that the conductivity in carbons is realised by $\pi$-electrons moving along hexagonal aromatic planes in the system of conjugated bonds. Carbons should be considered as a transition phase between organic substances (insulators) and graphite (electron conductor). Hence, their conductivity is strongly dependent on the extent of the structural regularity of crystallites. These begin to form at relatively low temperatures (300-500 °C). At higher treatment temperatures the crystallites form a more orderly pattern and thus create the conjugated bond structure. The electrical resistivity of activated carbons is in the range of $10^3 - 10^2 \Omega\text{cm}$.

Electronic structure of carbon can be represented by an electronic energy band model as proposed by Mrozovski and Loebner. This model covers the transition from simple organic crystals through disordered structures of chars and carbons up to single crystal graphite depending on the temperature of heat treatment. The model is based on the notion that carbon materials possess an energy gap differing from zero. The width of this gap is dependent on the size, electronic structure and relative positions of crystallites in the carbon specimen. As the temperature of heat treatment increases the energy gap decreases gradually with the increase of molecular size (crystallite diameter) throughout the range from raw cokes through baked carbons and
polycrystalline graphite and finally disappears for infinitely large graphite crystals or may even end in an overlap of the $\pi$ and conduction bands.

A one-dimensional energy band diagram, showing the energy gap and the Fermi level as a function of heat treatment, is presented in Figure 2.3\textsuperscript{11}. During the course of carbonisation an increase in the concentration of holes in the $\pi$-band is observed. This is due to the removal of hydrogen and other radicals when the organic substances are subjected to temperatures exceeding 600°C. Bare valences that are formed act as electron traps. They are normally located on various defect sites, e.g. on the edge atoms of broken carbon bonds and carbon layers. The formation of holes finishes at temperatures above 1600°C.

![Energy band diagram for carbon solids.](image)

Detection of electron spin resonance (ESR) signals is direct evidence of the existence of free valences and hole-type centres. This method allows the detection of signals of different intensity and width. These signals are dependent on various factors such as conditions of thermal treatment, surrounding atmosphere, presence of impurities in the sample, introduction of acceptor additives, etc. ESR spectra are categorised into two types such as free valency (edge radicals) and hole-type spectra. The latter appear due to deformations in the $\pi$-electron system\textsuperscript{12, 14, 15, 16}.

Carbon materials heat treated between 700 and 3000°C are characterised by positive thermoelectric power $\Theta$\textsuperscript{9, 11, 17}. This indicates preferential hole-type conductivity.
Therefore, in contrast to crystalline graphite possessing metal-type conductivity the transitional forms of carbon (including activated carbons) are characterised by semiconductive properties.  

2.2 Porous Structure in Carbons

Microcrystalline structure of active carbons allows for the occurrence of non-uniformities (voids). During the process of carbon activation the space between the elementary crystallites becomes cleared of various carbon-containing compounds and non-organised carbon. Carbon is also removed partially from the graphitic layers of the elementary crystallites. This results in formation of voids which are termed as pores. The spectrum of pore sizes in active carbons extends from molecular dimensions to defects with millimetre dimensions in large granules. Because all aspects of active carbon utilisation are related to the pore size, Dubinin introduced a classification of pores into three groups: micropores, transitional pores and macropores. The effective radius of micropores, according to Dubinin, is less than 1.8-2 nm. The order of their size corresponds to that of molecules. Adsorption in active carbons is mainly due to dispersion forces. The higher adsorption energy in micropores is the major reason for the relatively high adsorption capacity of a microporous sorbent compared with less finely porous sorbents of the same chemical type. Adsorption in micropores proceeds through the volume filling mechanism. The volume of micropores for different active carbons is approximately from 0.15 to 0.6-0.8 cm³/g. Their specific surface area usually amounts to at least 95% of the total specific surface area. Transitional pores (mesopores), in accordance with the classification, are those in which capillary condensation with the formation of a meniscus of the liquified adsorbate can take place. This phenomenon usually produces the hysteresis loop between the adsorption and desorption isotherms. Transitional pores, besides their significant contribution to adsorption, also act as the

---

* International Union of Pure and Applied Chemistry (IUPAC) adopted a somewhat different pore size classification, according to which the definitions of pore diameters are: ultra-microporosity (< 0.5 nm); microporosity (0.5 - 1.4 nm); super-microporosity (1.4 - 2.0 nm); mesoporosity (2.0 - 50 nm); macroporosity (> 50 nm) (IUPAC definitions, Pure and Appl. Chem. 1985, 57, p. 603)
main transport arteries for the adsorbate. The size of transitional pores is in the range of effective radii from approximately 2 to 50-100 nm. The volume of these pores is normally from 0.02 to 0.10 cm$^3$/g (sometimes up to 1.5 cm$^3$/g$^{21}$) and their specific surface area does not exceed 5% of the total surface of the active carbon. Pores with an effective radius greater than 50-100 nm are classified by Dubinin as macropores. The pores of this size cannot be filled by capillary condensation. Their volume is between 0.2 and 0.5 cm$^3$/g. They provide a very little contribution to the surface area in active carbons (0.5-2.0 m$^2$/g). Consequently, macropores are not of great importance in the process of adsorption. They act as transport channels rendering the internal parts of carbon grains accessible to the particles of adsorbate.

The shape, size, interconnectivity and pore size distributions are a function of:

- The origin of the active carbon,
- The process (e.g. rates) of pyrolysis and carbonisation as the original polymer system is transformed into a carbon system,
- The final heat treatment temperature of the carbon (as the heat treatment temperature increases so the carbon lattice becomes more planar and aromatic, and hence pore shape must change),
- The process of activation / chemical modification used to enhance pore volume and surface area$^{22}$.

Various methods of porous structure investigation have been used and their results indicate that there are pores with a contracted entrance (ink-bottle shaped)$^{23,24}$, pores in a shape of capillaries open at both ends or with one end closed, pores in the shape of more or less regular slits between two planes$^{24,25}$, V-shaped pores, tapered pores, and other forms$^{26}$. Generally, it is rather difficult to determine in a given carbonaceous material what shape and proportion of pores are present.

The complexity of porous structure in carbons is such that no single experimental method can offer all the information needed to fully characterise the structure of porosities. Thus, adsorption data describe thermodynamic equilibria, and diffusivities measure the kinetic properties of adsorption. X-ray techniques provide only crude statistical information. Microscopy provides information about only a minute fraction
of the sample. High-resolution, fringe-imaging, transmission electron microscopy is probably one of the best methods available to indicate the relationship between structure (within the carbon atom assemblies) and porosity. The following list presents the variety of techniques which have been used to understand structures within porous materials 22,27:

- Adsorption isotherms
  a) Effective surface area (m²/g);
  b) Micropore volume (cm³/g);
  c) Isotherm constants (energetics), e.g. ‘b’ of the Langmuir equation and ‘c’ of the BET equation;
  d) Gradient of plot of log n₄ against log² p/p₀ (Dubinin-Radushkevich equation) as an indication of pore size distribution and mean pore diameter;
  e) Distributions of characteristic energies of adsorption.

- Transmission electron microscopy
  f) Phase-contrast, fringe-imaging, high resolution transmission electron microscopy (TEM), to reveal structure;
  g) Dark-field TEM, indicating stacking order of lamellar constituent molecules (LCM).

- SAXS and SANS (Small angle X-ray scattering techniques)

- Molecular sieve experiments.

- Pre-adsorption of n-nonane.

- Scanning tunnelling microscopy (STM),
  h) To reveal atomic surface features.

- Atomic force microscopy
  i) To reveal atomic surface features.

- Calorimetry
  j) To measure the energetics of adsorption and desorption: surface functionalities;
  k) To measure the dynamics of adsorption and desorption.

- Mercury porosimetry (mainly for macro- and mesoporosity).

- Computer molecular modeling.
  l) To model and simulate structures using minimum energy calculations.
A large amount of research was dedicated to the carbon porous structure investigation. This work is summarised in many papers, reviews and books. 28-38

2.3 Surface Chemistry in Carbons

Active carbons, like other types of carbon materials, are essentially composed of elemental carbon associated with other chemical elements chiefly hydrogen and oxygen. In fact, all types of carbon, particulate solids (cokes, chars or activated carbons, etc.), powders (carbon blacks), bulk materials (synthetic graphites, glassy carbons, pyrocarbons, etc.), fibres and filaments contain more than 90 % by weight of elemental carbon. Depending on the nature of the carbon precursor, nitrogen, sulphur and phosphorus may also be present in small amounts. Moreover, inorganic impurities originating from the precursor or added during carbonisation and activation process may exist in the carbon. These foreign compounds may affect to some extent the chemical properties of the carbon sample and they usually have to be removed before characterisation. The properties of active carbons can also be altered by deposition of various chemicals (oxides, sulphides, organic compounds) in their pores. The chemical properties of 'impregnated carbons' are governed by the interactions between the carbon surface and the modifier.

In most carbon materials, the carbon atoms are arranged in aromatic rings which build up lamellae, i.e. basal planes of various size and stacking height. The aromatic layers are usually not structurally perfect. Various types of defects may be present: stacking faults, single and multiple atom vacancies, dislocations, etc. These types of defects consist of vacancies in the outer basal plane on the carbon surface and also in lamellae edges and steps which build up the prismatic edges of the carbon surface. The chemical reactivity of the carbon atoms located at defects is much higher than that of the basal planes. In particular, chemisorption of various gases, for instance oxygen, hydrogen and halogens, can take place and build up surface functional groups or surface complexes. Many of the surface reactions of charcoals and carbon blacks
The surface chemistry of carbons is determined by the number of fixed foreign atoms and by the characterisation of the chemical bonding with the carbon atoms, i.e. the nature of the surface functional groups or complexes. Oxygen is the most common foreign chemical element present on carbon. Carbon-oxygen surface compounds are by far the most important in influencing surface reactions, surface behaviour, wettability, and electrical and catalytic properties of carbons. Thus, hydrophilicity of a carbon black can be enhanced by the introduction of acidic oxygen-containing groups. Cationic or anionic exchange capacity can be observed for carbons depending on the prevailing surface functionality (acidic or basic). Surface charge and zeta potential of carbon particles in aqueous suspensions is also conditioned by the nature of the surface functional groups. In a similar way, the adsorptive properties of active carbons can be modified by the presence of surface groups.

As early as 1863, Smith was probably the first to suggest that when oxygen is adsorbed on a carbon surface it undergoes a chemical change. He found that adsorption of oxygen on charcoal did not cease even after a month. While nitrogen and other gases adsorbed on charcoal could be easily removed, oxygen could only be removed as carbon dioxide by strong heating. It was shown in later studies that purely physical interaction with oxygen occurs only at very low temperatures. Thus, Shah showed that oxygen would chemisorb on sugar charcoal at 0°C, but not at -78°C, since all the oxygen adsorbed at the lower temperature could be recovered unchanged. There is some evidence that slight chemisorption of oxygen on carbon materials occurs at temperatures as low as -183°C. Ward and Rideal found that the heat of oxygen adsorption on charcoal, even at 0°C, was of the order of 40 kcal/mole, suggesting the chemical nature of the interaction involved. Other researchers reported even higher values ranging between 60 to 84 kcal/mole and sometimes over 200 kcal/mole for temperatures exceeding 200°C. Lobstein and Deitz studied chemisorption of oxygen on a few carbon adsorbents at 200°C. They differentiated between oxygen involved in chemisorption and oxygen used in combustion. This process is accompanied by the
release of gaseous carbon oxides (up to 150 - 160°C these oxides are not formed). In all those reactions up to 15 % or even 25 % of the oxygen is bonded to the carbon surface. Now it is well known that almost all types of carbons are covered with oxygen complexes, unless special care is taken to eliminate them. These complexes are often the source of the properties which make a carbon useful or effective in certain applications.

Numerous investigations have shown that carbons which have chemisorbed oxygen at room temperature (conventional activated carbons or H-carbons) are significantly different from those carbons which have chemisorbed oxygen at high temperatures (oxidised carbons or L-carbons). Garten and Weiss proposed that oxygen is present on carbon surfaces as organic functional groups. The concept of 'organic functional surface groups' was further developed in the 1960’s in particular by Boehm and Donnet. The existence of different types of functional groups was evidenced by means of organic chemical detection methods and titration techniques. More recently the study of surface groups has also been undertaken by spectroscopic methods, chiefly FT-IR, X-ray photoclectron spectroscopy (XPS), NMR and by radiometric tracer technique. It is well accepted now that the acidic or basic character of carbon is developed as a result of surface oxidation. Surface functional groups can originate from the precursor of active carbon. This is particularly related to active carbons originated from oxygen-rich raw materials (wood, sucrose, phenol-formaldehyde resins, etc.) followed by their incomplete carbonisation. Substantial quantities of oxygen can be introduced in the course of production, e.g. during the activation process of coal by oxidising gases (steam, air). Thus, activated carbon prepared from sucrose at 550°C contains 30 atoms of hydrogen and 9 atoms of oxygen per 100 atoms of carbon. Larger amounts of oxygen can be introduced into the carbon surface by subjecting it to chemical modification. The oxidising agents involved in this modification are divided into two groups:

- Gaseous oxidising agents (oxygen, air, steam, ozone, nitrogen oxides, etc.)
- Liquid oxidising agents (nitric acid, hydrogen peroxide, sodium hypochlorite, potassium permanganate, etc.)
Depending on the type of the agent used and on the conditions of the modification process, the amount of oxygen-containing surface functional groups can vary over a wide range, as can the reactivity.

Oxygen surface compounds are usually divided into two major types: functional groups of acidic nature (neutralised by bases) and basic groups (neutralised by acids).

2.3.1 Acidic surface groups

Several types of oxides with an acidic character have been clearly identified. The most important ones are the carboxylic and phenolic groups. Their existence has been established by different types of techniques, specific organic reactions, potentiometry, FT-IR and XPS. From the two structural groups, several other groups may be built up at the carbon surface: anhydrides, lactones and lactoles as presented in Figure 2.4 (b to d). Titration methods are generally used for the measurement of acidic groups. Because the acidity constants of the various groups (carboxyles, phenoles and lactones) differ by several order of magnitude, an estimate of their relative amount can be obtained by titration with different strength bases. Boehm et al ⁵⁸ proposed an identification method for functional groups which consists of using alkaline solutions of increasing strength: sodium hydrogen carbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH) and sodium ethoxide (NaOC₂H₅). Accordingly, carboxylic groups can be titrated with NaHCO₃, lactones with Na₂CO₃, phenols with NaOH, and groups of weaker acidic strength with NaOC₂H₅ solutions. This method provides a good way of determining the distribution of the acidic strength of functional groups present on the carbon surface.

Carbonyl groups are also present on the carbon surface as isolated or conjugated structures like quinones (Figure 2.4 f and g). Chemical evidence has been given for existence of quinone type structures ⁵⁶. Potentiometric techniques and cyclic voltammetry are suitable for measuring the amount of weakly acidic groups and quinones present ⁵⁹. Ether-type functions (Figure 2.4 h) stable even at high temperature are also currently postulated.
The simultaneous presence of various types of organic groups may lead to more complex surface structures. There is a strong evidence that surface structures with mesomeric forms may give a better description of the chemistry of the surface groups \(^6^1\). Analogous structures may also be present on graphene planes (Figure 2.5).

It should be emphasized that oxygen containing functional groups, even of a given type, can display some, or even fairly substantial differences in reactivity due to direct interactions with adjacent groups of the same or other type, or to electronic
interactions, via surface carbon crystallites, with more distant groups. The quantity of oxygen combined with the surface in the form of functional groups cannot only be increased via oxidation but also decreased as a result of burn-off of active carbon at temperatures exceeding 1000°C in vacuum or in an inert atmosphere. Under such conditions, oxygen-containing functional groups thermally decompose to yield gaseous carbon oxides, water and hydrogen.

2.3.2 Basic surface groups

Oxygenated functions with a basic character have been proposed in order to account for the adsorption of acids by active carbons \(^{54, 48, 62}\). When active carbon is heat treated over 700°C, it acquires a basic character after cooling in an inert atmosphere and re-exposure to oxygen at room temperature. In order to explain the uptake of acids Garten and Weiss \(^{54, 48}\) proposed a chromene structure, but \(\gamma\)-pyrone-like structures appear more plausible \(^{61}\). These structures are schematically shown in Figure 2.6 and 2.7. There is also some evidence that protons can be adsorbed on basal planes due to the \(\pi\)-electron system of the basal planes and probably both mechanisms, reaction with pyrones and donor-acceptor interaction have to be considered \(^{63}\).

![Figure 2.6. Reaction of proton with pyrone-like structure \(^{62}\).](image)
2.3.3 Other heteroatoms in carbons

Chemical modification allows various functional groups to be synthesised on the carbon surface. These groups may contain not only oxygen but also sulphur, phosphorus, nitrogen, etc. Introduction of relatively small amounts of these elements (up to 10 %) changes physico-chemical and sorptive properties of carbons sharply. Thus, carbon-sulphur surface complexes of high stability and non-stoichiometric composition can be formed by heating (400-600°C) a variety of chars, activated carbons or carbon blacks with sulphur-containing gases and vapours (elemental S, H₂S, SO₂, CS₂) 37. Several types of surface groups such as sulphoxide, sulphide, polysulphide, hydrosulphide, thioquinone and thiophenol have been identified. This was established by using X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structures (XANES), FT-IR, etc. 64, 65. There were some indications that sulphur can also be incorporated into carbon structure as C-S-C and C-S-S-C complexes. Introduction of sulphur adversely affects the adsorptive properties of carbon due to appreciable narrowing of pores and enhanced hydrophobicity.
However, sulphur-containing carbons acquire an exceptional selectivity towards zinc, cadmium and mercury ions.

In order to introduce nitrogen onto the surface, carbon is treated with ammonia or amines at high temperatures. Impregnation of carbon precursor with different chemical compounds such as melamine, ammonium salts or urea followed by carbonisation results in the formation of nitrogen-containing groups. Introduction of nitrogen can also be performed by carbonising various nitrogen-containing polymeric precursors (vinyl-pyridine, acrylonitrile, etc.). Nitrogen compounds of basic nature are formed on the carbon surface. The suggested compounds are amine groups and pyridinic type structures. The carbon-nitrogen complexes are found to be highly stable. Nitrogen can be recovered only on heating at high temperatures (up to 1200°C) mostly as free nitrogen, hydrogen cyanide, cyanogen and ammonia. Active carbons containing this heteroatom bonded to their surface exhibit enhanced anion-exchange properties and improved catalytic activity.

Phosphorisation of active carbons with phosphoric acid, phosphorus trichloride or phosphorus oxychloride vapours at high temperatures results in formation of complex oxygen-phosphorus structures on the carbon surface. The limited amount of information regarding phosphorus-containing carbons indicates the existence of organophosphorus surface compounds like oxides of ternary phosphines or polyphosphates. Similarly with nitrogen, phosphorus may be introduced through a polymeric resin precursor with subsequent pyrolysis. Prior to carbonisation polymeric material is refluxed in phosphorising agent in toluene. The resulting material is pyrolised to yield a carbon with structural heteroatoms. Such treatment allows creation of both P-O-C and P-C bonds. The phosphorus functionality imparts hydrophilicity and improves ion-exchange properties to the carbon surface.

2.4 Sorption of Electrolytes

Active carbons have long been known as very effective adsorbents for gases, vapours and organic compounds. Besides these properties, active carbons behave as ion-exchangers in solutions of electrolytes. Sorption of electrolytes on active carbons
from aqueous solutions is the subject of a considerable amount of research aimed at establishing the mechanism of this process. The published work regarding ion sorption process by active carbons suggests that surface chemistry governs these properties.

The study of surface chemistry of carbonaceous sorbents began in the 1920's when it was found that technical grade carbons can remove cations and anions from strong electrolyte solutions. This fact required some explanation and was considered either as an ordinary molecular sorption or as a result of the presence of mineral admixtures in the carbon\textsuperscript{73, 74}. Systematic investigation of electrolyte adsorption by activated carbon started after the research work published by Bartell and Miller\textsuperscript{75, 76, 77}. These researchers studied carbon adsorbents prepared from purified sugar which were then activated at high temperature (900-1000°C). It was revealed that this carbon caused a change of pH when brought into contact with solutions of neutral salts (e.g. sodium chloride or sodium acetate). This carbon removed anions and released an equivalent amount of hydroxyl-ions. Bartell and Miller considered this phenomenon as the result of hydrolytic splitting of salts by water followed by selective removal of corresponding acids by the carbonaceous adsorbent. Hence this phenomenon was termed "hydrolytic adsorption".

Conventional active carbons with anion-exchanging properties are relatively unstable. When they are exposed to air or oxygen at room temperature they slowly convert to a more stable modification, so-called oxidised carbon. At temperatures of 400-450°C this process is significantly accelerated. In contrast to the conventional active carbon, the latter preferentially removes cations from aqueous solutions of electrolytes. As this takes place, protons are released causing acidification of the solution. Therefore, oxidised carbon acts as a special type of cation-exchanger in hydrogen form. The formation of this carbon modification was originally discovered by Dubinin\textsuperscript{78} and Kruyt and de Kadt\textsuperscript{79, 80}. These researchers found that when charcoal, which was heated at 900°C in inert atmosphere (and which adsorbs acids but not inorganic bases), was reheated at 400°C in oxygen, it acquired the property of adsorbing bases. This property can be destroyed by again heating at the higher temperature. They then postulated the formation of substances of an acidic nature on the surface of the
charcoal by heating in oxygen at lower temperatures. At the higher temperature the acidic surface compounds are destroyed. For rapid formation of the acidic surface compounds it is necessary to heat the charcoal at 300-400°C in the presence of air and water vapour.

Several theories were proposed to explain the adsorption of electrolytes on different types of carbon. Shilov et al. observed that charcoals heated at lower temperatures took up bases. From this and other facts they postulated a chemical theory of surface compounds. Adsorption of acids, bases and salts by charcoal takes place through interaction with acidic and basic oxides of carbon on its surface. According to the researchers, basic oxides are formed when a charcoal, outgassed in vacuum at high temperatures, is allowed to come into contact with oxygen only after cooling. Acidic surface oxides are formed when a charcoal is heated in oxygen at temperatures between 300 and 500°C. The structures, presented in Figure 2.8, were proposed.

According to the investigators, oxides A and B react with acids and oxide C interacts with alkalis.

![Figure 2.8. Surface oxides proposed by Shilov et al.](image)

The character of ion sorption is determined, as it is in the case of synthetic ion-exchangers, by the chemical nature of the surface functional groups. From this point of view, anion-exchanging properties of conventional active carbon are related to the
presence of basic surface oxides of carbon whereas the ability of oxidised carbon to sorb cations is attributed to the presence of acidic functionality.

Ion-exchange on active carbon and its oxidised modification can be represented by the following schemes:

$$R - OH + K^+ + A^- \rightarrow R - A + K^+ + OH^- \quad \text{(anion exchange)}$$ (1)

$$R - H + K^+ + A^- \rightarrow R - K + H^+ + A^- \quad \text{(cation exchange)}$$ (2)

where $K^+$ is cation, $A^-$ is anion, and functional groups $R$ can be ascribed with one or another structure.

It should be noted that there is insufficient clarity regarding the composition of basic structures on the carbon surface. It is perhaps related to the fact that it is rather difficult to imagine a purely basic functional group consisting of atoms of carbon, hydrogen and oxygen. Shilov et al.\textsuperscript{81} proposed the basic structures represented in Figure 2.8 (oxides A and B). Garten and Weiss related the basic properties of active carbon to the existence of surface quinones and chromene (benzpyran) structures (Figures 2.6 and 2.7) with localisation of positive charge on the carbonium (benzpirilium) ions or on oxygen\textsuperscript{48}.

Contrary to Shilov's theory, Frumkin\textsuperscript{82,83} put forward a theory according to which the process of electrolyte sorption on active carbon is related to the potential drop at the carbon-solution interface and the capacity of electrical double layer. The extent of the potential drop depends on the amount of electrochemically active gases (oxygen and hydrogen) adsorbed by the carbon surface and on polarisation of the carbon electrode under application of a potential. Conventional active carbon in an air atmosphere behaves as an oxygen gas electrode. Negatively charged hydroxyl ions, formed in aqueous solutions, create the outer boundary of the electrical double layer. Oxygen chemisorbed by carbon ionises by the following scheme:

$$C_xO + H_2O \rightarrow C_x + 2OH^- + 2\Theta \rightarrow C_x^{2+} \cdots 2OH^- \quad (3)$$
where $C_x^{2+}$ represents the positively charged surface of carbon with hydroxyl ions in the electrical double layer. When active carbon interacts with electrolyte solutions, the exchange of hydroxyl ions for anions occurs by the following schemes:

$$C_x^{2+} \rightarrow 2OH^- + 2H^+ + 2A^- \rightarrow C_x^{2+} + 2A^- + H_2O$$ \hspace{1cm} (for acids) (4)

$$C_x^{2+} \rightarrow 2OH^- + 2K^+ + 2A^- \rightarrow C_x^{2+} + 2A^- + 2K^+ + 2OH^-$$ \hspace{1cm} (for salts) (5)

where $A^-$ is the anion, and $K^+$ is the cation.

The electrical double layer in active carbons possesses a relatively high capacity because of its large specific surface area. Consequently active carbons have notable anion-exchange properties. Acid sorption can also proceed by a more complicated scheme:

$$C_xO_2 + 2H^+ + 2A^- \rightarrow C_x^{2+} + 2A^- + H_2O_2$$ \hspace{1cm} (6)

The possibility of a purely electrochemical mechanism of ion removal is confirmed by the following fact. Complete removal of oxygen or the introduction of a minor amount of platinum (less than 1 %) onto the carbon surface results in the complete recharge of the surface with the change of gas atmosphere. Thus, if platinised carbon is placed into a hydrogen atmosphere it begins functioning as a conventional hydrogen electrode. The electric double layer of such carbons consist of hydrogen ions. As a consequence, such carbons acquire cation-exchanging properties. The interaction of carbon with cations proceeds as follows:

$$C_x^{2-} \rightarrow 2H^+ + 2K^+ + 2A^- \rightarrow C_x^{2-} + 2K^+ + 2A^- + 2H^+$$ \hspace{1cm} (7)

This process is accompanied by the equivalent acidification of the solution.

Convincing evidence of the electrochemical nature of ion-exchange sorption on active carbons was presented by Burshtein \(^8^7\). He showed that sorption of anions and cations can be performed without electrochemically active gases, instead polarising
carbon by an external source of current. Carbon can be charged either positively or negatively.

Cation sorption by an oxidised variety of active carbon, in accordance with electrochemical theory, may be attributed to the presence of the oxide layer on the carbon surface. This oxide layer, as mentioned previously, is slowly formed at room temperature. This process is rapid when carbon is heated in oxygen at about 400°C. As a result of this process, the formation of a layer of orientated $C^+\cdot O^-$ dipoles on the carbon surface causes a positive potential drop between the carbon and the solution. The carbon surface is recharged and the outer layer of the electric double layer of this negative oxygenated carbon consists of protons. These take part in ion-exchange with cations of electrolytes. Theoretically the oxidised modification of active carbon should only adsorb bases. In practice both acids and bases are adsorbed. This is because oxidised carbon never has a uniform surface. During the oxidation process there are always moments in which a new carbon surface is set free and so the surface oxidised sites are intermingled with the pure carbon surface.

It is necessary to underline that due to the complexity of the chemical nature of the active carbon surface and its electrochemical non-uniformity, a purely electrochemical approach is not in itself enough to explain the ion-exchange and sorptive behaviour of carbonaceous sorbents. Thus, it was shown that the cation-exchange on oxidised carbon is caused not only by acidic surface functional groups (carboxylate, phenolate, etc.) but also by protons which are easily detachable from the surface. The bonding between these protons and the surface is of an electrochemical nature (electric double layer). Owing to the special electrophysical properties of carbons, (namely the presence of delocalised $\pi$-electrons easily transferable in conjugated systems of bonds) the carbonaceous sorbents are endowed with significant electrical conductivity. The properties of functional groups attached to the carbon surface and non-conductive polymeric matrix (ion-exchange resins) should diverge considerably. The strengths of real protonogenic surface groups (primarily carboxylic groups) in carbons should increase since the negative charge builds-up close to the surface of oxidised carbon. This is demonstrated by the fact that cation-exchange on oxidised carbons, contrary to carboxylic resins, begins at pH values below 2. Taking into account the above
considerations, the structure of electrical double layer of active and oxidised carbons as well as the ion-exchange can be represented by the scheme shown in Figure 2.9.

![Diagram showing ion sorption by active and oxidised carbons]

Figure 2.9. Schematic representation of the ion sorption by active and oxidised carbons.

Active carbon is a remarkable type of adsorbent with functional groups connected together by an electrically conducting system of bonds. This important property of such a structure was illustrated by the electrochemical studies outlined above. It was suggested that such an adsorbent may act as an electrode, i.e. can be positively or negatively charged and be a donor or acceptor of electrons. As a result, the adsorbent
can participate in reductive and oxidative processes with electrolytes in aqueous solutions. It was proposed to term this type of sorbent as a "redox adsorbent".

Activated carbon has long been used for noble metals recovery from aqueous solutions of high saline content. A comprehensive investigation of the selective sorption mechanism for these metals by active carbon has been recently presented. Thus, it was shown that activated carbon can selectively extract such metal ions as gold, platinum and palladium over nickel. The researchers showed that the selective adsorption of palladium, platinum and gold proceeds through the formation of surface complexes with charge transfer and the subsequent formation of clusters (for gold) or the reduction to the metal state (for palladium and platinum).

Electrochemical reduction is thermodynamically enabled if the equilibrium potential for metal ions is more positive than the potential of the active carbon surface. Therefore, the sorption of palladium and platinum is accompanied by their reduction to the metallic state whereas nickel cannot be reduced under such conditions. The comparative investigation of redox process potentials for different metals shows that electrochemical reduction is likely for $[\text{AuCl}_4]^-$, $[\text{PtCl}_4]^{2-}$, $[\text{PdCl}_4]^{2-}$ and is unlikely for $[\text{RhCl}_6]^{3-}$, $[\text{Pd(NH}_3)_4]^{2+}$, $[\text{Au(CN)}_2]^-$, $\text{Ni}^{2+}$.

2.5 Concluding Remarks

The information provided in this chapter clearly shows the relation between the surface properties of carbons and their physical and chemical structure. The graphite-like microcrystalline structure is the basic structural unit of active carbon. This type of structure allows for the existence of a wide variety of pores which make active carbons excellent adsorbents for organics. Electrophysical studies of carbons indicate the presence of excess electrons due to peripheral carbon atoms with free, unattached valencies. The existence of delocalised $\pi$-electrons and unsaturated valencies in the system of hexagonal aromatic planes gives rise to diverse electrochemical, chemical and sorptive properties.
The surface of activated carbons is not uniform either in structural or in energetic respects. The surface carbon atoms are in a different electronic state than those in the bulk phase, especially on the edges of carbon layers, in the places where defects, dislocations and discontinuities of the layer planes are present. Such sites are associated with high concentrations of unpaired electron spin centres and therefore, play a significant role in the chemical and adsorptive interaction of carbon with different compounds. The result of such interactions is the association of active carbons with appreciable amounts of various heteroatoms. Oxygen is the most important amongst them. It determines the way active carbons interact with electrolytes in aqueous solutions. The ion-exchange properties of carbons can be described by:

- **Electrochemical mechanisms:**
  a) ion-exchange in electric double layer (carbon behaves as a gas electrode when brought into contact with hydrogen or oxygen),
  b) electrochemical reduction of electropositive metal ions,
- **Ion-exchange involving surface functional groups** (oxidised and chemically modified carbons).

The mechanisms discussed for electrolytes sorption on carbon materials are not contradictory but complement one another.

There are a great number of options in altering the physical and chemical properties of active carbons. It is concluded that carbonaceous adsorbents are very important and interesting materials for continued study.

### 2.6 References


50. Kruyt, H.R. and de Kadt, G.S. *Kolloid Z.* 1929, 47, p. 44.


73. Michaelis, L. and Rona, P. *Biochem. Z.* 1919, 97, p. 57.


79. Kruyt, H.R. and de Kadt, G.S. *Koll. Z.* 1929, 47, p. 44.


86. Ivanova, L.S., Grabchak, S.L., Strazhesko, D.N., and Matskevich, E.S. *Adsorbsiya i Adsorbenty (adsorption and Adsorbents).* 1972, 1, p. 18.


Chapter 3: Removal of Metals by Active Carbons

3.1 Introduction

For many years the ion-exchange properties of active carbon have been the object of considerable theoretical and practical interest. Active carbons, if compared to polymeric ion-exchange resins and mineral ion-exchangers, exhibit a number of advantages. For example, specific ion-exchange properties may be relatively easily altered in a desired manner and ion sorptive capacity may also be readily controlled. Furthermore, carbon materials show high chemical stability in aggressive solutions. Both commercial active carbons and those prepared on a laboratory scale demonstrate some ion-exchange properties even when they are untreated. However, in order to enhance these properties, as well as to change them in a desired way, the carbon surface is usually chemically modified. One such treatment involves incorporating various heteroatoms onto the surface. Most often these atoms are oxygen, hydrogen, nitrogen, phosphorus and sulphur. They constitute the principal components of surface functional groups e.g. oxygen and hydrogen in carboxylic or phenolic groups of oxidised carbons. The heteroatoms may also be part of a carbon lattice e.g. pyridinic-type or pyrrolic-type structures in nitrogen-containing carbons. Both untreated and chemically modified carbons are currently used in various technological processes. The most important are the removal of traces of toxic heavy metals from waste water and potable water conditioning, recovery of precious metals in hydrometallurgical processes, removal of undesirable ionic species from concentrated electrolyte solutions, and as catalysts and catalyst supports.

3.2 Heavy Metal Contaminants in Water

The presence of heavy metals in the environment can be detrimental to a variety of living species. Therefore, the elimination of heavy metals from waters and wastewaters is important to protect public health. Heavy metals is the classification which is generally applied to those metals of particular concern in water treatment:
copper, silver, zinc, cadmium, mercury, lead, chromium, iron, and nickel. Other metals which may be considered to be in this category are tin, arsenic, selenium, molybdenum, cobalt, manganese, and aluminium. Most heavy metals found in water and waste water treatment processes are in inorganic form. However, in some cases these metals are present in the organic form (e.g. textile and dyeing industry wastes).

The most common method for removal of inorganic heavy metals is chemical precipitation. Typical estimates of final concentration levels obtainable by chemical precipitation are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Achievable concentration, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0.3</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>0.05</td>
</tr>
<tr>
<td>Chromium, total</td>
<td>0.5</td>
</tr>
<tr>
<td>Copper</td>
<td>0.5</td>
</tr>
<tr>
<td>Iron</td>
<td>1.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 3.1. Typical concentration levels obtainable through chemical precipitation.

The data presented in the Table 3.1 suggests that the precipitation technique is not sufficient to bring heavy metal concentrations to the regulations set by European Council Directive 80/778/EEC relating to the quality of water intended for human consumption. Table 3.2 shows typical values for metal concentrations adopted by EU legislation. Hence, additional methods of water treatment are required to comply with the legislation requirements for heavy metal concentration in water.
3.3 Application of Active Carbons for Metals Removal

Active carbon is being widely used in water and waste water treatment to remove undesirable organic compounds. The advantages of this sorptive material are well documented in the scientific literature \(^3\), \(^4\). However use of active carbon for the removal of inorganic species from water is rather rare.

The ability of active carbons to remove cations or anions from aqueous solutions of electrolytes has been known for a long time. Bartell and Miller \(^5\), \(^6\), \(^7\), Kruyt and de Kadt \(^8\), \(^9\), Kolthoff \(^10\), and other researchers \(^11\), \(^12\) reported that carbonaceous sorbents can remove cations or anions from electrolyte solutions depending on the preparation method. A substantial amount of fundamental research into metals removal by active carbons was carried out by the scientists from the Soviet Union \(^13\), \(^14\), \(^15\), \(^16\). To date, only a limited number of publications have been translated into English \(^17\), \(^18\), \(^19\), \(^20\).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Guide level, µg/l</th>
<th>Maximum admissible concentration, µg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Copper</td>
<td>100* – 3000**</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>Lead</td>
<td>50</td>
<td>50 (in running water)</td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Zinc</td>
<td>100* – 5000**</td>
<td></td>
</tr>
</tbody>
</table>


* At outlets of pumping and/or treatment works and their substations.
** After the water has been standing for 12 hours in the piping and at the point where the water is made available to the customer.

Sigworth and Smith \(^21\) were probably the first to review previous research on the utilisation of active carbon for the removal of trace heavy metals from water. Their
review highlighted the potential for the removal of antimony, arsenic, bismuth, chromium, tin, silver, mercury, cobalt, zinc, lead, nickel, titanium, vanadium and iron by carbon materials. Nevertheless, systematic investigation was not carried out to determine the metal sorption mechanism. Their work indicated that sorption of heavy metals by active carbons was inversely proportional to the solubility of metal complexes in aqueous solutions. The researchers concluded that heavy metals could be better adsorbed by the carbon when water conditions rendered the heavy metals less soluble.

House and Shergold investigated the sorption of multivalent metal species such as aluminium, calcium, cobalt, copper, iron, lead and zinc by active carbon and graphite from aqueous solutions. They reported that the sorption strongly depends on pH and occurs at 1 to 2 pH units below the value that is required for precipitation of the bulk metal hydroxide. The researchers argued that the structuring of water molecules near a charged sorbent surface will lead to a reduction in the dielectric constant, which will reduce solubility in the proximity of the surface and thus produce conditions which are favourable for metal hydroxide precipitation in the sorbent pores. The results of the research suggest that the mechanism of the sorption of multivalent metal species on active carbon may not be different to that of graphite. This indicates a similarity in the surface chemistry of both graphite and active carbon.

Sorption of copper, lead, nickel and zinc by fourteen various brands of active carbon was thoroughly studied by Corapcioglu and Huang. Emphasis was put on the effect of key factors (such as pH, temperature, carbon type and surface loading) on the extent of metal removal. It was found that the removal efficiency of the activated carbon increased as the pH was raised up to 10. The results clearly show that two carbons (Nuchar SA and Nuchar SN) exhibit the highest adsorption capacity for metals in the acidic region. However, at alkaline pH values, these two carbons appeared to be less effective for heavy metal removal. The high sorption capacity of these carbons may be attributed to their acidic character and to the presence of phosphoryl compounds on their surface. Corapcioglu and Huang stated that the sorption capacity of heavy metals varies significantly with pH. For cations, the magnitude of sorption increases abruptly at a specific pH value that is a characteristic
of the individual metal. The specific pH value which is required for an increase in sorption is determined by the acid-base behaviour of the activated carbon.

3.3.1 Agricultural waste-based active carbons

The need for the purification of potable and waste waters from different contaminants, exhaust gases from sulphur dioxide, etc., requires the development of new methods for the production of highly efficient adsorbents. In this respect carbon-based adsorbents have attracted special attention because of their well developed porous structure, large active surface area and good mechanical properties. However these materials are relatively expensive and therefore their use requires the development of regeneration procedures. Hence, it is necessary to consider relatively cheap initial materials such as agricultural by-products, used automotive tyres, low cost coals, etc. Thus, in India a technology has been developed for producing activated carbons using local raw materials - nut and coconut shells, peanut hulls, pine timber, pine scraps, etc. \(^{24,25}\). The granulated carbons prepared are characterised by their mechanical strength, density and high adsorption activity. These properties enable them to be used for adsorption of gases and vapours as well as for metals removal from water. Some research has been carried out on the preparation of active carbons derived from other agricultural by-products.

Gergova et al \(^{26}\) investigated the physico-chemical and structural characteristics of active carbons prepared from apricot stones, cherry stones and grape seeds. It was found that the adsorption characteristics and porous structure of derived carbons are dependent upon the nature of the raw material. The experimental results obtained show the possibility of production of activated carbons with well developed porous structure, high surface area and appreciable sorptive capacity. Almond and pecan shells were chosen as hard, lignocellulosic precursors for the production of granular active carbons in order to create sorptive materials for both organic compounds and metals \(^{27}\). The carbons were activated either chemically (phosphoric acid) or physically (carbon dioxide). A portion of the carbon obtained was modified by surface oxidation. The simultaneous removal of organics and metals (copper) was investigated. The results of this study show good potential for the production of effective, bi-functional active carbons for the adsorption of both metals and organic
compounds. The researchers concluded that the non-polar organics are sorbed in the non-polar (hydrophobic) micropores while metals are taken up on oxygen-containing sites which are located in the more open meso-and macropores. Ferro-Garcia et al.\textsuperscript{28} studied the sorption of zinc, cadmium and copper from aqueous solutions by three different carbonaceous sorbents. These carbons were derivatives of almond shells, olive stones and peach stones. The influence of the solution pH on the sorption processes was investigated as well as the influence of various anions (Cl\textsuperscript{-}, CN\textsuperscript{-}, SCN\textsuperscript{-}) and complexing agents (EDTA). The obtained data indicated that the presence of Cl\textsuperscript{-}, CN\textsuperscript{-} and SCN\textsuperscript{-} increased the amount of metal ions removed whereas the presence of EDTA hindered the sorption process. The authors suggested that an enhanced metal uptake in the presence of anions is due to the formation of some complex anions. These complex compounds would be more readily sorbed onto active carbons as anions rather than cations because of a positive carbon surface charge potential. The lower sorption in the presence of EDTA is suggested to be because of the size of the EDTA-metal complexes. A large proportion of carbon pores would be inaccessible to this compound and therefore sorption would be lower. The influence of the solution pH on the sorption extent was related to the carbon surface charge variation.

Other researchers\textsuperscript{29} also studied the removal of lead, copper, zinc and cadmium from aqueous solutions by active carbons prepared from agricultural wastes (apricot stones and coconut shells). The results presented indicate that all active carbons show an ability to remove metal ions from aqueous solutions with the capacity increasing in the order: cadmium<zinc<copper<lead. Sorption of these metals is negligible at low pH values but increases considerably in the range of pH 3-4. The presence of other ions in solution decreases the sorption of each of them. The authors suggested several determining factors for the extent of metal sorption such as ionic radius, ionic potential q/r (q-ionic charge; r-ionic radius), chemical properties and hydrolysis.

3.3.2 Coal-derived active carbons

Natural coal may be employed as a precursor for production of active carbon because of its low cost and availability. 28% of total activated carbon production in the world is based on coal\textsuperscript{3}.
Munoz-Guillena et al 30 dealt with various types of Spanish coals as precursors for active carbon preparation. In order to understand the relationship between the adsorption properties of different types of activated carbons, the coal precursor, and the method of preparation, different feed stocks covering coals from anthracite to high-volatile bituminous have been tested. The results revealed that the selection of coal precursor influences the pyrolysis process, the porosity of the char and consequently the rate of activation and characteristics of the resulting carbon. Active carbons derived from lower rank coals have higher surface areas and a much more highly developed pore structure than those prepared from higher rank coals.

Two types of brown coal, oxyhumolite and peat have been studied with regard to their ability to remove lead, zinc and copper from waste waters 31. The results have shown that the calcium loaded form of these materials can be effectively used for metal extraction by ion-exchange with calcium. These ion-exchangers have been effective for concentrations of metals less than 10 mmol/l.

3.3.3 Oxidised active carbons and metals removal

Conventional activated carbons are relatively unstable when brought into contact with oxygen or air at room temperature. At this temperature they are gradually transformed into the more stable modification of oxidised carbon. This process is significantly enhanced at temperatures of 400 - 450°C 16. As shown in the previous chapter, surface modification by oxidation may be carried out in a liquid phase by a variety of oxidising agents (nitric acid, hydrogen peroxide, etc.). Oxidation of carbon leads to a significant increase in the amount of surface oxygen-containing functional groups of acidic character. Strazhesko and Tarkovskaya 32 regarded oxidised carbons as weakly acidic polyfunctional cation exchangers, the capacities of which are determined primarily by their surface carboxylic and phenolic groups. Kuzin, Plachenov and Taushkanov 33 showed that the sorptive properties of carbons depend on the structure and the degree of surface oxidation. The cation-exchange groups enable the carbon surface to become hydrophilic 34 and highly selective to heavy metal ions 35,33.

A significant number of publications relating to the use of oxidised carbons for metal ion separation from aqueous solutions was generated in the USSR between the 1950's
and 1970's. Thus, Kuzin and Strashko \textsuperscript{36} developed a process to separate zirconium, thorium and uranium on oxidised carbon. The researchers showed that under a variety of experimental conditions, i.e. the presence of nitric or sulfuric acid, molarity of the acids, etc., quantitative separation of these metals can be achieved. Strashko et al \textsuperscript{37} carried out a chromatographic separation of lithium, sodium, potassium and caesium using oxidised carbon. This separation (elution) was performed using hydrochloric acid of varying normality. The researchers concluded that the exchange capacity depends upon the charge and ionic radius of the sorbed cations. The extent of alkali metals separation is dependent upon their ratio in the feed solution and upon the degree of carbon oxidation. Extraction of thallium from industrial solutions was investigated by Kovyrshin et al \textsuperscript{38}. It was shown that phenolic groups of oxidised carbons exhibit enhanced selectivity with respect to thallium. A solution from a lead-manufacturing plant was used in this study. Table 3.3 presents the composition of the solution studied.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thallium</td>
<td>0.125</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>27.3</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>1.7</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1.1</td>
</tr>
<tr>
<td>Rhenium</td>
<td>0.01</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.08</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.024</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 3.3. The composition of solution used for thallium separation \textsuperscript{38}.

Despite the considerable sodium ion content (thallium : sodium = 1 : 795), the total dynamic capacity of the oxidised carbon for thallium was relatively high (0.79 meq/g). Strazhesko et al \textsuperscript{39} studied the sorption of monovalent (sodium) and bivalent (calcium and cobalt) ions by oxidised carbon from aqueous-organic and non-aqueous media.
The researchers found that as the amount of organic solvent component increases in the supernatant solution the bonding between metal ion and carbon surface becomes stronger. An electrochemical mechanism of sorption (see previous chapter) was used to explain the results.

Research concerning the removal of various cations by oxidised carbons has been summarised by Tarkovskaya et al.\textsuperscript{40} and Strazhesko and Tarkovskaya\textsuperscript{16}. The authors showed that significant differences in sorption of various metal ions by oxidised carbons are observed over a wide range of pH values (Figure 3.1). The authors presented a selectivity series compiled on the basis of both batch and dynamic experiments:

Selectivity series for cations Me\textsuperscript{2+} on H\textsuperscript{+}-form of oxidised carbon:

\[
\begin{align*}
\text{Na}^+ &< \text{Sr}^{2+} < \text{Cd}^{2+} < \text{Mn}^{2+} < \text{Ca}^{2+} < \text{Zn}^{2+}, \\
\text{Co}^{2+} &< \text{Ni}^{2+} < \text{Cr}^{3+} < \text{La}^{3+}, \\
\text{Sc}^{3+} &< \text{Cu}^{2+} < \text{Fe}^{3+}
\end{align*}
\]

The exchange constants for the series Me\textsuperscript{2+}-H\textsuperscript{+} as determined by chromatographic method is follows:

\[
\text{Sr}^{2+} < \text{Cd}^{2+} < \text{Mn}^{2+} < \text{Ca}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cr}^{3+} < \text{La}^{3+} < \text{Sc}^{3+} < \text{Fe}^{3+}
\]

The exchange constants for the series Me\textsuperscript{2+}-H\textsuperscript{+} as determined from sorption isotherms is:

\[
\text{Na}^+ < \text{Cd}^{2+} < \text{Ca}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{La}^{3+} < \text{Cu}^{2+}
\]
Figure 3.1. pH dependence of cation sorption by air oxidised FOU carbon. (reproduced from original article)

These results regarding the uptake of cations indicate significant differences of bond strength between individual metal ions and the oxidised carbon surface. This also shows that oxidised carbon is a highly selective ion-exchange material. The authors related their observations to the surface structure and physico-chemical properties of carbons.

Although the existence of acidic surface functional groups in carbons is widely accepted, there are very few Western publications dedicated to the preparation and applications of oxidised active carbon. Thus, Bautista-Toledo et al. investigated sorption of chromium (III) and chromium (VI) from aqueous solutions using conventional active carbon and its oxidised variety. The uptake of chromium (III) by carbons is essentially determined by the presence of surface oxygen complexes rather than by the surface area and porosity of the solid. A similar effect was observed for chromium (VI). The uptake is found to be relatively low (0.14mmol/g for unoxidised carbon and 0.28mmol/g for oxidised carbon). The authors suggested that chromium (VI) is reduced to chromium (III) on the surface of the carbon at acidic pH and sorbed as a cationic species.
Oxidised anthracite was used for the removal of zinc, copper, cadmium and lead from aqueous solutions\textsuperscript{44, 45}. This sorptive material may be considered as equivalent to oxidised active carbon. The effect of solution pH on the extent of sorption was determined. A comparison of the chemical composition data of both the starting and oxidised anthracite revealed a six-fold increase in oxygen by weight for the oxidised sample. The oxygen content is related to the concentration of the acidic groups on the surface of anthracite. The results presented in the article indicated that oxidised anthracite possesses an ability to adsorb copper, lead, zinc and cadmium with decreasing capacity in the order $\text{Cu}^{2+}>\text{Pb}^{2+}>\text{Zn}^{2+}>\text{Cd}^{2+}$. The adsorption of metal ions increases considerably in the range of pH 3-4. The presence of all ions in the solution in equal quantities decreases the adsorption of each of them. Apart from the fact that selective adsorption of the metals is observed, the ions, which are preferentially adsorbed, completely prevent the adsorption of other species.

3.3.4 Removal of lead by active carbons

Lead is an important chemical element which has been used by man for many centuries. It can be regarded as a longstanding environmental contaminant. Mining, smelting and refining of lead, as well as the production and use of lead based products give rise to the release of lead into the environment. This takes the form primarily of either lead-rich aqueous effluent streams, or the emission of air-borne fumes and dust. It is also well known that lead is a heavy metal poison which, acting by complexing with oxo-groups in enzymes, virtually affects all steps in the process of haeme synthesis and porphyrin metabolism\textsuperscript{46}. The toxicity of lead in most tissues is similar, regardless of the inorganic or organic nature of its compounds\textsuperscript{47}. All these facts prompt the setting up of experimental methods to obtain the most efficient removal of lead from a contaminated medium.

3.3.4.1 Lead contamination of drinking water

An important source of lead leading to human exposure is that contained in drinking water. Drinking water can become contaminated with significant amounts of lead in the distribution system as a result of corrosion and leaching from lead pipes and Pb/Sn-soldered joints associated with copper service lines commonly used in...
household plumbing. In Britain, it is estimated that approximately 7 million households have lead somewhere between the water main and the tap \(^{48}\). Many households may thus be exposed to elevated levels of lead in their drinking water. Lead levels up to 1000 \(\mu g/l\) can be detected in the first samples drawn after water has been standing in the pipes overnight or for long periods \(^{49,50}\). Lead content of water is subject to regulation in many countries. The European Community Directive 80/778/EEC on the quality of water for human consumption specifies 50 \(\mu g/l\) as the maximum admissible lead concentration \(^2\).

The only way to guarantee low lead levels in drinking water is to replace all lead pipework and fittings. However this is a costly exercise. It has been estimated for Britain that this would cost around £ 2500 million and take many years to complete \(^{48}\). A cheaper alternative would be to treat the water to reduce lead content, essentially by producing a relatively inert coating to the lead pipe. This can be achieved by raising the pH to greater than 8 and causing a precipitate of basic lead carbonate \((Pb(OH)\times 2PbCO_3)\) to line the pipe. This approach, however, cannot guarantee low levels of lead especially in waters which already have an alkalinity greater than 100 mg/l expressed as \((CaCO_3)\) and as yet there is no wholly satisfactory treatment approach to this problem \(^{48,51}\). Removal can be achieved by other means such as simple water filters applied at the 'point of use' but these usually consist of a fabric filter or contain activated carbon which are not particularly effective in reducing or removing lead.

### 3.3.4.2 Active carbons for lead decontamination

Numerous investigators have evaluated the potential of active carbon to remove lead from aqueous solutions. Sigworth and Smith \(^{21}\) reported on the relationship of solution pH and the adsorption of inorganics by activated carbon. Laboratory studies performed with aqueous solutions containing different lead salts showed little adsorption at pH 2 but fairly good removal at pH 5. The authors suggested that active carbon has good prospects for lead removal from water at pH 7.

Netzer and Hughes \(^{52}\) extensively studied the adsorption of lead and other heavy metals on ten different kinds of activated carbon. The investigation revealed that one
carbon (Barney Cheney NL 1266) was superior for lead removal at low pH. The rest of the carbons demonstrated a large variation in their ability to adsorb lead from aqueous solutions. The investigation showed that the adsorption capacity of activated carbons for lead is twice as high as for copper and ten times higher than for cobalt. The researchers concluded that a large number of different factors affect the adsorption of heavy metals, such as the surface chemistry of carbon and the water chemistry. No single carbon property appears to be dominant in determining its metal adsorptive characteristics from aqueous solutions.

Research performed by Corapcioglu and Huang \(^{23}\) demonstrated that the pH of the solution is a critical parameter in the sorption of lead by active carbons. They reported that the amount of heavy metal sorbed increases from a low value to nearly 100\% in a narrow pH range. This was referred to as the pH-adsorption edge for activated carbon and is specific for the heavy metal and carbon type. The researchers also revealed that the beginning of the adsorption edge depends upon the surface loading with the metal. Experimental results showed that increasing the concentration of the metal species, while keeping the active carbon amount constant, shifts the pH-adsorption edge to more alkaline pH values.

Rivera-Utrilla et al \(^{53}\) examined lead removal by active carbons derived from olive stones and commercially available carbonaceous sorptive materials (Table 3.4). Several parameters which can influence metal sorption were investigated. These were the chemical nature of the carbons, textural characteristics, solution pH, equilibration time, zero point of charge of the sorbents, feed solution concentration, and the influence of other ions present in the feed solution. The authors concluded that pH of the solution, chemical nature of the carbons and zero point of charge have a determining effect on the extent of sorption. The remaining parameters are found to have less influence on the metal uptake.
3.3.4.3 Sorption of low levels of lead by active carbon

New requirements for drinking water standards have encouraged recent research activity on lead adsorption from aqueous solutions. The reason for the new move to lower lead levels in drinking water is based upon evidence collected by the US Environmental Agency (USEPA), which indicates that low levels of lead, even at the current maximum admissible concentration, may cause adverse health effects \(^{51}\). The US Environmental Protection Agency proposed a new maximum contaminant level (MCL) for lead of 5 ppb and an MCL goal of 0 ppb. An action level of 10 ppb for lead at the customer's tap was also proposed \(^{51}\). Similar recommendations were also outlined in the Guidelines for Canadian Drinking Water Quality \(^{54}\). Water supply companies will find these proposed guidelines for lead levels in drinking water extremely difficult to meet since the problem arises after the water has been treated. This has prompted many researchers to evaluate the effectiveness of active carbon for the removal of low levels (ppb range of concentrations) of lead from water.

Kuennen et al \(^{51}\) and Taylor and Kuennen \(^{55}\) carried out an extensive evaluation of a point-of-use (POU) granular active carbon (GAC) fixed-bed adsorber for removing soluble and insoluble lead from drinking water. The sorptive material used in these studies was basic in nature (H-type) active carbon. The feed solution in column experiments contained 150 ppb of lead chloride. Several factors which influence lead removal by GAC were assessed, such as carbon type and solution pH. A limited amount of work on competitive interactions was also performed. Mini-columns were

### Table 3.4. Sorption (%) of lead ions on activated carbons (H-8 and M) in the presence of added cations \(^{53}\).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>No cations added</th>
<th>Mg(II)</th>
<th>Ca(II)</th>
<th>Sr(II)</th>
<th>Ba(II)</th>
<th>Fe(III)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-8 (basic)</td>
<td>90</td>
<td>98</td>
<td>95</td>
<td>94</td>
<td>89</td>
<td>81</td>
<td>98</td>
<td>94</td>
<td>91</td>
<td>84</td>
</tr>
<tr>
<td>M (acidic)</td>
<td>98</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>97</td>
<td>94</td>
<td>100</td>
<td>100</td>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>
used to evaluate the capacity of carbon for lead under a variety of experimental conditions. The influence of the surface chemistry of the carbon and the relationship between the pH of the water and lead reduction was shown. The authors used the surface complex formation mechanism in order to explain the surface – metal ion interactions in aqueous solutions. It was concluded that a properly designed fixed bed adsorber can reduce lead in drinking water to below the EPA action level of 15ppb.

Cheng et al \(^{54}\) examined lead removal using a commercially available active carbon (Calgon Filtrasorb 400) with the aim of adding more information in the area of competitive sorption and on the role of solute speciation in influencing the sorption process. Parameters affecting the sorption of ppb levels of lead from water by carbon were investigated. The data presented (Figure 3.2) suggested that high dosage (1 g/l) of carbon allows nearly 90% removal of lead from 50 ppb solution maintained at pH 7-8.

![Figure 3.2. Effect of foreign cations on lead uptake by active carbon \(^{54}\)](image)

The presence of foreign ions (calcium, magnesium, aluminium, and iron) notably influences the extent of lead removal. Thus, calcium at concentrations higher than 80 mg/l significantly limited the uptake. The introduction of low concentrations of
aluminium (10 mg/l) and even lower concentrations of iron (2 mg/l) completely suppressed lead removal. However as the amount of iron added was increased, more and more lead was removed from the solution. The final uptake appeared to be greater than that obtained using active carbon alone. The researchers suggested that this phenomenon is in agreement with the known high affinity of precipitated iron hydroxide towards lead.

3.3.5 Removal of cadmium by active carbon

The problem of removing pollutants from water is becoming more important with the ongoing increase in industrial activity. Cadmium is an example of a heavy metal which is included in List I of the Council Directive 76/464/EEC as a particularly dangerous substance. Cadmium is an industrial pollutant which has reached high concentrations in certain estuaries, for example, the Severn estuary which receives drainage waters from old zinc-smelting works in South Wales. The unpleasant consequences of excessive intake of cadmium by mammals include kidney damage, sterility and cancer. It is toxic to fish in concentrations as low as 10 µg/l. Cadmium acts synergistically with other elements such as copper and zinc to increase toxicity. The metal is not implicated in damage to plant life.

Because the trace elements in water are so numerous, only a non-specific process like sorption seems to be appropriate for their removal. Active carbon has been tested by several researchers as a potential sorbent for cadmium removal.

Reed et al used granular activated carbon (GAC) columns to treat cadmium- and lead-bearing waste waters. Artificial waste waters were used in this research. The influence of acetic acid and EDTA on the adsorption of cadmium and lead was examined. The researchers found that the presence of acetic acid did not appear to significantly affect cadmium removal. The authors were not certain why the increase in acetic acid concentration did not decrease uptake. It was postulated that the solution chemistry of cadmium was responsible. The presence of EDTA decreased both lead and cadmium uptake. Regeneration processes have also been performed. It was reported that a dramatic improvement in column performance was observed if a regeneration step was applied to the original carbon. The authors suggested that this
could be attributed to an increase in OH-groups available for surface and pore liquid precipitation as well as an increase in the number of sites available for adsorption. The authors also concluded that feed solution chemistry as well as influent pH play a key role in metals removal by active carbon.

Cadmium removal by Merck active carbon, an active carbon oxidised by hydrogen peroxide and a carbon heat treated in argon at 1400 K was examined by Dobrovolski et al 59. The authors employed an isotope exchange technique in order to investigate the equilibrium exchange kinetics. These experiments showed that exchange was very fast in the initial stages at high pH values. The researchers attributed this finding to the exchange of cadmium at easily accessible surface sites and micropores. The slow exchange at low pH values was attributed to metal physisorption into deep micropores. The authors suggested that sorption of cadmium on carbon is due to physisorption in the micropores and ion-exchange with surface functional groups. Higher uptake of metal on the oxidised sample was also observed. It was concluded that a higher concentration of ion-exchanging groups on the surface was responsible for increased metal removal. Heat treated carbon was found to sorb cadmium only at pH greater than 7. Cadmium sorption by the heat treated sample was inferred to be due to the precipitation of cadmium hydroxide occurring at pH 8.

### 3.3.6 Nickel removal by active carbon

Owing to increasing industrial activity the input of nickel to the environment and into soils in particular may exceed output. Consequently soils may be accumulating nickel. This could be serious in the long term since nickel is one of the most poisonous elements to plants. There are large areas of land which are unsuitable for agriculture because of naturally high concentrations of nickel 57. There are relatively few reports of nickel toxicity to man except in the factories where large amounts of the metal are handled. Apart from causing dermatitis, nickel dusts were held responsible for some cases of lung cancer 57. European Community legislation adopted a maximum admissible nickel concentration in drinking water of 50 μg/l ².

Laboratory studies on a nickel chloride solution treatment with active carbon are reported by Sigworth and Smith 21 and showed no adsorption at pH 2, slight removal
at pH 5.4, and noticeably better uptake at pH 7.5. Tomashevskaya et al.\(^{17}\) and Mironov and Taushkanov\(^{60}\) used oxidised active carbon for the removal of various metals including nickel from aqueous solutions. A special feature of oxidised carbon is the formation of surface complex compounds between the surface functional groups and metal ions sorbed. The exchange constants and stability constants for a large number of cations were determined in order to characterise the bond strength between the sorbed cations and the surface functional groups in carbon. High stability constants were found for alkaline and alkaline earth metals whereas polyvalent metals exhibited very low stability constants. This indicates that polyvalent metals form stronger complexes on the surface. Nickel is found to be bound to the surface more strongly than alkaline and alkaline earth metals and some transitional metals (e.g. zinc and cobalt).

Emelyanov et al.\(^{13}\) examined the sorption of ammonium complex compounds of nickel and other metals by platinised active carbons. An attempt was made to establish the sorption mechanism of complex compounds. The experiments were carried out in a hydrogen atmosphere and in air. The authors revealed that sorption of ammonium complexes predominately follows an electrochemical mechanism. It was shown that cations of \([\text{Zn(NH}_3)_4\text{]}^{2+}\), \([\text{Cd(NH}_3)_6\text{]}^{2+}\), and \([\text{Ni(NH}_3)_6\text{]}^{2+}\) are only removed by hydrogenated carbon. Complete desorption was observed when the gas atmosphere was changed. Figure 3.3 presents the sorption isotherms for ammonium complexes of zinc, nickel and cadmium.
3.3.7 Copper sorption by active carbon

Copper is an essential element to the human body and the adult daily requirement has been estimated at 2.0 mg. Large oral doses may, however, produce emesis and, if prolonged, may result in liver damage. Copper is a relatively inert element and widely used in water distribution and domestic plumbing. EC legislation adopted a relatively high concentration allowed in drinking water (100-3000 µg/l).

A significant number of papers on copper sorption have been published to date. Sorption process modelling is a current topic of interest for the prediction of metal partitioning between an aqueous solution and a solid surface. Copper is regarded as a model metal ion in the characterisation of sorptive properties of different sorbents since its presence is easily determined by various analytical techniques and its chemistry in aqueous solutions is relatively well understood. Thus, copper sorption by granular active carbon (Calgon Filtrasorb 400) has been reported by Chen et al. The carbon used was characterised by pH-titration and on this basis the point of zero charge was found to be at pH 9.5. The surface charge was observed to increase with pH decreasing. Copper sorption strongly depends on solution pH and increases from...
10 to 95 % over the range pH 2.3 to 8. In order to describe the metal sorption the two-pK triple-layer model was employed. Sorption kinetics algorithm (KINEQL) was used to represent the experimental data. The authors found that the model correlates with the experimental measurements of surface charge, sorption equilibrium and kinetics of sorption reasonably well. According to the calculations, copper removal is attributed to the formation of the surface-metal complexes SO' Cu^2+ and SO'CuOH^+ (a hydrolysis product of complexes SO-Cu^2+) in the outer layer around the surface of carbon (S represents carbon surface). It was also suggested that mass transfer controls the sorption rate indicating that sorption occurs in the micropore region where both external mass transfer and diffusion are important. The authors however admitted some disagreement between experimental and modelled results, attributing this to some other unknown reactions.

Seco et al 63 investigated the removal of copper, nickel, zinc and cadmium by granular active carbon Darco 12 - 20 mesh (Aldrich). Metal uptake increased with pH whereas the growth in initial metal concentrations at constant carbon dose had an opposite effect on metal removal. The sorption processes were modelled using the surface complex formation (SCF) Triple Layer Model (TLM) with an overall surface bidentate species. According to the SCF theory, the increase in metal removal as pH increases can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower coulombic repulsion with the sorbed metal. The TLM surface complexation model successfully predicted experimental pH-removal curves for the sorption of single copper and nickel, although at lower metal concentrations, model predictions slightly underestimate copper and cadmium removal and overestimate nickel uptake. Sorption from aqueous solutions of binary metal mixtures of copper-nickel, copper-cadmium and copper-zinc showed competition for the available sorptive surface sites. Copper appeared to have a stronger attraction to the carbon, and also showed higher removal percentage at the same pH as the other three metals. The presence of competitive metals hardly affected the removal of copper.
3.4 Reductive Sorption of Metals by Active Carbons

The interaction of electrolytes with active carbons is not solely restricted to adsorption. Different chemical processes usually accompany adsorption. These processes result in conversion of the compounds sorbed and sometimes change the properties of the carbon itself. Redox processes are often observed in the presence of active carbons. The ability of active carbons to reduce various compounds and ions (e.g. transition metals) has been known for a long time. Avery 64, later followed by Bartell and Miller 6,65 and other researchers 66,3,67,21 demonstrated that gold, silver, platinum, mercury, etc. on contact with active carbon can be reduced to ions with lower valency and even to a free metal state 6. The reduction of iron, copper, chromium, etc. by active carbons is also documented in the literature. 13,67, 68,21

The reduction process can occur entirely by an electron transfer mechanism e.g. the reduction of iron (III) to iron (II) on active carbon 69:

$$C_x + Fe^{3+} + 3Cl^- \rightarrow C_x^+ \ldots \ldots Cl^- + Fe^{2+} + 2Cl^- \quad (1)$$

In other cases where stronger oxidising agents are involved (gold(III), silver(I), chromium(VI), etc.) the oxidation of carbon occurs. The carbon can be oxidised to form various surface oxides (functional groups) and even to form carbon monoxide and carbon dioxide. In this case, the reduction is often accompanied by acidification of solution 65,64:

$$4AuCl_3 + 6H_2O + 3C \rightarrow 4Au + 12HCl + 3CO_2 \quad (2)$$

Electron-exchange properties of carbons strongly depend on the chemical nature of the carbon surface. Different authors related the electron-exchange properties of carbons to the existence of certain redox-groups on the surface 70. 71. 72. 73. Thus, Huang and Blankenship 73 studied mercury removal by various acidic and basic active carbons. Mercury sorption is found to follow two mechanisms, i.e. sorption and reduction. The authors distinguished between mercury removed by these two mechanisms. It was suggested that surface functional groups are responsible for
mercury reduction. However the researchers failed to specify which particular groups act as reducing agents. An important observation was made indicating that Filtrasorb 400 active carbon has a higher reducing capability despite its lower sorptive capacity for the metal. Acidic carbons, Nuchar SA and Nuchar SN, are shown to possess lesser metal reducing properties. Masutin et al 72 investigated oxidation-reduction process in the iron(III)-iron(II) system using various active carbons. The researchers determined the amount of different surface functionalities such as aldehyde, quinone, peroxide and other groups. Based on the results of the experiments, the authors concluded that aldehyde and alcohol functionalities are responsible for the reduction of iron(III). -Iron(II) is found to be oxidised by quinone and peroxide groups. Matskevich et al 69 established the link between the function of carbon as an oxygen electrode and the ability of carbon to reduce oxidising ions in solution. The authors showed that the reducing ability of carbon deteriorates as the degree of carbon oxidation increases.

Strelko 74, 75 argued that reduction is not accomplished by the surface functional groups but by direct interaction of oxidising ions with the carbon surface. Carbon materials being semiconductors possess free electrons in the \( \pi \)-conjugated system (Chapter 2). These electrons can be relatively easily accepted by any electrophilic group. The formation of a positive charge on carbon accompanied by negatively charged hydroxyl ions in the double electric layer can be described by the sequence of processes starting from the formation of highly reactive anion-radical \( \mathbf{O}_2^- \):

\[
\begin{align*}
\text{Carbon} + \mathbf{O}_2 & \rightarrow \text{Carbon (+) + } \mathbf{O}_2^- \\
\end{align*}
\]  

These anion-radicals are easily identified by ESR technique. Further transformations in the water-carbon system are presented by the following schemes:
These schemes describe the mechanism of oxygen reduction of the carbon surface and indicate that hydroxyl-anion is a final product of all the transformations, neutralising the positive charge on the carbon surface (the hole-type centre of the semiconductor). The electron transfer schemes considered in the carbon-oxygen-water system can be confirmed by characteristic redox reactions with polyvalent oxidising ions such as iron(III), gold(III), chromium(VI), manganese(VII), etc.

Oxidised carbon is a significantly less energetic reducing agent than active carbon with basic properties. The study of electron-exchange properties in oxidised carbons is important both theoretically and practically since these sorbents are often used for the removal of transition metal species. These metals may possess variable valencies and they can often change valency during interaction with carbon materials. The selectivity of oxidised carbons towards different valency forms of metals can significantly vary. For example, the selectivity of the carbon towards iron(III) is much higher than that for iron(II) \(^{76}\). Besides conventional ion-exchange on oxidised carbons, other surface processes can occur. These can be surface complex formation, hydrolysis, non-equivalent cation removal, anion sorption, and redox reactions. Thus it has been found that oxidised carbon can selectively remove metal ions in anionic form from aqueous solutions \(^{76,14}\). This phenomenon was observed during the study of molybdenum(VI) removal from aqueous solutions. It has been shown that molybdenum(VI) is sorbed well by anion-exchange resins and active carbons with anion-exchange properties \(^{77}\). However, further study \(^{14,76}\) revealed that the presence of foreign ions in the solution has an adverse effect on molybdenum(VI) removal.
However, if oxidised carbon (cation-exchanger) is used as sorbent, the removal of molybdenum(VI) is not hindered by the presence of foreign ions. Effective sorption of metal was observed for both anionic and cationic species i.e. Mo$^{5+}$ and MoO$_4^{2-}$. The maximum metal uptake was achieved in the pH interval of 2-3 (Figure 3.4).

Molybdenum is sorbed by active carbon and its oxidised modification according to different mechanisms. Active carbon removes anionic species of the metal whereas the presence of oxidised carbon initiates the equilibrium shift between cationic and anionic species$^{76}$:

\[
 m\text{MoO}_4^{2-} + H^+ \Leftrightarrow \text{(polymolybdates @ pH<7)} \Leftrightarrow (\text{H}_2\text{MoO}_4 \times x\text{H}_2\text{O})_m \Leftrightarrow \]
\[
 \Leftrightarrow [H^+] + m/n[(\text{MoO}_y)_n]^{2+} \quad (@ \text{pH}=1.1)
\]  

(9)

Cationic species are then selectively sorbed by oxidised carbon. Consequently, during the interaction between molybdenum and oxidised carbon, the metal can undergo changes between cationic and anionic forms, reduction to lower valency, and polymerisation in the pores of the sorbent.

![Figure 3.4. pH dependence of molybdenum(VI) removal by different active carbons$^{14}$](reproduced from original article)
3.5 Humic Compounds in the Removal of Heavy Metals by Active Carbons

Humic substances are abundant and important components in the natural environment. They are a constituent of natural organic matter (NOM) which forms part of the complex matrix of organic compounds present in natural waters. In surface waters, heavy metals may form complexes with NOM, particularly with ill-defined humic and fulvic acids. For example, Table 3.5 presents lead speciation in surface water indicating the existence of lead - humic/fulvic acid complexes. The role of humic compounds in binding organic or inorganic pollutants has been investigated by scientists for many years. Metal ion sorption on humic substances has also been thoroughly studied. Thus, removal of heavy metals such as chromium, lead, copper, cadmium, silver, lithium and cobalt by humic acids was investigated by Yu et al. Single ion and multiple ion sorption studies were reported. A comparison of different metal ions sorbed on a mass basis by humic acids is listed in Table 3.6. The percentage amount of metal removed by humic substances was in order Cr(III) > Pb(II) > Cu(II) > Cd(II) > Ag(I) > Li(I) = Co(II). Chromium and lead showed greater sorption amongst the seven metals from the single ion system.

The presence and competitiveness of chromium in a multiple ion mixture greatly reduced the amount of all other metals sorbed.

The molecular size and chemistry of humic and fulvic acid significantly affects their ability to be adsorbed. Humic acids are generally large molecules, equivalent to spherical particles with diameters of 60-100 Å whereas fulvic acids generally have a molecular size of 20-30 Å. At high sample concentrations, low pH, and high amounts of neutral electrolytes, humic and fulvic acids behave like rigid "spherocolloids". In contrast, flexible linear colloids are observed at low sample concentration, neutral pH, or low ionic strengths. The large molecular size will generally prevent the substances from entering the micropores of sorbents. However, many granular active carbons posses mesopores (20-100 Å), which accelerate their adsorption kinetics of humic and fulvic acids.
### Table 3.5. Lead species in water

<table>
<thead>
<tr>
<th>Metal species</th>
<th>Free Metal Ions</th>
<th>Inorganic ion pairs: Organic chelates</th>
<th>Organic complexes</th>
<th>Metal species bound to high molecular weight organic material</th>
<th>Metal species adsorbed on colloids</th>
<th>Metals incorporated with organic particles and remains of living organisms</th>
<th>Mineral solids: Metals adsorbed on solids: Precipitates and co-precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example</td>
<td>Pb$^{2+}$</td>
<td>PbHCO$_3^+$</td>
<td>Pb-fulvic acid</td>
<td>Pb-humic acid</td>
<td>Pb-Fe(OH)$_3$</td>
<td>Pb-organic solids</td>
<td>Pb-clay</td>
</tr>
<tr>
<td></td>
<td>Pb-EDTA</td>
<td>Pb-EDTA</td>
<td>Acid</td>
<td></td>
<td>Pb-MnO$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The table above lists the various forms of lead species in water, categorized by size and solubility. The table includes examples of lead species in different forms, such as Pb$^{2+}$, PbHCO$_3^+$, and Pb-EDTA.
<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Amount sorbed, (mg mg$^{-1}$)</th>
<th>Percentage sorbed, (%)</th>
<th>Amount sorbed, (mg mg$^{-1}$)</th>
<th>Percentage sorbed, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>0.294</td>
<td>81.0</td>
<td>0.294</td>
<td>65.0</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>0.793</td>
<td>53.0</td>
<td>0.277</td>
<td>13.0</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.189</td>
<td>39.0</td>
<td>0.014</td>
<td>3.0</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.129</td>
<td>17.0</td>
<td>0.005</td>
<td>1.0</td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.014</td>
<td>3.0</td>
<td>9.85 x 10$^{-4}$</td>
<td>0.0</td>
</tr>
<tr>
<td>Ag(I)</td>
<td>0.075</td>
<td>10.0</td>
<td>0.014</td>
<td>2.0</td>
</tr>
<tr>
<td>Li(I)</td>
<td>0.002</td>
<td>4.0</td>
<td>0.000</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3.6. Comparisons of sorption results of single ion vs. multiple ion in humic acids.\textsuperscript{80}

(reproduced from original article)

Frederick et al\textsuperscript{82} found that calcium sorption can be correlated to NOM loading onto active carbon F 400. A linear relationship was observed between the NOM loading and calcium uptake. Calcium tends to catalyse burn off resulting in a reduction of the carbon mass and surface area during thermal regeneration. Karanfil et al\textsuperscript{83} suggested that surface oxidation of F 400 reduced the uptake of NOM. Heat treatment of the carbon surface did not increase the uptake suggesting that the low degree of oxygen functionality did not interfere with the removal. Lafrance et al\textsuperscript{84, 85} studied the adsorption of humic substances on F 400 active carbon in the presence of sodium salts. They also observed that the increase in capacity was due to the neutralisation of the negative charges on the humate molecules and surface functional groups on the carbons, thus reducing the electrostatic repulsion. Newcombe\textsuperscript{86} investigated the adsorption of the fulvic acid fraction, since humic acids were generally removed by conventional water treatment processes of coagulation, settling and sand filtration. He observed Langmuir type isotherms suggesting that F 300 had a high affinity for fulvic acid. At low surface concentrations he concluded that the molecules were adsorbed
by ion pair formation between the carboxyl groups of the humic material and positive groups on the surface of the carbon.

The effect of humic substances on chromium(III) and chromium(VI) sorption from aqueous solution by conventional active carbon and its oxidised modification was studied by Bautista-Toledo et al. The presence of humic compounds can influence the removal of metal ions from aqueous solutions (Figure 3.5).

![Figure 3.5](image)

**Figure 3.5.** Relative Cr(III) and Cr(VI) uptake on conventional (M) and oxidised (MO) active carbons in the presence of humic acid (HA). (reproduced from original article)

Humic substances can change the surface charge density of the sorbent, block some adsorption sites and form complexes with trace metals. The authors reported that a large decrease in chromium sorption was observed at low concentrations of humics for conventional active carbon. As the concentration of humics increased, a sharp rise in chromium(III) removal was observed. This was explained on the basis of a blockage effect of the adsorbed humics on the carbon surface. When the humic acid concentration increases, the surface of carbon is increasingly covered by the acid molecules. It was suggested that chromium(III) interacts with negatively charged unbound functional groups of humic compounds adsorbed by the carbon.
Chromium(VI) removal remained very low and was scarcely affected by the increase in humic concentration. This behaviour was attributed to the sorptive competition between CrO$_4^{2-}$ ions and humic molecules sorbed on the carbon. It was suggested that active carbon has higher selectivity towards humic substances. As far as oxidised carbon is concerned, the decrease in metals removal was observed at low humic acid concentrations. The increase in the humic concentration did not affect the removal of both chromium valent forms. The authors argued that oxidised carbon possesses a higher affinity for chromium(III). It was suggested that chromium(VI) is partially reduced to lower valency and then preferentially removed by the carbon.

### 3.5.1 Oxidised carbons and humic compounds

Active carbons oxidised by hot air $^8$ and nitric acid $^{88}$ are known to possess high selectivity with respect to multivalent metal ions $^{36, 38}$. In a number of cases these carbonaceous materials are more effective than ion-exchange resins for extraction of certain metal ions from complex solutions $^{76, 14}$. However when carbon is oxidised in the liquid phase and brought into contact with alkaline solution the latter acquires a brown colour. This colour is deeper with increasing degree of carbon oxidation $^{89, 36}$. The colouration is produced by leaching of certain substances formed on the carbon surface during the oxidation process. These compounds are found to belong to the class of humic acids $^{90}$ which are very strong complexing agents $^{91, 92}$. Kuzin and Strashko $^{36}$ studied the infrared spectra of the by-products of carbon oxidation in an attempt to gain additional information on the nature of the surface compounds. The authors also tried to relate the selective properties of oxidised carbons to the presence of humic substances on the carbon surface. The research revealed that the humic compounds extracted from the carbon surface were similar in nature to those obtained from other sources i.e. naturally occurring humic substances. The authors also discovered structural similarity between the carbon surface and the humic acid molecules. It was suggested that oxidised carbon should exhibit selectivity towards the metal ions which form complex or insoluble compounds with humic acids.

Earlier research performed by Chuveleva et al $^{93, 94, 95, 96}$ revealed that the sorptive and selective properties of soil-extracted humic acid are identical to those of the carboxylic ion-exchange resin (KB-4). Humic compounds however dissociate in a
more acidic medium than the carboxylic acid resin. Like oxidised carbons, humic acids possess two major types of functional groups: carboxylic and phenolic. Sulphonic acid resin (KU-2) is shown to possess a much lower selectivity towards heavy metals than humic substances.

\section*{3.6 Radionuclides Removal by Active Carbons}

The presence of radioactivity in the environment may be due to a variety of sources. Human activities involving nuclear weapons and the nuclear fuel cycle (including mining, milling, fuel enrichment, fabrication, reactors, spent fuel stores, reprocessing facilities and waste storage) are important, leading to significant creation and release of radioactivity. The burning of fossil fuels also releases pre-existing natural radionuclides into the atmosphere. Besides planned radioactivity discharges arising from operations associated with the nuclear fuel cycle, radionuclides may enter the environment as a consequence of accidental releases. Some important non-routine releases which have occurred include that due to an explosion in a high-level waste storage tank at Kyshtym, USSR (1957), and those involving nuclear reactors at Windscale, UK (1957); Three Mile Island, USA (1979) and Chernobyl, USSR (1986). The majority of radionuclides generated in these processes have a very short half-life and decay to stable chemical elements in a relatively short time (e.g. barium-143 has a half-life of only 12 seconds). However there are several radioactive isotopes which possess a very long decay time (e.g. the beta-decay half-life for technetium-99 is $2.1 \times 10^5$ years).

In the recent years, public concern about environmental issues has risen tremendously and the regulations for discharging liquid radioactive effluents and dumping solid waste into the environment are becoming more stringent day-by-day. In order to meet these strict requirements, researchers are facing the challenge of improving existing treatment techniques and developing new decontamination methods. The search for new sorptive materials for effluent treatment as well as for conditioning and purification of potable water is still a major challenge.
Radionuclides in liquid wastes from nuclear installations are mostly removed by primary treatments such as evaporation, ion-exchange and precipitation methods. Evaporation is an energy inefficient process. Precipitation is a batch process and involves the filtration of large volumes of liquid. Ion-exchange possesses the obvious advantage that it can be used on a semi-continuous basis in a set of fixed columns. However, ion-exchange utilises costly inorganic or polymeric materials which are affected by elevated levels of radiation and increased temperatures. They are also unstable in corrosive media and are not highly selective. Carley-Macauly presented a comparison of polymeric resins and inorganic ion-exchangers with respect to their potential applications in the nuclear industry (Table 3.7). Therefore, the development of a new sorptive material which would be free of the drawbacks mentioned above would make the task of treatment and disposal much easier.

Active carbon can provide an alternative to other expensive ion-exchangers because of its high mechanical and chemical stability, high selectivity, cheap and simple manufacturing process, possibility of volume reduction by incineration, and possibility of altering the physical and chemical properties according to requirements of a particular process.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Organic Resins</th>
<th>Inorganic Sorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal stability</td>
<td>Fair-Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Radiation stability</td>
<td>Fair-Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Resistance to oxidation</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Exchange capacity</td>
<td>High</td>
<td>Low-High</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Available</td>
<td>Available</td>
</tr>
<tr>
<td>Regeneration</td>
<td>Good</td>
<td>Uncertain*</td>
</tr>
<tr>
<td>Specificity</td>
<td>Not Known</td>
<td>Available</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Good</td>
<td>Variable*</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>Low-High*</td>
</tr>
<tr>
<td>Availability</td>
<td>Good</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Immobilisation</td>
<td>Limited</td>
<td>Good</td>
</tr>
<tr>
<td>Handling</td>
<td>Good</td>
<td>Fair-Variable</td>
</tr>
</tbody>
</table>

Table 3.7. General comparison of organic and inorganic ion-exchangers. *Information is limited mainly to that available from small-scale research work.
The current use of active carbon in the nuclear industry is restricted to gas phase applications. Carbon materials are used in nuclear power plants to prevent the release of radioactive gases and vapours into the atmosphere e.g. radioactive iodine, organic iodides (mostly methyl iodine) and noble gases (krypton, xenon and helium). The gases are not captured entirely, but their passage is delayed long enough to allow the radioactive decay of short-lived species. Active carbons are also used to eliminate radon, a toxic radioactive gas associated with the mining of uranium $^{101,98}$.

The limited amount of research conducted with active carbons has shown promising results in the removal of certain radionuclides from aqueous solutions. Rivera-Utrilla et al $^{102}$ reported on the removal of radioactive caesium, thallium, strontium and cobalt by three active carbons from aqueous solutions. The carbons used were different in surface chemical nature and structural characteristics. The removal of radionuclides as a function of time was investigated. The authors observed low sorptive capacity (selectivity) for all active carbons towards caesium. On the other hand, the amount of thallium removed by the sorbents was found to be high (approaching 100 %). The researchers attempted to relate metal ion removal to ionic and hydrated radii and carbon pore structure. It was suggested that because of the low polarising power of $\text{Cs}^{+}$ (as deduced from the ratio of ion charge to ionic radius), the carbon-caesium interaction is too weak and therefore caesium ions are retained only on those surface centres which exhibit a high negative surface charge density. The paper, however, failed to satisfactorily explain why thallium, being similar to caesium with respect to ionic and hydrated radii, is removed much better. It is also not clear why single valent thallium is sorbed better than double valent strontium and cobalt.

Radioactive pertechnetate ion ($\text{TcO}_4^-$) sorption from aqueous solutions has been compared for activated carbons derived from different precursors $^{99}$. The carbons used in this study were alkaline in nature. The best technetium uptake is found to be in the acidic pH region. This phenomenon was attributed to the reaction of pertechnetate-anion with oxonium ions generated by the interaction of $\text{H}^+$ with the functional groups of activated carbon. The authors concluded that active carbons derived from coconut shell and oil pitch are the most suitable for technetium removal.
The article however fails to provide any information on the capacities of the sorbents for the pertechnetate ion.

Litman et al.\textsuperscript{103} performed an investigation using active carbon (F 400) to remove such radioactive metals as chromium-51, cobalt-60, zinc-65, caesium-137, iron-59 and antimony-124 and other radionuclides from liquid waste generated by a small nuclear reactor. Most of the waste arose as a result of ion-exchange resin regeneration. The sorption experiments with active carbon were carried out in an acidic medium (pH 3). The results revealed that active carbon treatment of aqueous reactor wastes can substantially remove certain radioactive elements. Those which are removed to the most significant extent were chromium-51, zinc-65, iron-59, cobalt-60, tungsten-181 and caesium-137. It was suggested that the carbon adsorbs H$_3$O$^+$ ions; the total amount adsorbed depends on the mass of carbon and the pH of the influent solution. The carbon surface, once coated with H$_3$O$^+$, can act as a complexation site for negatively charged ions. This paper however did not provide any quantitative results.

The removal of cobalt-60 by active carbons was investigated by Litman et al.\textsuperscript{104} and Paajanen et al.\textsuperscript{105}. Metal removal was studied at different pH values and in the presence of various ionic species such as chloride, borate and citrate. Increased removal of cobalt was observed at higher pH values (Table 3.8).

<table>
<thead>
<tr>
<th>Time, min</th>
<th>pH</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.49</td>
<td>13</td>
</tr>
<tr>
<td>20</td>
<td>7.80</td>
<td>90</td>
</tr>
<tr>
<td>40</td>
<td>7.87</td>
<td>90</td>
</tr>
<tr>
<td>60</td>
<td>7.93</td>
<td>92</td>
</tr>
<tr>
<td>120</td>
<td>7.89</td>
<td>99</td>
</tr>
<tr>
<td>240</td>
<td>7.86</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 3.8. Variation of cobalt removal efficiency with time\textsuperscript{104}.

Solution composition: 25ml of 160ppb of Co, 600ppm of boric acid, 0.16ppm of Li. Mass of carbon: 1g
It was suggested that at higher pH values there is a larger percentage of conjugate base species of weak acids $\text{H}_2\text{C}_2\text{O}_4$, $\text{H}_3\text{BO}_3$ ($\text{C}_2\text{O}_4^{2-}$, $\text{B(OH)}_4^-$). These Lewis-type bases could be acting as complexing agents for metal ions such as cobalt, yielding anionic complexes. These complexes are then removed by carbon material.

### 3.6.1 Radiation stability of resins and carbons

The removal of radionuclides from nuclear wastes is usually performed by ion-exchange. However, the use of organic ion-exchange resins for this purpose is somewhat limited due to their low stability in ionising radiation fields. Thus, Dessouki et al.\(^{106}\) reported on radiation stability of strongly acidic cation-exchange resin based on styrene-DVB copolymers. Radiation stability was assessed on the basis of changes in exchange capacity, loss of weight, change of swelling behaviour, etc. A loss in capacity of up to 44% was observed for specimens of resin in $\text{H}^+$-form irradiated to 1000 Mrad. The reduction in capacity was accompanied by a loss of weight and a decrease in the degree of swelling of the irradiated resin. The authors also detected the formation of carboxylic and phenolic groups on the resin surface.

The study carried out by Kuzin and Semushin\(^{107}\) revealed that oxidised carbons may provide an alternative to polymer-based ion-exchange resins. The researchers compared the radiation stabilities of weakly acidic resins KFU, KB-4P-2 and KMT to that of oxidised carbon under the action of $\gamma$-radiation generated by cobalt-60. The influence of $\gamma$-radiation upon the ion-exchange properties of the sorbents investigated is presented in Table 3.9. The authors concluded that the oxidised carbon and KFU resin are very stable under irradiation whereas KB-4P-2 and KMT resins drastically lose their ion-exchange capacity and stability under increased levels of $\gamma$-radiation. The degree of swelling for these two resins rises sharply in the alkaline solution after exposure to radiation. Kuzin et al.\(^{108}\) studied the effect of $\gamma$-radiation from cobalt-60 on the cation- and anion-exchange properties of active and oxidised carbons. The carbons investigated were irradiated with a dose rate of 200 roentgen/s. The ion-exchange capacity, moisture capacity and pore volume of all the carbon samples remained virtually unchanged in the radiation exposure range from 0 to $1.5 \times 10^8$ roentgen. Furthermore, in contrast to polymeric resins, there were no visible changes, gas release or irradiation products observed for the sorbents studied.
Table 3.9. The influence of γ-radiation on the ion-exchange properties of some sorbents.

(reproduced from original original article)

The nature of the surface oxidation also remained unchanged. Similar observations were also reported by Nair. Evidently the carbon atoms of the crystallites and of the amorphous carbon in the active carbons are able to disperse the energy of the ionising radiation without a noticeable change in the structure of the sorbent. It was concluded
that ion-exchange materials based on active carbon are very promising sorbents for use in the treatment of highly active solutions.

3.6.2 Radionuclide removal by oxidised carbons

Unplanned release of radioactive elements into the environment is often associated with accidents at nuclear installations. The most serious accident to have occurred in the history of nuclear reactor operation was in April 1986 at the Chernobyl nuclear power plant located in Ukraine. After 10-days of radionuclide release following the accident, some $2 \times 10^{18}$ Bq of activity, due to condensable radioactive fission and transuranium activation products, was present in the environment. Radioactive elements released after the Chernobyl accident were detected throughout the northern hemisphere $^97$. This event boosted the development of new sorptive materials for environmental decontamination. The possibility of radioactive elements removal by oxidised carbons was studied by Strelko et al $^{109, 110}$. The carbons used in this research were derivatives of polymeric resin, apricot stones and wood. The selectivity series for sorption of various radionuclides on oxidised carbons from solutions of different nature (i.e. potable water, sea water, fluids of human organism) were determined as follows:

$$^{140}La > ^{141}Ce > ^{103}Ru > ^{95}Zr > ^{95}Nb > ^{90}Sr > ^{140}Ba > ^{137}Cs$$

Nair $^98$ carried out a detailed investigation of the removal of caesium and strontium by modified commercial active carbons. The modification of carbons was performed in hot air and in nitric acid. The maximum uptake of radionuclides from buffered solutions was at pH 8.5 whereas very low sorption levels were observed below pH 2. Sorption from radionuclide mixtures by oxidised carbons was reported by Nair $^98$. The selectivity sequence was found to be determined by ionic charge:

$$\text{Eu}^{3+}, \text{Am}^{3+} > \text{Sr}^{2+}, \text{Co}^{2+} > \text{UO}_2^{2+} > \text{Cs}^+$$

The predominant mechanism of radionuclide removal by carbon materials was determined to be ion-exchange.
3.7 Concluding Remarks

The use of carbon materials for the removal of heavy metals from aqueous solutions has relatively good coverage in the available literature. However the metal removal mechanism is not completely understood. Sorption of metals from aqueous solutions by carbons is a complex phenomenon. Sorption is determined by several factors such as physico-chemical properties of carbons, metal ion chemistry in the solution, the presence of complexing agents, competition between the ions, solution pH, etc. An example of the complex nature of sorption on carbons can be illustrated with some multivalent metal ions. Quite often the removal of these ions is not limited to ion-exchange only. It is usually accompanied by some parallel processes, such as oxidation, reduction, formation of insoluble metal hydroxide substances, and decomposition of metal complex compounds in the solution as well as alteration of the properties of carbon itself, e.g. as an ion-exchanger (gas electrode).

There is now great concern about the levels of heavy metals present in the environment. Active carbon is already in use in water treatment processes for the removal of organic pollutants. It would be advantageous if carbon materials were further investigated for the removal of heavy metals. There is strong evidence that modification of active carbons helps improve their sorption capacity and most importantly their selectivity towards heavy metal ions. It is necessary to emphasise that information on the carbon surface acidity is crucial to the satisfactory achievement of metal removal from aqueous solutions. Although this area has been relatively well investigated there is still a need to study this phenomenon further together with surface characterisation of carbonaceous materials.

3.8 References


81. Stumm, W. and Bilinski, H. Trace Metals in Natural Waters: Difficulties of Interpretation arising from our Ignorance of their Speciation; in Advances in Water


Chapter 4: Experimental

4.1 Sorptive Materials

A wide range of carbon sorbents have been prepared possessing different porous structure in the micropore and meso/macropore region as well as differing in surface chemistry. One of the carbons was also modified to introduce relatively strong acidic phosphonic and phosphoric surface groups which essentially alters the interactions between the adsorbent surface and the heavy metals in aqueous solution. This phosphorus-containing carbon was synthesised in collaboration with Dr. O. Kozynchenko, the Institute of Sorption and Endoecology Problems, Kiev, Ukraine, during his work in Loughborough (EC INTAS research grant No 94-3033).

Several sorptive materials were selected for this project. Activated carbons derived from agricultural by-products, designated as KAU, were precursors for oxidised activated carbons used in this study. Some adsorbents were provided by the Institute of Sorption and Problems of Endoecology (ISPE), National Academy of Sciences (NAS) of Ukraine, Kiev. These were polymer-based carbon CKC and oxidised KAU carbon (designated as KAU-1.6). The carbons studied were compared with carboxylic resin Purolite C 104 and commercially available Filtrasorb 400 activated carbon. The sorbents tested in this project are summarised in Table 4.1.

Polymer-based synthetic carbons were chosen for this project because of their unique crystalline structure. These carbons possess more perfect graphite-like planes in the carbonaceous matrix (i.e. fewer structural defects because of the absence of mineral impurities). As a consequence these sorbents possess remarkable sorptive, catalytic and electrochemical properties and differ from technical grade conventional active carbons produced from naturally occurring raw materials.

All sorbents were obtained in large particle size (approx. 850-1500 µm). These sorptive materials were size reduced by grinding into different fractions. The
fractions were washed thoroughly with distilled water to remove fine particles and then dried in an oven at 105°C overnight before use. After drying, the materials were stored in air-tight containers. The term “as received” has been used for these sorbent fractions.

<table>
<thead>
<tr>
<th>Sorptive Material</th>
<th>Precursor</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU carbons</td>
<td>Apricot stones</td>
<td>ISPE</td>
</tr>
<tr>
<td>Filtrasorb 400</td>
<td>Coal</td>
<td>Chemviron</td>
</tr>
<tr>
<td>CKC</td>
<td>Styrene/DVB copolymer</td>
<td>ISPE</td>
</tr>
<tr>
<td>PGP-P</td>
<td>Phenol-formaldehyde</td>
<td>Dr. O Kozynchenko, ISPE, (EC INTAS research grant No 94-3033)</td>
</tr>
<tr>
<td>C 104 carboxylic resin</td>
<td>-----</td>
<td>Purolite</td>
</tr>
</tbody>
</table>

Table 4.1. List of sorptive materials used.

4.2 Preparation of Fruit Stones-Based Active Carbons (KAU)

Granulated porous carbons derived from polysaccharides (cellulose) are remarkable sorptive and ion-exchange materials for several reasons. Firstly, the feedstock for production of these sorbents originates from vegetal matter and is abundant in nature. Secondly, the matrix is formed by a rigid carcass of biopolymer which is cross-linked in three dimensions. There is an optimal ratio between hydrogen, oxygen and carbon in the matrix. This makes the material particularly suitable for thermal treatment (carbonisation). However, crushed fruit stones cannot be used for the production of high quality carbonaceous materials without a special pretreatment. Fruit stones are not porous and they contain large amounts of various compounds (lignin, pectin, proteins, vegetable fats, etc.) which drastically reduce the quality of the final carbon obtained by direct thermal carbonisation. These undesirable components form a large quantity of amorphous carbon residue which obstructs the release of pyrolitic gases during carbonisation. As a result, the polysaccharide-derived carbonaceous framework becomes structurally damaged by trapped gases. The final ‘defective’
carbon carcass is not uniform i.e. it is contaminated with unstructured amorphous carbon residue. This leads to the development of additional stress within the carbon lattice and consequently, destruction of particles of carbonaceous adsorbent. Furthermore, lignin pyrolysis is accompanied by the formation of free radicals capable of initiating cellulose destruction. This results in poor mechanical properties of the final product.\textsuperscript{2,3}

Treatment of precursor (cellulose materials) with hot solutions of strong alkalis prior to carbonisation eliminates the majority of the impurities and creates a porous structure in the carbon precursor. Lignin is almost completely removed from the cellulose carcass at this stage thus creating a well developed network of pores. Lignin-free cellulose material still contains hemi-cellulose and mineral admixtures. Treatment of the precursor with hot hydrochloric acid solution results in hydrolysis and partial wash-out of hemi-cellulose and a majority of the mineral impurities. This process further enhances the porous structure of the precursor. The presence of alkaline metals (alkaline treatment) hinders the processes of cross-linking in cellulose necessary to form a rigid lattice. Acid treatment eliminates the adverse effect of various cations by regenerating hydroxyl groups in cellulose thus enabling cross-linking processes to take place.

Preparation of active carbons from agricultural by-products is carried out in six stages as follows:

- Treatment of crushed fruit stones with hot solution of strong alkali;
- Washing with water to bring pH of solution down to 10;
- Treatment of crushed fruit stones with hot hydrochloric acid;
- Washing with water to bring pH of solution up to 4;
- Carbonisation at 350-700°C;
- Activation with steam at 800-850°C.

A simplified chemical scheme to illustrate the carbonisation of cellulosic material carbonisation is presented in Figure 4.1.
4.3 Preparation of Synthetic Polymer-Based Carbons (CKC)

The utilisation of synthetic polymers as precursors for the preparation of carbon materials could be a convenient industrial process. It allows the shaping of sorbents in a desired manner during polymer preparation (pelletisation, spherical granulation, shaped products) to generate the required porous structure, to introduce various heteroatoms and regulate their content, and to control the mechanical properties of the final products\(^4,5\).

The main industrial organic synthesis products which may be used as starting materials for synthetic carbon production are:

- styrene/divinylbenzene copolymers;
- vinylpyridine/divinylbenzene copolymers;
- acrylonitrile polymers;
- acrylonitrile/divinylbenzene copolymers;
- phenol-formaldehyde and other polycondensation resins.

4.3.1 Styrene/DVB copolymer-based carbon (CKC)

Linear polystyrene yields no carbonaceous residue\(^6\). Therefore, styrene polymers are not particularly suitable materials for carbon production. There are two ways to increase the yield of carbon material. The first way is the utilisation of copolymers with a high degree of cross-linking (20-60 % DVB). The yield of carbonaceous solid...
derived from cross-linked polystyrenes increases with the degree of cross-linking of the polymeric precursor. A necessary condition for polystyrene pyrolysis is partial oxidation of the polymer during the course of carbonisation. In the absence of oxygen the yield of carbon is virtually zero regardless of the divinylbenzene content. A chemical scheme for styrene/DVB copolymer carbonisation is presented in Figure 4.2.

![Chemical scheme of styrene/DVB copolymer carbonisation](image)

**Figure 4.2.** Chemical scheme of styrene/DVB copolymer carbonisation. (reproduced from original paper)

The second way of increasing carbon yield is the introduction of oxygen-, sulphur- and chlorine-containing groups into the polymer precursor. Chemical modification prior to thermal treatment increases the yield of carbon and permits the use of copolymers with a low degree of cross-linking (10 % DVB). Additional cross-linking prevents degradation and depolymerisation of precursor in the course of carbonisation. A chemical scheme for carbonisation of chlormethylated styrene/DVB copolymer is shown in Figure 4.3.
4.3.2 Phenol-formaldehyde resin-based phosphorus-containing carbon*

The presence of heteroatoms in the carbon lattice should significantly alter the physico-chemical properties of the sorptive material due to the different electronic structure. Heteroatoms can be introduced into the polymeric material-precursor of carbon. The polymer-precursor is carbonised to yield carbon in which heteroatoms are uniformly distributed in the bulk of the matrix. Phosphorus-containing polymeric materials can be produced by thermal treatment of phenol-formaldehyde (polycondensation) resins phosphorylated with phosphorus oxychloride (POCl₃). Preparation scheme of phosphorus-containing carbon is shown in Figure 4.4 ⁸,⁹.

* Synthesised by Dr. O. Kozynchenko
4.3.2.1 Preparation of polycondensation phenol-formaldehyde resin

The process of emulsion polycondensation in a reactor with a spade-shaped stirrer was applied for granulation of a matured ethanediol solution of precondensed resins. Transformer oil was used as an inert medium (water-in-oil system).

A resin solution was matured in a standard three-necked round bottom glass reactor (1 litre capacity) equipped with a mechanical stirrer, thermometer and air condenser, and heated to the desired temperature in a water-bath placed on a heater.

The granulation process was performed in an enamel-coated metal vessel with a stirrer made of Teflon. Granules of resin were separated by filtration followed by washing with hot distilled water. The washed resin was dried at room temperature in air. The air-dried resin usually contains 40-50 % of solid material (the rest is moisture and transformer oil) and can be used for further treatment.

4.3.2.2 Phosphorilation of polycondensation resin

A sample of the resin was washed with water, dried, washed with iso-propanol-diethyl ether 1:1 (v/v) solution and dried in air at 80°C until constant weight was achieved. 40.0 g of the resin was placed into a 0.5 litre three-necked round bottom flask equipped with a stirrer, thermometer and water-cooled condenser fitted with a drying tube (Figure 4.5).
Figure 4.5. The apparatus for resin phosphorilation. (1) - glass reactor; (2) - stirrer paddle; (3) - thermometer; (4) - water-cooled condenser; (5) - heater; (6) - stirrer motor; (7) - plastic stopper with a glass tube (8) inside; (9) - drying tube.
Dry toluene (200 mL) was added and the mixture was left to stand overnight. Then phosphorus oxychloride (28 mL, 46 g, 0.3 mole) was added to the stirred suspension. The mixture was stirred at room temperature for 2 hours and left to stand overnight. Next day the stirred mixture was heated at a rate of 15°C/hour until boiling temperature (110°C) was reached. Hydrogen chloride was released throughout the course of heating and diminished as the temperature approached boiling point. The reaction mixture was then cooled, and the resin was separated by filtration, washed on the filter with toluene (2 × 50 mL), ether (5 × 50 mL) and dried in air at room temperature first, then at 50°C until air dried.

4.3.2.3 Carbonisation of phosphorilated resin

The phosphorilated resin was placed into a quartz-glass reactor and heated in a furnace at a rate of 5°C/min in a constant flow of oxygen free nitrogen (OFN) at a rate of 150 ml/min until a temperature of 700°C was achieved. A Bunsen burner was placed at the outlet of the reactor to combust the volatile products of carbonisation. Heat treatment of the resin was continued at this temperature for 3 hours. The sample was cooled down in the reactor in the OFN flow to 350°C. Then the quartz reactor with carbonised material was removed from the furnace and further cooled to room temperature in the OFN flow. The apparatus used for high temperature treatment is shown in Figure 4.6.

4.3.2.4 Washing

The carbon produced (yield 20.7 g, about 52 %) was washed in boiling distilled water several times. The carbonaceous material was then treated with a boiling solution of 0.1 N sodium hydroxide followed by washing with distilled water to achieve slightly alkaline solution pH (pH 8-9). The carbon was then washed with hydrochloric acid solution (pH 1) until constant pH. This was followed by washing with deionised water until neutral pH of washings was reached. The final product was dried in air at 80°C until constant weight was achieved.
Figure 4.6. Apparatus for high temperature treatment. (1) - furnace; (2) - control unit; (3) - gas cylinder with OFN; (4) - flow-meter; (5) - quartz-glass reactor with a sample to be treated; (6) - heater; (7) - water-bath; (8) - flask with water and adapter for steam-supply; (9) - Bunsen burner. Route (a) - for carbonisation; route (b) - for activation.
4.3.2.5 Experimental equipment

All high temperature treatments were carried out using an SSL TF-75-45-12N furnace (Severn Science Ltd.). The temperature was maintained using a PyroTherm Furnaces control unit. The flow of oxygen free nitrogen (OFN) from a cylinder supplied by BOC Ltd. was maintained by a Platon flow-meter. The furnace was calibrated before use to establish a zone (Zone A) of minimal temperature gradient (<10°C).

All the weighings for the resin preparation and the determination of carbon burn-offs were made to an accuracy of ± 0.1 g (Sartorius 3703 balance). The bulk density of the carbon was found by weighing the sample into a measuring cylinder and agitating until the sample settled to a constant volume. Density was calculated as weight (g) / volume (cm³).

The structural parameters of the phosphorus-containing carbon are listed in Table 4.2.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity for Na⁺, (mmol/g)</td>
<td>2.1</td>
</tr>
<tr>
<td>Phosphorus content, (mmol/g)</td>
<td>2.55</td>
</tr>
<tr>
<td>Bulk density, (g/cc)</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Table 4.2. Structural parameters of phosphorus-containing carbon.

4.4 Modification of Active Carbons

Various methods of chemical modification of active carbon are described in the scientific literature (Chapter 2). These modifications are aimed at improving ion-exchange properties, and permit different functional groups to be introduced onto the carbon surface. Oxidation is by far the most important carbon modification. Oxidised carbons possess a number of interesting properties such as relatively high ion-exchange capacity and chemical stability, enhanced selectivity related to complexing ability of surface functional groups, and good catalytic activity. These properties can be effectively exploited in many industrial applications such as removal of cationic and anionic contaminants from ultrapure compounds, purification of large volumes of industrial solutions and as catalysts or catalyst supports.
Several simultaneous processes may occur during the course of carbon oxidation. These are redox reactions between carbon and the oxidising agent resulting in the formation of surface functional groups, catalytic decomposition of the oxidant, partial destruction of sorbent matrix and release of humic substances into solution. Active carbon can be oxidised by both liquid and gaseous oxidising agents (e.g. nitric acid, hydrogen peroxide, hot air, etc.). It should be emphasised, however, that synthetic carbons (e.g. CKC type) possess enhanced chemical resistance. Therefore, the oxidation of these carbons by hydrogen peroxide is not applicable due to vigorous catalytic decomposition of the oxidising agent on the carbon surface. Oxidation of synthetic carbon with hydrogen peroxide produces a limited number of surface functional groups. Surface modification with sodium hypochlorite in strong alkaline medium results in severe wash out of humic compounds in sodium form. As a consequence, physico-chemical characteristics of the carbon are adversely affected.

4.4.1 Oxidation of active carbon with liquid reagents.
Oxidation of carbon materials by nitric acid is favored over other oxidation techniques. This method was described in detail by Kuzin et al.\textsuperscript{10, 11, 12}. The liberation of humic compounds from the carbon surface in alkaline solutions is also a characteristic of this modification method. However if the degree of oxidation is not high (capacity not exceeding 2-3 meq/g), coloured compounds can be removed from carbon by washing in alkaline solutions. This oxidation technique is technologically viable and provides good reproducibility allowing uniform sorptive materials to be obtained.

4.4.1.1 F 400 oxidation
The following method of oxidation by nitric acid was used for F 400 modification. Oxidation of carbon was carried out using the apparatus similar to that shown in Figure 4.5.
A five-litre round-bottomed flask with three openings was placed into a temperature controlled water bath. The temperature of the solution was monitored by a thermometer placed in one of the flask openings. A water-cooled condenser was fitted to the flask to prevent liquid loss by evaporation. Activated carbon was added to 8 N nitric acid in the carbon to acid ratio of 1 to 3 by volume. A variable speed stirrer with glass impeller was used to agitate the carbon-nitric acid suspension. The experiment was carried out in the temperature range of 90-95°C for 24 hours. The nitric acid was replaced after 12 hours. After cooling to room temperature the carbon was separated from the solution and washed with distilled water. Washing was continued until solution pH increased to 2-2.5. In order to remove humic substances from the carbon, alkaline washing was applied. Washing was performed in hot 0.1 N sodium hydroxide solution with constant stirring for 5 hours. During washing the solution was replaced several times. Washing was continued until the solution over the carbon became almost colourless. Further washing with 0.1 N hydrochloric acid was carried out under conditions of constant stirring. This was followed by final washing with deionised water. The carbon was washed repeatedly until the solution pH reached 3.5. The carbon was then separated by filtration and dried at ambient temperature until “air dry”. Further drying was performed in an oven at 105°C over night. The carbon was cooled and stored in an air tight container.

4.4.1.2 Oxidation of KAU carbon by nitric acid

Oxidation of KAU active carbon by nitric acid was carried out using the following method developed at the Institute of Sorption and Endocoeology Problems, National Academy of Sciences, Ukraine. The oxidation was performed using apparatus similar to the experimental set-up depicted in Figure 4.5.

Active carbon was demineralised (inorganic components) with 6-10 % (wt.) hydrochloric acid solution at 95-100°C for 2 hours. Demineralisation was followed by several washes with boiling distilled water. The carbon was transferred to a glass reactor containing a 20 % (wt.) solution of nitric acid. The carbon to acid ratio was 1 to 3 by volume. The oxidation was performed in thermostatic conditions at 90-95°C for 15 hours. The oxidant was replaced every 4 hours. Vigorous release of brown
fumes (nitrogen oxides) is taken as the beginning of the oxidation process. Samples of carbon were extracted from the reactor at different time intervals.

The removal of humic compounds from the sorbent includes the following steps: washing the remains of nitric acid with distilled water until pH 2; treatment with hot 1-3 % (wt.) solution of sodium hydroxide until the yellow colouring (leaching of humic substances) in alkaline solutions almost completely disappears; washing the residual of sodium hydroxide with distilled water until pH 9. The conversion of the ionite into hydrogen form was accomplished by treatment with a 2-5 % (wt.) solution of hydrochloric acid. This was followed by a final washing with distilled water until pH 3.5-4. The sorbent was dried at room temperature until 'air dry'. Further drying was performed in an oven at 105°C over night. The carbon was cooled and stored in an air tight container.

4.4.1.3 Oxidation of KAU carbon by hot air

The 'classic method' of carbon oxidation by air is summarised in many scientific publications 13, 14. The apparatus for air oxidation experiments is presented in Figure 4.7. The oxidation of carbon was performed as outlined below.

A sample of carbon (approx. 50 g) was put in a quartz reactor. The reactor then was heated in a tubular furnace equipped with a temperature control unit. Oxidation was carried out in moist air flowing over carbon at a rate of 6-8 litre/hour. The temperature and the time of carbon exposure was variable between 410 and 450°C and between 3 to 5 hours respectively. The quartz reactor containing the carbon sample was occasionally rotated during the course of oxidation. Compressed air from a gas cylinder was used in these experiments. The regulated air flow was conducted to the reactor in the furnace via water in a glass vessel (moist air).

After oxidation the carbon samples were cooled down in the reactor with no air flow and then transferred to air tight containers. The bulk density of the sorptive materials was determined using a Sartorius balance (accuracy ± 0.0005 g)
Figure 4.7. Apparatus for hot air oxidation. (1) - furnace; (2) - temperature control unit; (3) - gas cylinder with air; (4) - flow-meter; (5) - quartz-glass reactor with a sample to be oxidised; (6) - flask with water and adapter for moist air supply.
4.4.2 Static exchange capacity

The static exchange capacity of sorbents for sodium from 0.1 N sodium hydroxide solution is taken to be a measure of the sorbent's oxidation degree\textsuperscript{15, 12}. The static exchange capacity measurements were carried out in a following manner:

200 mg of sorbent was placed in a 50 ml glass conical flask. Then 20 ml of sodium hydroxide of known concentration (approx. 0.1N) was added to the flask. The flask was sealed with Parafilm and then continuously agitated for 24 hours at a constant temperature of 22 ± 2°C. After that an aliquot of 5 ml was extracted from the flask using a Luer plastic syringe and 0.45 µm PVDF disposable microfilter (Whatman). The aliquot was titrated with hydrochloric acid solution of known concentration (approx. 0.1N). The indicator used in this test was ethanol-water solution of methyl red. Each titration was repeated twice and the average value of the two experiments was taken. The capacity was calculated from the decrease in alkali concentration. Sodium capacity was expressed as the number of milliequivalents of sodium hydroxide removed per gram of dry sorptive material (meq/g).

Table 4.3 presents the conditions of oxidation and some properties of the materials produced.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Oxidising agent</th>
<th>Exposure time, h</th>
<th>Temperature, ( ^\circ \text{C} )</th>
<th>Bulk density, ( \text{g/cm}^3 )</th>
<th>( \text{Na}^+ \text{capacity, meq/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td></td>
<td></td>
<td></td>
<td>0.33</td>
<td>0.4</td>
</tr>
<tr>
<td>KAU-1.5</td>
<td>HNO\textsubscript{3}</td>
<td>2</td>
<td>90-95</td>
<td>0.30</td>
<td>1.7</td>
</tr>
<tr>
<td>KAU-1.9</td>
<td>HNO\textsubscript{3}</td>
<td>5</td>
<td>90-95</td>
<td>0.34</td>
<td>2.0</td>
</tr>
<tr>
<td>KAU-2.2</td>
<td>HNO\textsubscript{3}</td>
<td>10</td>
<td>90-95</td>
<td>0.34</td>
<td>2.6</td>
</tr>
<tr>
<td>KAU-2.7</td>
<td>HNO\textsubscript{3}</td>
<td>15</td>
<td>90-95</td>
<td>0.37</td>
<td>2.8</td>
</tr>
<tr>
<td>KAU-0.8</td>
<td>Air</td>
<td>2</td>
<td>410</td>
<td>0.32</td>
<td>0.8</td>
</tr>
<tr>
<td>KAU-1.2</td>
<td>Air</td>
<td>3</td>
<td>430</td>
<td>0.31</td>
<td>1.3</td>
</tr>
<tr>
<td>KAU-1.8</td>
<td>Air</td>
<td>5</td>
<td>450</td>
<td>0.32</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 4.3. Conditions of oxidation and some properties of the oxidised carbons.
4.5 Characterisation of Sorbents

4.5.1 Elemental analysis

Major structural components (i.e. carbon and hydrogen) of the carbon matrix and of structural heteroatoms (i.e. nitrogen, sulfur, phosphorus) were determined by elemental analysis. An elemental analysis oxidised F 400, KAUini, KAU-2.7, PGP-P and CKC was performed in the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow. The samples were analysed on a Perkin Elmer Series II 2400 elemental micro analyser. The estimated error for each element analysed was ± 0.5%.

4.5.2 Phosphorus analysis

A sample of phosphorus-containing carbon (20mg) was placed in an Ehrlenmeyer flask. A mixture of perchloric and nitric acid with a ratio 2 : 1 (v/v) was added to the flask. The flask was heated on a hot plate until the carbon sample was dissolved and white fumes were produced. The flask was then allowed to cool to room temperature. The fluid from the flask was quantitatively transferred into a 100 ml volumetric flask using distilled water (resistance > 15 MΩ). A 5 ml aliquot of this solution was transferred into a 100 ml volumetric flask followed by the addition of 3.5 ml of perchloric acid, 4.5 ml of amidole solution and 3.5 ml of ammonium molybdate solution. The mixture was made up to 100 ml of solution and allowed to equilibrate for 30 minutes. Measurements of phosphorus were performed using a Perkin Elmer Lambda 12 UV-VIS spectrophotometer at 700 nm. A calibration curve for the spectrophotometer was prepared in mg of phosphorus per g of salt using potassium hydrophosphate (K₂HPO₄) as standard.

4.4 g of ammonium molybdate was added to 50 ml of distilled water to prepare ammonium molybdate solution.

- amidole solution was prepared in the following manner (for 4 samples):
- amidole (0.28g) + 0.05 g for each subsequent sample;
- sodium sulphite (Na₂SO₃) 2.8g + 0.5g for each subsequent sample;
- water 19.6g + 3.5g for each subsequent sample;
- concentrated sulphuric acid 0.756g + 0.135g for each subsequent sample;
• water 5.6g + 1g for each subsequent sample.

It is important to prepare amidole solution freshly and each sample must be duplicated.

4.5.3 Surface Area and Pore Size Distributions

Surface area and pore size distributions were made using a Micromeritics ASAP 2010 automatic gas adsorption analyser fitted with an optional high stability 1 torr pressure transducer. Samples of the sorbents were prepared by outgassing for a minimum of 24 hours at elevated temperature (usually at 110°C) on the degas ports of the analyser. The degassed adsorbent mass was determined by subtracting the weight of the empty sample tube from the nitrogen backfilled adsorbent sample tube. Seal frits, inserted into the top of the sample tubes, prevent the degassed samples from being contaminated by exposure to air.

Adsorption isotherms were generated by dosing nitrogen (> 99.99 % purity) onto the adsorbent held within a bath of liquid nitrogen at approximately 77 K. The analysis and cold trap Dewars were filled with liquid nitrogen to approximately 5 cm from the top. An isothermal jacket was then placed over the neck of the sample tube before connection to the analysis port of the analyser. Insulated Dewar covers were then placed on the top of both Dewars.

The ASAP 2010 software contains a number of predefined input files which define the run conditions for a number of different types of measurement. The pressure table chosen for all the samples was “High Resolution Nitrogen Adsorption/Desorption”. However a number of other parameters were varied according to the sample being analysed (e.g. slow evacuation for fine particles). The dosing mode of “Rate of Adsorption” was selected to enable kinetic effects to be investigated prior to data collection. The equilibration interval was initially set at 45 seconds so as to enable adequate diffusion of the nitrogen into the micropores. However, this selection led to excessive analysis times. The effect of equilibration interval was investigated by analysing samples at intervals of 5, 10, and 45 seconds. An interval of 10 seconds was finally selected since no observable effect was seen on the pore size distribution.
or the isotherm with the reduction in the equilibration time. The microporous nature of the adsorbents necessitated the free space determination to be measured after the nitrogen adsorption isotherm, since helium is sometimes retained. The molecular drag pump was turned on for all measurements.

4.5.4 Boehm's titration

In order to quantitatively assess the ion-exchange properties of the sorbents it is necessary to determine the concentration of different surface functional groups and their ability to dissociate in aqueous solutions. The distribution of surface functional groups is usually determined by Boehm's method. This technique consists of using alkaline solutions of increasing strength: sodium hydrogen carbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH) and sodium ethoxide (NaOC₂H₅). Accordingly, carboxylic groups can be titrated with NaHCO₃, lactones with Na₂CO₃, phenols with NaOH, and groups of weaker acidic strength with NaOC₂H₅ solutions.

Samples of sorptive materials in hydrogen form were mixed with 0.1 M solutions of sodium hydroxide, sodium hydrogen carbonate, sodium carbonate and sodium ethoxide. The sodium hydroxide and sodium carbonate were volumetric standards purchased from Aldrich Chemicals. The sodium hydrogen carbonate and sodium ethoxide solutions were prepared from analytical reagents also from Aldrich. The sodium ethoxide solution was dissolved in HPLC grade ethanol to prevent degradation of the compound caused by reaction with water. 200 mg quantities of dried adsorbents, in the particle size range 75 - 100 µm, were weighed into 50 ml glass conical flasks prior to the addition of 20 ml of the different bases. The flasks were then sealed using parafilm and agitated using an orbital shaker for 72 hours at 22 ± 2°C. Blank solutions of each base were also shaken. The equilibrated solutions were filtered using 0.45 µm PTFE syringe top filters to remove the adsorbent particles. Aliquots of 10 ml were then titrated with a 0.1 M volumetric HCl standard using a water-ethanol solution of methyl red as the indicator.
4.5.5 pH-titration

The relationship between the ion-exchange capacities of sorbents and the solution pH can be found from pH-titration curves. Based on these curves, inferences may be drawn concerning the acidic and basic properties of ion-exchangers and the nature of their surface functional groups.

Titration curves for the sorbents studied were generated as follows. Twenty samples of carbon (particle size under 45 µm), nominally 20 mg each, were accurately weighed using a Sartorious BP210D balance (accuracy ± 0.0005 g) and then transferred into 50 ml glass conical flasks before the addition of 10 ml of 0.1 M sodium chloride. A known volume (usually between 0.1 ml and 4 ml) of 0.1 M sodium hydroxide or 0.1 M hydrochloric acid solution (both supplied by Aldrich) was then added to each flask using a precision micropipette. The flasks were sealed with parafilm and agitated for 24 hours at 22 ± 2°C. Equilibrium pH was then measured for each sample using a Mettler-Toledo 340 digital pH meter. A blank experiment with no sorbent present was also performed.

4.5.6 Electrophoretic measurements

Electrophoretic measurements were carried out using the following method. The sorptive materials were initially crushed using a Waring blender followed by grinding with an agate mortar and pestle. The sorbents were screened to obtain a particle size fraction less than 45 µm. 20 sorbent samples (approx. 20 mg each) were placed in 50 ml glass conical flasks with 30 ml of 0.1 N sodium chloride as a supporting electrolyte. This provided an optimum concentration of particles for zeta potential analysis at approximately 3500 counts/sec. Variable amounts of 0.01 N sodium hydroxide (from 0 to 4.5 ml) and 0.1 N or 0.5 N hydrochloric acid (from 0.1 to 4 ml) were added in order to adjust the pH of the sorbent suspensions. Samples were shaken for 24 hours at a constant temperature of 22 ± 2°C. Prior to zeta potential measurements the pH of the sorbent suspension in each flask was recorded. Samples of the suspension were collected in plastic Luer syringes and injected directly into the electrophoretic cell. After each measurement the cell was flushed with DECON 90 detergent solution followed by several rinses with distilled water. Electrophoretic
measurements were carried out using a Zetamaster (Malvern Instruments, UK) designed to provide rapid and accurate measurement of colloid electrophoretic mobility. Determinations are based on an analysis of the frequency of interference fringes created by laser light scattered by the particle suspension and captured by a photon-counting detector and digital correlator.

4.5.7 FT-IR spectroscopy
Fourier Transform Infra Red (FT-IR) spectroscopy was applied to the determination of functional groups on the surfaces of carbons.

All spectra were recorded on a Nicolet 20-DXC FT-IR spectrometer with a dry air purge, liquid nitrogen cooled MCT (mercury-cadmium-telluride) detector, and a Spectra-Tech diffuse reflectance accessory. Samples of carbon were crushed using an agate mortar and pestle and sieved to a particle size range under 45 µm. Finely divided FT-IR grade potassium bromide (obtained from Aldrich) was ground, dried at 105°C, and stored in a desiccator prior to use. The samples were mixed with the dried FT-IR grade potassium bromide (KBr) to make a 0.025 % (wt/wt) solid solution and pressed into thin pellets (approx. 0.1 g) to enable transmittance values of less than one to be recorded.

Background spectra of potassium bromide and water vapour were recorded every 100 minutes. Spectra were recorded at a resolution of 4 cm⁻¹ using a minimum of 200 scans and an aperture setting of 15. The samples were allowed to equilibrate in the instrument for 10 minutes prior to recording the spectra to ensure their dryness.

4.5.8 Scanning electron microscopy
Microscopy provides valuable information regarding external and internal features of the particles of materials studied. Low magnification electron micrographs (40 - 10,000 x) of the adsorbents were taken by Mr. F. Page at IPTME, Loughborough University, using a Cambridge Stereoscan 360 scanning electron microscope at an accelerating voltage of 10kV. All samples were dried in an oven for 24 hours at
105°C and stored in a desiccating vessel over silica gel. The specimens of sorbents were glued to aluminium platforms and sputter-coated with gold. Investigations were made into whole and crushed sorbents.

4.5.9 Solid state nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS)

The valency and chemical state of phosphorus on the carbon surface may be determined by means of nuclear magnetic resonance spectroscopy and X-ray photoelectron spectroscopy.

Samples of phosphorus-containing carbon were sent to $^{31}$P solid state NMR facility based in the Department of Chemistry at Cambridge University and at the Institute of Colloid Chemistry and Chemistry of Water, Kiev, Ukraine. Analysis was performed using a Bruker spectrophotometer. 85 % phosphoric acid was used as a standard.

XPS spectra for the analysis of carbons were obtained with a Varian IEE-15 spectrometer (Varian USA) equipped with a monoenergetic Al $k_{\alpha}$ X-ray source. XPS measurement were carried out at the Institute of Physics of Metals, Kiev, Ukraine.

4.6 Sorption Studies

4.6.1 Kinetic experiments

Sorption rate was studied by the finite batch method. In a finite batch experiment, a known amount of solute in solution is vigorously stirred with a known amount of sorptive material. The extent of sorption is monitored by measuring the change of solute concentration with time. These experiments are simple to carry out and give good first-hand information on the sorption kinetics, though theoretical interpretation of experimental results is difficult.

Experiments were carried out in an agitated round-bottomed batch reactor with a capacity of 2 litres, from which fluid was extracted and pumped through a three-way solenoid valve (Cole-Parmer) before returning to the vessel. The valve was
synchronised with a fraction collector and controlled by a Mitsubishi FXo 14 I/O programmable logic controller PLC unit. A schematic diagram of the apparatus is shown in Figure 4.8. The fluid was extracted from the flask through a 20 µm PTFE filter (to separate sorbent particles) and circulated using a Masterflex Cole-Parmer peristaltic pump. The pump was set to a flow rate of 3 – 4 ml/sec. The vessel contents were agitated at 300 rpm using a two-bladed Teflon paddle attached to a glass rod, at a constant temperature of 22°C ± 2°C. Pseudo-equilibrium contacts were carried out over fixed time intervals not exceeding 24 hours. Sampling intervals were carefully planned in order to keep the volume and the number of samples extracted to a minimum.

0.8 g of sorbent was placed in the flask followed by addition of 1 litre of distilled water. The mixture was stirred for several hours. This procedure was necessary to wet the sorbent and purge air trapped in pores and attached to the particle surface. 1 litre of feed solution containing double the concentration of metal ion required for the experiment was prepared from analytical grade reagents. This solution was then added to the reaction vessel. This was taken as the start of the experiment. During the course of the experiment, samples of solution were collected at intervals using a fraction collector controlled by a programmable PLC unit.

The particle size of the sorbents used was between 150 and 250 µm. The initial pH in all experiments was about 5. The experiments were conducted without pH control. 3 ml samples were extracted from the batch flask at fixed time intervals and then analysed using a Varian SpetAA-200 atomic absorption spectrophotometer in flame mode with an air-acetylene flame. The wavelength used for lead (Pb) detection was 283.0 nm.
Figure 4.8. Schematic diagram for metals sorption rate experiments. (1) reactor; (2) filter with a 20μm frit; (3) glass stirrer with a Teflon paddle; (4) stirrer motor; (5) peristaltic pump; (6) programmable PLC unit; (7) 3-way solenoid valve; (8) fraction collector
Chapter 4

4.6.2 Batch sorption experiments

Active carbon has been employed for the removal of gaseous contaminants from gas streams for many years. Adsorption data can be found in the literature and methods exist for the design of adsorbers, sometimes without doing any preliminary tests. It is not, however, possible to predict the effectiveness of carbon in treating a given liquid on a purely theoretical basis. In most cases, therefore, tests have to be carried out and each application has to be considered individually.

If a sorbent is being considered for a new application, a laboratory investigation is essential to determine:

- its efficiency;
- the relative advantages in the specific application.

A complete laboratory investigation consists of at least two parts: a preliminary batch test (so-called sorption isotherm test) and a mini-column test.

Batch sorption experiments are performed purely to investigate the feasibility of a sorptive material system and to calculate the theoretical capacity and minimum sorbent dosage. For a specific metal ion, the sorption capacity of the adsorbent is related to the concentration of that metal ion in aqueous solution. The objective of the batch sorption experiment is to measure the sorption capacity of an adsorbent for different levels of impurity concentration.

4.6.2.1 Sorption experiments at parts per million concentration range

Sorptive material (particle size under 45 µm) was accurately weighed into 250 ml conical flasks. Five weights of carbon between 0.01 and 0.1 g were used. 200 ml of metal feed solution was then added to the carbon. Apart from the metal studied, this solution also contained 0.5 M of sodium ions as sodium nitrate. This was added in order to maintain constant ionic strength of the feed solution. The flasks were sealed with Parafilm and kept in an orbital shaker at a constant temperature of 22°C ± 2°C.

* Amount of sorbent rather than solution concentration was variable in the batch sorption tests.
Subsequently, solutions were separated using a Luer syringe and a disposable PVDF 0.45 µm filter and then used for determination of equilibrium concentrations.

Sorption isotherms were measured at controlled solution pH 4.8 by addition of known amounts of sodium hydroxide or nitric acid to the batch flasks using a disposable plastic pipette. Every 24 hours, the pH of each sample was measured and adjusted to pH 4.8 by addition of a several drops of alkali (NaOH, 1 M / 0.1 M). The samples were taken to have achieved equilibrium when no significant change in solution pH (± 0.2 pH units) was observed over a 48 hour period.

The equilibrium metal concentration in each sample was measured using a Varian SpectrAA-200 atomic absorption spectrophotometer (AAS) in flame mode with an air-acetylene flame. The wavelengths used for metal detection were: lead (283.0 nm), copper (324.7 nm), cadmium (228.8 nm) and nickel (232.0 nm).

4.6.2.2 Nomenclature

The following terms have been used in this work:

- \( m, (g) \) – weight of sorbent in batch, in grams;
- \( C_{eq}, (mg/l, mmol/l, meq/l) \) - equilibrium metal concentration, in milligrams/millimoles/milliequivalents of metal ion per litre of solution;
- \( C_{ini}, (mg/l, mmol/l, meq/l) \) - initial metal concentration, in milligrams/millimoles/milliequivalents of metal ion per litre of solution;
- \( x, (mg/l, mmol/g, meq/g) \) - amount of impurity removed, in milligrams/millimoles/milliequivalents of impurity per litre of solution;
- \( V, (l) \) - volume of batch, in litre;
- \( m \div V, (g/l) \) - ratio of weight of sorbent and volume of feed solution in a batch, in grams per litre;
- \( x \div m, (mg/g, mmol/g, meq/g) \) - mass of metal ion sorbed per unit mass of sorbent (uptake), in milligrams/millimoles/milliequivalents of metal ion per gram of sorbent.

Mass of metal ion sorbed per unit mass of sorbent was determined using the following equation:
The uptake \((x/m)\) is plotted against equilibrium metal ion concentration \((C_{eq})\).

**4.6.2.3 Sorption experiments at parts per billion concentration range**

Equilibrium sorption experiments in the parts per billion range of concentrations were performed as follows. 5 sorbent samples, nominally 10, 30, 60 and 120 mg were weighed into Nalgene polypropylene bottles of 500 ml nominal capacity with leak proof screw tops. 500 ml of solution containing a known quantity of metal ions was added to each bottle. Sorption isotherms were generated at fixed solution pH 4.8. Since the concentration of the sorbent in plastic containers was so small, it was not necessary to adjust the pH of supernatant solution in order to keep the pH constant. The batch samples were equilibrated at a temperature of 22°C ± 2°C in an orbital shaker for 10 days. Prior to equilibrium metal concentration measurements the amount of sample required (approx. 1.5 ml) was filtered using a Luer syringe and a disposable PVDF 0.45 µm filter.

The equilibrium metal concentration in each sample was measured using a Varian SpectrAA-200 atomic absorption spectrophotometer with a GTA-100 graphite furnace attachment. The wavelengths used for metal determination were, copper (324.7 nm) and lead (283.0 nm). The uptake capacity \((x/m)\) was expressed in micromoles of metal removed per gram of sorbent \((\mu mol/g)\) and was calculated using equation 1.

**4.6.3 Mini-column sorption experiments**

The mini-column experiments were carried out in isolute SPE columns of nominal capacity 3 ml, supplied by Jones Chromatography Limited, (Mid-Glamorgan, UK) using 20 µm polyethylene frits as bed supports and column adapters to seal the column and attach tubing.

A known quantity of dried sorbent sample (particle size 45-90 µm) was weighed and transferred into a mini-column. The sorbent was wet packed into the column to a bed...
volume of approximately 0.65 cm³ (8.7 mm diameter, ~ 10 mm height). The column was then washed using distilled water to eliminate any fines and purge air trapped in the pores. A schematic diagram of the mini-column apparatus is shown in Figure 4.9. Feed solution was pumped at a known flow rate to the top of the carbon bed using a Masterflex peristaltic pump. The level of the solution above the bed was maintained by forced flow. The effluent from the column was directed either to the fraction collector or to waste using a three-way PTFE solenoid valve (Pharmacia). The volume of fraction collected varied during the mini-column operation but was usually between 5 and 10 ml. The fraction collector was controlled using a Mitsubishi FX0 14 I/O programmable logic controller (PLC) connected to a data access panel which enabled alteration of the timer constants.

After saturation the mini-columns were regenerated using 0.5 M nitric acid. Fractions from the outlet were collected into 2 ml plastic containers. Each effluent sample was diluted up to 1 litre. Metal content in the samples was analysed using an atomic absorption spectrometer in flame mode. The volume of the feed/regenerant solution passed through the sorbent bed was expressed in bed volumes (BV).

4.6.4 Sorption of radionuclides
Sorption experiments with radionuclides were carried out at the Harwell Laboratory, AEA Technology plc, Oxfordshire. The objective of these experiments was to investigate the selectivity of a variety of sorbents towards radioactive isotopes in complex waste streams. The use of radioactive facilities, experimental techniques and operator assistance were courtesy of the company. The work was performed as a part of the Novel Absorber Evaluation Club programme designed to test sorbents for the removal of radionuclides supplied by different manufacturers.

4.6.4.1 Reference waste streams
Low activity reference waste streams were used in this study, known as NAEC (Novel Absorber Evaluation Club) S1, S3, S4 and S5. All waste streams were 0.05M in sodium nitrate to reduce peptisation of the sorbent. Table 4.4 shows the metal ion content of the streams used.
Figure 4.9. Schematic diagram of the mini-column apparatus. (1) - feed tank; (2) - peristaltic pump; (3) - mini-column; (4) - 20µm frits; (5) - sorptive material; (6) - three-way solenoid valve; (7) - pH-meter probe; (8) - U-shaped glass tube.
<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Metal Ion Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAEC S1</td>
<td>$^{137}$Cs, $^{60}$Co, $^{65}$Zn, $^{51}$Cr, $^{59}$Fe, $^{54}$Mn, $^{106}$Ru, $^{109}$Cd, $^{110m}$Ag, $^{203}$Hg at the 100 Bq/ml level</td>
</tr>
<tr>
<td>NAEC S3</td>
<td>$^{239}$Pu(IV) at 2 Bq/ml, $^{241}$Am at 1 Bq/ml, $^{90}$Sr at 5 Bq/ml</td>
</tr>
<tr>
<td>NAEC S4</td>
<td>$^{137}$Cs, $^{60}$Co, $^{65}$Zn, $^{51}$Cr, $^{59}$Fe, $^{54}$Mn, $^{106}$Ru, $^{109}$Cd, $^{110m}$Ag, $^{203}$Hg at the 100 Bq/ml level, 0.25 g/l EDTA in sodium form, 0.15 g/l citric acid</td>
</tr>
<tr>
<td>NAEC S5</td>
<td>$^{239}$Pu(IV), $^{241}$Am and $^{237}$Np(V) at 1Bq/ml, 1 g/l NaHCO$_3$</td>
</tr>
</tbody>
</table>

Table 4.4. The metal ion content of the waste streams used in this study.

The test solutions were adjusted to the required pH value and then kept for at least 24 hours at room temperature before use so as to allow equilibration of ionic species.

Streams NAEC S1 and S4 were analysed by gamma spectrometry with a limit of detection of 1 Bq/ml or less. Streams NAEC S3 and S5 were analysed by both alpha and beta scintillation counting.

4.6.4.2 Sorbent conditioning

Prior to use, sorbents were conditioned by washing with water adjusted to the experiment pH value using sodium hydroxide. Washing was continued until the pH of the wash remained at its original value for 2-3 hours. The sorbents were used in wet condition after decanting the wash fluid and removing any excess moisture with a cellulose tissue.
4.6.4.3 Batch sorption experiments

1 ml samples of the conditioned sorbent were measured into 200 ml screw-top plastic containers using a syringe modified to provide a ‘full-bore’ syringe. A known amount of a reference waste stream was added to the containers to make up the starting concentration of radionuclides (100 Bq/ml). The containers were agitated using a constant temperature orbital shaker at 20 ± 2°C. 1.5 ml aliquots of supernatant solution were extracted from the containers after 1, 2, 4, 6 and 24 hours, centrifuged and then 1 ml removed for analytical measurements. A blank experiment with no sorbent present was also included. All the experiments were performed in duplicate, and results averaged.

All analytical results are presented as Bq/ml and also as a calculated decontamination factor with reference to the original waste stream activity level:

Decontamination Factor (DF)=activity per ml in feed / activity per ml in effluent sample  \( (2) \)

No correction was made for the volume changes resulting from sampling.

4.7 References


Chapter 5: Physical characterisation

5.1 Introduction

Carbonaceous sorbents based on agricultural by-products (KAU carbons), coal (F 400), and synthetic polymeric materials (CKC and PGP-P carbons) possess large internal surface area due to their well developed porous structure. The porous nature of these materials influences their sorption characteristics for metal removal in aqueous solutions. This chapter discusses the porous properties of active carbons using nitrogen adsorption and optical measurement techniques.

5.2 Scanning electron microscopy (SEM)

Oxidation of carbons may cause a significant loss of weight (up to 40-60 %). The available literature on oxidation of carbons does not provide any information regarding the appearance and mechanical properties of carbon granules. Nevertheless, this is very important since carbon materials used in water treatment should be capable of withstanding significant mechanical wear.

Figures 5.1–5.3 show low magnification SEM photographs of polymer-based carbons CKC and PGP-P and coal-based F 400. The polymer-based carbon particles are perfect spherical beads. This shape derives from the spherical synthetic polymeric precursors. In contrast, particles of F 400 have an irregular shape.

Prolonged exposure of carbons to oxidising agents usually results in loss of particle strength. However polymer-derived active carbons can withstand (without significant loss of particle strength) prolonged oxidation much better than conventional active carbons. It is also important to mention that synthetic carbons are less susceptible to oxidation than ordinary active carbons. During oxidation of carbon, surface groups are usually formed at defects in the carbon matrix i.e. stacking faults, atom vacancies, dislocations, etc. (Chapter 2 and 3). Polymer-derived carbons possess more regular
structure and consequently have fewer defects than those derived from natural materials (i.e. coal, fruit stones, etc.). This feature of synthetic carbons results in their greater resistance to oxidation and erosion. The effect of carbon oxidation can also be seen in Figure 5.4 and 5.5. Oxidation increases the width of surface cracks indicating the corrosive nature of this process.

The uncrushed surface of synthetic carbons appears to be virtually dust-free in contrast to F 400. These carbons also possess a very smooth surface. These interesting features of synthetic carbons permit them to be used as adsorbents for blood purification (haemosorption) since they do not inflict mechanical damage to the blood cells \(^1\). Figures 5.3 and 5.6 illustrate the irregular particle shape of F 400 showing a significant amount of fine particles attached to the surface. Crushing of carbons produces irregular shaped particles and generates a significant amount of dust.

The brittle nature of F 400 and rough shape of the particles results in the release of a large amount of fines. Operation of mini-columns packed with carbonaceous sorbents suggests that the fines gradually migrate through the sorbent bed and block the supporting frits (bed support). This results in excessive backpressure causing the feed solution flow rate to drop.

The extremely high mechanical strength of synthetic carbons derived from polymeric precursors allows them to be activated at high (up to 85%) burn-off values (burn-off values do not exceed 50% for conventional activated carbons). The microphotographs show a dramatic difference between surfaces of synthetic carbons and conventional active carbons (Figures 5.8 and 5.9). Higher magnification of the surface of PGP-P presented in Figure 5.9 does not reveal any particular features whereas the microphotograph of KAU 2.7 (Figure 5.8) shows many cavities and large pores. This texture originates from the natural precursor (apricot stones) and is well preserved during carbonisation and activation.

High-resolution scanning electron microphotographs (Figure 5.10) reveal the uniform globular structure of the synthetic carbons. This structure is derived from polymeric precursors (Figure 5.11) and remains practically unchanged during high temperature treatment. The external surface of the synthetic carbons appears to be 'glazed' (shiny
and smooth) in comparison with cross sectional views. As mentioned above, the ‘glazed’ surface allows them to be used in medical applications.

Figure 5.1. SEM of CKC.
Figure 5.2. SEM of PGP-P.

Figure 5.3. SEM of F 400.
Figure 5.4. SEM of the surface of unoxidised F 400.

Figure 5.5. SEM of the surface of oxidised F 400.
Figure 5.6. SEM of crushed F 400.

Figure 5.7. SEM of crushed CKC.
Figure 5.8. SEM of the surface of KAU 2.7.

Figure 5.9. SEM of the surface of PGP-P.
Figure 5.10. SEM of cross sectional view of CKC.

Figure 5.11. SEM of cross sectional view of styrene/DVB resin.
5.3 Nitrogen adsorption isotherms and pore size distribution

Gas adsorption is the most widely used method of characterising the pore structure of solids. Although various gases may be utilised (argon, carbon dioxide), nitrogen at its boiling point of 77 K is used most extensively.

It is known from the literature that the kinetic curve (on a logarithmic scale) of ion sorption on oxidised carbons consists of two independent parts (more details will be provided in further chapters). From our point of view this phenomenon is related to the presence of micropores, the size of which are comparable to that of the metal ions sorbed. Therefore it is necessary to investigate the porous structure of adsorbents using modern methods of pore structure analysis.

Pore size distribution and surface area of solids are usually determined in a routine manner, though the complex nature of both the pore structure and the mechanisms of adsorption make it necessary to be cautious in the interpretation of experimental results. However, adsorption measurements provide useful information regarding the microstructure of the solid and this information is essential if the material is to be used for various applications related to adsorptive and catalytic processes.

In order to generate an adsorption isotherm, the amount of nitrogen adsorbed (mmol/g) is plotted against the equilibrium adsorbate partial pressure \( p/p^0 \) at constant temperature. The isotherms for the adsorbents studied are presented in Figures 5.12 and 5.13.
Figure 5.12. Overlaid nitrogen adsorption isotherms for KAU carbons.

Figure 5.13. Overlaid nitrogen adsorption isotherms for various adsorbents.
The nitrogen adsorption-desorption isotherms for active carbons (particularly for KAU carbons and F 400) are Type I. This isotherm type is typical of microporous solids with a small external area and indicates that micropore filling occurs predominantly at relatively low partial pressures \(< 0.1 \, \text{p/p}_0\). The adsorption process is complete at \(\sim 0.5 \, \text{p/p}_0\). Nitrogen adsorption by CKC carbon is typical of a Type IV isotherm. The characteristic feature of this isotherm type is the hysteresis loop, which is associated with capillary condensation occurring in mesopores, and the limiting uptake over a range of high \(\text{p/p}_0\)\(^5\).

Figure 5.12 also suggests that carbon oxidation decreases nitrogen adsorption capacity (KAU carbons) with KAU 2.7 having the lowest.

The hysteresis loop in the isotherms (Figure 5.14) provides information about the mesoporous structure of the solids. In accordance with IUPAC classification \(^5\), the carbonaceous adsorbents possess Type II 4 hysteresis. Inspection of adsorption isotherms suggests that all the carbon materials are predominantly microporous. These materials have greatest capacity for nitrogen.

Figure 5.14. Representative nitrogen adsorption-desorption isotherm for active carbons (KAU 0.8).
A hysteresis loop at $p/p^0 = 0.40 - 1.00$ indicates the presence of mesopores in the carbons (Figure 5.14). Hysteresis occurs because the mechanism of adsorption in mesopores is different to that of desorption. The hysteresis shape in adsorption-desorption isotherms is similar to that found for slit-shaped pores, as expected for mesopores in activated carbons. Considering mesopores as capillaries, hysteresis may be explained by capillary condensation whereby the capillary empties during desorption at a lower $p/p^0$ than it fills during adsorption. Capillary condensation can be described by the Kelvin equation for cylindrical pores:

$$r_k = \frac{2\sigma V_m}{RT\ln(p/p^0)}$$  \hspace{1cm} (1)

where $\sigma$ is the surface tension of the liquid, $V_m$ its molar volume, $r_k$ is the mean or Kelvin radius of the capillary.

Pore size distribution and surface area can be determined from adsorption isotherms by mathematical modelling. This has become the standard method of determining the microporous nature of adsorbents, due to the simplicity compared with other methods such as mercury intrusion. However, the derived results are extremely dependent upon which model is used to calculate the pore size distribution.

The specific surface area ($m^2/g$) of highly porous materials is usually determined from gas adsorption measurements using the Brunauer-Emmett-Teller (BET) method. Over the past fifty years this method has remained the most widely used procedure for the determination of the surface area of porous solids and is widely accepted by the scientific community. BET surface area is generally considered to be correct and beyond dispute. The BET method is based on specific assumptions, extended from the Langmuir mechanism, that the first layer (the monolayer) is localised on surface sites of uniform adsorption energy and that the second and subsequent adsorbed layers (the multilayers) build-up by a process analogous to condensation of the liquid adsorbate. Molecules in the first layer act as sites for molecules in the second and higher layers and the evaporation and condensation properties of all layers above the first are very similar to those of the liquid adsorbate. On the basis of these
assumptions, the rates of condensation and evaporation can be equated for each adsorbed layer. Summation of the amounts adsorbed produced the linear form of the well-known BET equation

\[
\frac{p}{n(p^0 - p)} = \frac{1}{cn_m} + \frac{(c-1) p}{cn_m p^0}
\]

(2)

where (for the unit weight of adsorbate) \(n\) is the molar amount adsorbed at relative pressure \(p/p^0\), \(n_m\) is the amount of adsorptive required to cover the surface as a monolayer (the monolayer capacity), and \(c\) is a dimensionless constant which, in accordance with the theory, is related exponentially to the heat of first-layer adsorption.

According to equation 2, the plot of \(p/n(p^0-p)\) against \(p/p^0\) should be linear, and it is easy to calculate both \(n_m\) and \(c\) from the slope and intercept. In practice, the linearity of the 'BET plot' is always restricted to the lower part of the isotherm \(^7\). In many cases the range of linearity extends over \(p/p^0 = 0.05 - 0.3\), however with graphitised and microporous carbon materials linear BET plots are obtained at \(p/p^0 < 0.1\). Differing tangents to the curve result in surface areas which vary by up to 200 m\(^2\)/g. In order to obtain a positive \(y\)-intercept on the BET plot, the linear range of 0.06 - 0.12 was selected for the surface areas presented in Table 5.1.

The BET equation is subject to severe limitation when applied to active carbons. BET surface areas as high as 4000 - 5000 m\(^2\)/g have been reported for some active carbons but are unrealistically high, since the calculated surface area for an extended graphite layer plane, counting both sides, is about 1800 m\(^2\)/g \(^2,8\).

Active carbons have a very disordered structure consisting of a twisted network of defective carbon layer planes and an interconnected network of slit-shaped micropores formed by the spaces between the carbon layer planes and the gaps between stacks of layer planes. Constrictions in the microporous network control access to much of the pore space. This disordered structure makes interpretation of adsorption very difficult. Firstly, gases are strongly adsorbed at low pressure in micropores, because there is enhancement of adsorption potential due to overlap of the force fields of opposite pore walls. Secondly, microporous constrictions cause activated diffusion
effects at low adsorption temperatures when the adsorbate has insufficient kinetic energy to fully penetrate the micropore space. Thirdly, microporous carbons can exhibit molecular sieve behaviour, i.e. the selective adsorption of small molecules in narrow micropores. Carbons also exhibit molecular shape selectivity by preferential adsorption of flat molecules, as expected from the slit-shape micropores. Adsorption in micropores does not actually take place by successive building-up of molecular layers, as suggested by the BET theory. Rather, the enhanced adsorption potential in micropores induces an adsorption process described as primary or micropore filling. Nevertheless, the BET surface area continues to be used for microporous carbons because of its widespread use for other adsorbents, but its limitations should be recognised.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Coefficient 'c'</th>
<th>BET surface area, m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td>149</td>
<td>1823</td>
</tr>
<tr>
<td>KAU-1.5</td>
<td>147</td>
<td>1732</td>
</tr>
<tr>
<td>KAU-1.9</td>
<td>133</td>
<td>1694</td>
</tr>
<tr>
<td>KAU-2.2</td>
<td>148</td>
<td>1553</td>
</tr>
<tr>
<td>KAU-2.7</td>
<td>159</td>
<td>1369</td>
</tr>
<tr>
<td>KAU-0.8</td>
<td>134</td>
<td>1865</td>
</tr>
<tr>
<td>KAU-1.2</td>
<td>117</td>
<td>1815</td>
</tr>
<tr>
<td>KAU-1.8</td>
<td>99</td>
<td>1870</td>
</tr>
<tr>
<td>CKC</td>
<td>-234</td>
<td>540</td>
</tr>
<tr>
<td>PGP-P</td>
<td>-111</td>
<td>301</td>
</tr>
<tr>
<td>KAU-1.6</td>
<td>250</td>
<td>845</td>
</tr>
</tbody>
</table>

Table 5.1. BET surface area results for the materials studied.

The characterisation of porous solids is of great interest since these materials are important in a variety of applications e.g. liquid and gas purification, catalysis, adsorption separation, etc. The increasing industrial use of active carbon materials has especially aroused interest in the pore size region of a few molecular diameters.
Nevertheless, current methods of obtaining pore size information in this region from gas adsorption data are still rather unsatisfactory.

Most routine methods employ nitrogen adsorption at 77 K and use the Kelvin equation (1) to correlate pore size with the pressure at which pore condensation takes place, together with a correction for the thickness of the adsorbed layer at the point of condensation. The method of Barrett, Joyner and Halenda (BJH) \(^{10}\) is typical and the thickness curves of de Boer, Halsey or Harkins and Jura are frequently employed \(^{11}\).

While the Kelvin equation may be regarded as exact at the large pore limit, its accuracy decreases as the pore dimensions become less than a large multiple of molecular size. Moreover, thickness curves are obtained from measurements on non-porous surfaces, hence tend to underestimate the thickness of the adsorbed film on the walls of small pores where adsorption forces are increased.

The determination of pore size distribution in the micropore region (defined as 20 Å and below) is less certain. Methods based on the potential theory of Dubinin et al \(^{12}\), \(t\)- or \(\alpha\)-plots \(^{8}\) or the MP method \(^{13}\) are widely used. In 1983, Horvath and Kawazoe \(^{14}\) published a quasi-thermodynamic method similar to the Kelvin equation. This method describes a step function mapping of equilibrium relative pressure of pore filling to micropore size modelled as width of slit-like pores. Saito and Foley have since developed this theory for cylindrical pores \(^{15}\). These authors acknowledge the 'Kelvin-like simplicity' of the method. It seems that the reality of adsorption in micropores is much more complex.

In recent years, great advances have been made in the understanding of the structure and thermodynamics of inhomogeneous systems of simple molecules, including surface tension and density profile of the free liquid-vapour interface. As a consequence, investigations have begun into the behaviour of fluids at free solid surfaces and fluids confined by parallel or cylindrical walls \(^{16, 17}\). Density functional theory has been especially useful in these studies.
The Density Functional Theory (DFT)\textsuperscript{18} is a new method which is based on the adsorbate-adsorbate and adsorbate-adsorbent interactions, similar to the Horvath-Kawazoe (HK) technique. However, the HK model assumes that the density of fluid near the walls of micropores is constant whereas the DFT models actually calculate the density. DFT is applicable to a broad spectrum of pore sizes up to 4000 Å which makes this technique very attractive. However, as with the original HK correlations, the DFT model is based on slit pores with graphite interaction energies.

Figures 5.15 - 5.22 present the DFT pore size distributions for the adsorbents studied. The plots demonstrate the microporous nature of the carbons. The effect is more apparent on the pore volume plots because larger pores contribute very little to the overall incremental surface area of the sorbents.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pore_size_distributions.png}
\caption{Pore size distributions for KAU carbons oxidised by nitric acid.}
\end{figure}
Figure 5.16. Pore size distributions for KAU carbons oxidised by air.

Figure 5.17. Pore size distributions for unoxidised and oxidised F 400.
Figure 5.18. Pore size distributions for miscellaneous carbons.

Figure 5.19. Surface area distribution for KAU carbons oxidised air.
Figure 5.20. Surface area distribution for KAU carbons oxidised by nitric acid.

Figure 5.21. Surface area distribution for oxidised and unoxidised F 400.
Figure 5.22. Surface area distribution for PGP-P and CKC.

Oxidation slightly reduces pore volume and surface area of the sorbents without significant changes in the pore size distribution (Figures 5.15 - 2.22). The pore size distribution for F 400 is somewhat different to the KAU carbons. Oxidised and unoxidised F 400 possess a significant amount of both micropores with a maximum at 8 Å and mesopores in the range 40 - 800 Å. KAU carbons appear to be mostly microporous with a maximum between 10 and 20 Å.

The porous structure of synthetic carbons can be tailored during the course of production. The pore size distribution of CKC clearly shows that. This material appeared to be bi-functional. The pore size distribution of CKC reveals a large quantity of mesopores with a maximum at 400 Å and some micropores in the range of 5 and 10 Å. Phosphorus-containing carbon appears to be mostly microporous with a low pore volume. This is reflected in a relatively slow metal sorption rate on this carbon (Chapter 7).
The apparent bi-modal pore size distribution in the microporous region is caused by deficiencies in the DFT model. The theory is not able to model pores between 8 and 10 Å which causes the smoothed data to have a slight dip in this range.

The results of DFT modelling of the surface area and pore volume are presented in Table 5.2. The values of surface area appear to be lower than those for BET surface area measurements presented in Table 5.1.

The term 'effective surface area' is applied to the values obtained from BET method. The basic problem is that the modelling used for the BET equation does not adequately describe the process of adsorption in such porous carbon materials. The results of DFT modelling seem to be more realistic. Nevertheless, similar trends are observed for both models. Longer exposure to the oxidising agent results in lower surface areas.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Total surface area, m²/g</th>
<th>Total pore volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td>1190.6</td>
<td>0.75</td>
</tr>
<tr>
<td>KAU-1.5</td>
<td>1142.8</td>
<td>0.73</td>
</tr>
<tr>
<td>KAU-1.9</td>
<td>1100.4</td>
<td>0.73</td>
</tr>
<tr>
<td>KAU-2.2</td>
<td>1075.7</td>
<td>0.66</td>
</tr>
<tr>
<td>KAU-2.7</td>
<td>949.1</td>
<td>0.58</td>
</tr>
<tr>
<td>KAU-0.8</td>
<td>1206.9</td>
<td>0.81</td>
</tr>
<tr>
<td>KAU-1.2</td>
<td>1164.4</td>
<td>0.78</td>
</tr>
<tr>
<td>KAU-1.8</td>
<td>1150.3</td>
<td>0.73</td>
</tr>
<tr>
<td>CKC</td>
<td>569.9</td>
<td>0.63</td>
</tr>
<tr>
<td>PGP-P</td>
<td>278.6</td>
<td>0.13</td>
</tr>
<tr>
<td>KAU-1.6</td>
<td>629.3</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 5.2. Surface area and pore volume results for the sorbents studied based on DFT model.
Oxidation may result in a number of functional groups being generated on the surface of the sorbent. These groups may block or occupy a percentage of the micropores resulting in lower values of surface area for the oxidised samples.

5.4 Conclusions

This chapter presents the results of physical characterisation of the sorptive materials studied. The differences between carbonaceous sorbents derived from different precursors were clearly shown. Scanning electron microscopy revealed some important features of the sorbents under investigation. The visible porous structure (macropores) of the carbons seem to be preserved after thermal treatment of the natural carbon precursors. SEM also provided interesting information regarding the resemblance between polymeric precursors and their derivatives - active carbons.

Gas adsorption measurements are widely used for determining the surface area and pore size distribution of porous solids. Although the role of gas adsorption in the characterisation of solid surfaces is firmly established, there is still disagreement about evaluation, interpretation and presentation of gas adsorption results. The complexity of most solid surfaces, particularly that of microporous active carbons, makes it difficult to obtain any independent assessment of the physical significance of the quantities derived (e.g. the absolute magnitude of the surface area and pore size). Consequently the calculation of true internal surface area of carbonaceous materials was considered more accurate using the DFT model than the BET equation.

The determination of pore sizes is still rather subjective despite the modelling applied to the experimentally derived information. Despite these drawbacks both models applied enable reasonable comparisons to be made between similar sorptive materials.

The carbonaceous sorbents possess all types of pores. The porous structure was found to be adversely affected by carbon oxidation, since the surface area and pore volume decrease as the degree of carbon oxidation increases. Synthetic carbons derived from polymeric precursors possess several advantages over the carbons originating from natural precursors. The porous structure of synthetic carbons may be tailored during
the preparation stage of the polymeric resin-precursor. These carbons also possess excellent mechanical properties i.e. exceptional mechanical strength, uniform shape (spheres), smooth outer surface, absence of dust, etc.

5.5 References


Chapter 6: Chemical Characterisation

6.1 Introduction

Active carbons are known to be excellent and versatile adsorbents and are therefore widely used to remove a broad spectrum of dissolved organic and inorganic species from both gas and liquid phases. Active carbons also represent an increasingly important share of the catalyst support market. This great flexibility in the application of active carbons arises not only from the very wide range of physical surface properties, but also the chemical properties of commercially available and/or specifically treated carbon materials. Consequently the techniques to modify and characterise the surface properties of active carbons have been of interest for many years. Increasingly strict clean air and water legislation prompts interest in more effective use of these materials in addition to better and easier surface chemical characterisation.

It has been shown earlier that sorption of a number of substances by active carbons is due to the presence of surface oxygen compounds which form surface functional groups. It is also known that surface functional groups in active carbons may contain other heteroatoms such as nitrogen, phosphorus, sulfur, etc. Functional groups may directly interact with metal species by an ion-exchange mechanism or by forming donor-acceptor bonds. The acidic or basic nature of the functional groups has a strong influence on the surface electrostatic charge of the sorptive materials allowing for attraction or repulsion of charged metal species.

The practical objective of this study is to explore in more detail the influence of progressive surface oxidation by different agents and of heteroatoms on ion-exchange properties of the sorptive materials. A variety of techniques such as Boehm's titration, pH-titration, elemental analysis, zeta potential measurements, solid state NMR, FT-IR, XPS, have been used to characterise the changes in carbon surface chemistry which take place during different treatments of carbonaceous materials.
6.2 Elemental Analysis

The elemental analysis data for the materials studied are presented in Table 6.1. This analytical technique does not permit the determination of oxygen. Since the analysis was performed gratis by Strathclyde University the number of samples analysed was kept to the necessary minimum. Two carbons from the KAU series and F 400 (ox.) were chosen in order to determine the influence of surface oxidation. Other materials analysed were polymer-derived carbons, some of them containing heteroatoms (nitrogen and phosphorus).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Elements, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>KAUini</td>
<td>94.73</td>
</tr>
<tr>
<td>KAU-2.7</td>
<td>82.41</td>
</tr>
<tr>
<td>CKC</td>
<td>81.04</td>
</tr>
<tr>
<td>F 400(ox.)</td>
<td>83.64</td>
</tr>
<tr>
<td>PGP-P</td>
<td>75.49</td>
</tr>
</tbody>
</table>

Table 6.1. Elemental analysis of the selected sorbents.

* Oxygen is determined by residual;

** -- analysis was not performed.

The starting active carbon KAUini has a relatively high oxygen content (4.78 %) due to the presence of a large number of oxygen-containing groups on the surface. This is however in accord with the oxygen values reported by Ferro-Garcia et al 1. These researchers obtained active carbon derived from agricultural by-products (fruit stones) containing approximately 5 % of oxygen.

It is well known that essentially all oxygen-containing groups are removed during the carbon activation process. However the resultant surface becomes very active and adsorbs significant quantities of oxygen upon re-exposure to air (O₂) at room temperature. Relatively high oxygen content is attributed to the stabilised form of
active carbon and is in agreement with the findings of Lau et al.\(^2\) on ageing effects in carbon blacks.

KAU-2.7 oxidised by nitric acid contains a larger amount of oxygen than the starting carbon KAUini. The formation of considerable quantities of oxygen surface groups during the nitric acid treatment is evident from the elemental composition of the starting and oxidised KAU carbons, which show a considerable increase in oxygen content (from 4.78 % to 16.46 %). Various authors reported different values of oxygen content for oxidised carbons. Thus Petrov et al.\(^3\) found that carbon oxidation results in the attachment of 16.99 % of oxygen. This value is in agreement with our findings. Bautista-Toledo et al.\(^4\) reported an unrealistically high oxygen content for nitric acid oxidised carbons (38.9 %). Although these authors associated oxygen with the formation of carboxylic acid groups and nitro and nitrate aromatic compounds, such high amounts of the element may not be solely attributed to the surface functional groups. The researchers also observed a dramatic drop in surface area of the modified sorptive material (from 1089 m\(^2\)/g to 164 m\(^2\)/g). It can therefore be assumed that some nitric acid remains trapped in the micropores of the material after this modification thus contributing to the high oxygen content.

Active carbons may contain elements other than carbon, hydrogen, oxygen and nitrogen. Alben S.\(^5\) used scanning electron microscopy combined with energy dispersive X-ray fluorescence (EDXRF) to identify the trace element distributions of F 400 granular active carbon. The author presented distributions for Al, Si, K, S, Cl, Ca, Ti and Fe. Table 6.2 shows the elemental composition of F 400 presented by the Calgon Corporation, the USA carbon producer.\(^6\) The total concentration of elements accounts for 4.4 % of the carbon weight although the percentage ash was measured at 7.4 %.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, mg/g</td>
<td>12.3</td>
<td>15.5</td>
<td>8.3</td>
<td>0.3</td>
<td>1.6</td>
<td>0.74</td>
<td>0.01</td>
<td>5.0</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 6.2. Elemental composition of F 400 (Calgon) active carbon.
Elemental analysis of the carbons studied has also revealed an interesting phenomenon. All the oxidised carbons analysed possess similar amounts of oxygen (± 1 %) regardless of their origin. This might be explained as follows. The easily accessible mesopore surfaces are oxidised at the start of the oxidation process. Further oxidation occurs on the less accessible micropore surfaces thus contributing to an increased oxygen content. Since all the oxidised carbons possess relatively similar pore size distributions it can be suggested that the amount of attached oxygen is also similar. The slightly larger amount of oxygen in CKC can be attributed to a greater surface area of mesopores.

The percentage of phosphorus in PGP-P was determined by the author using the molybdate method and was analysed independently at Strathclyde University, Glasgow. The results of both determinations appear to be similar. The author's determination yielded 6.8 % of the phosphorus content whereas the determination performed by Strathclyde University yielded 6.51 % of phosphorus. Elemental analysis also revealed the presence of nitrogen (1.15 %) in this material. The manufacturer suggested that there is a possibility of nitrogen introduction into the original polymer structure in the form of melamine. During carbonisation the melamine nitrogen is converted into pyridinic and pyrrolic-type nitrogen.

Oxidation of active carbons using nitric acid introduces very small amounts of nitrogen. Thus the comparison of the elemental composition of KAUini and KAU-2.7 reveals some nitrogen (0.76 %). CKC is based on a polymeric material which is completely nitrogen-free. Elemental analysis showed some nitrogen in this sorbent as well. Bautista-Toledo et al. attributed this nitrogen to the formation of nitro and nitrate aromatic compounds. There is also a possibility that some of the oxidising agent remained trapped in small pores despite the fact that the carbons were washed thoroughly with sodium hydroxide, hydrochloric acid and distilled water.

6.3 Boehm's titration

Carbonaceous materials may contain (apart from hydrogen) other chemical elements. The most important of these is oxygen. Whereas sulphur and nitrogen normally
originate from the carbon precursor, oxygen can be taken up during carbon formation or storage. Much more oxygen is chemisorbed on heating carbons in air (oxygen) or by treatment with liquid oxidants (e.g. HNO₃, NaOCl, etc.). The surface oxides formed in these reactions have a pronounced effect upon the surface properties of the carbon materials.

Carbons can exhibit basic or acidic properties in aqueous solutions. Acidic properties are attributed to the presence of acidic type surface functional groups, whereas basic properties are attributed either to the existence of basic surface oxides or to the presence of an electrical double layer near the surface of carbon (Chapter 2). It was shown recently that the π-electron system of the basal planes of carbon is sufficiently basic to bind protons from acidic aqueous solutions.

Various types of oxygen-containing surface compounds have been clearly identified using different physico-chemical methods. Titration methods are generally used for the determination of acidic groups. Since the acidity constants of the various surface groups (carboxyles, phenols and lactones) differ by several orders of magnitude, an estimate of their relative quantity can be obtained by titration with bases of different strength.

Boehm et al. presented a paper considering quantitative determination of surface oxides in carbon by neutralisation of the acidic functional groups. The authors used four bases of different strength (NaHCO₃, Na₂CO₃, NaOH, and C₂H₅ONa) to differentiate acidic groups of various strength. NaHCO₃ neutralised only ‘strong’ acidic groups such as –COOH. Lactones could be detected by the difference in the number of groups titrated by Na₂CO₃ and NaHCO₃, whereas weakly acidic groups (phenols) were neutralised by NaOH but not by Na₂CO₃. C₂H₅ONa in ethanol was able to titrate more groups than sodium hydroxide, and this was ascribed to carbonyl functionality. It is believed that sodium ethoxide reacts with the surface to form sodium salts of hemi-acetals. Verification of the type of functional groups, suggested by titration, was carried out by chemical modification of the acidic functional groups. Further research by Boehm confirmed the accuracy and assumptions of the titration method.
The concentration of functional groups on the surface of the carbons are presented in Tables 6.3 – 6.5.

### Table 6.3. Concentration of surface functional groups of KAU carbons oxidised by nitric acid.

*% to total non carbonyl capacity.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Carboxylic groups, meq/g</th>
<th>Lactones, meq/g</th>
<th>Phenolic groups, meq/g</th>
<th>Total (non carbonyl), meq/g</th>
<th>Carbonyl groups, meq/g</th>
<th>Total capacity, meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td>0.078</td>
<td>0.000</td>
<td>0.370</td>
<td>0.448</td>
<td>0.628</td>
<td>1.076</td>
</tr>
<tr>
<td></td>
<td>17.41</td>
<td>0</td>
<td>82.59</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-1.5</td>
<td>0.842</td>
<td>0.196</td>
<td>0.664</td>
<td>1.701</td>
<td>2.232</td>
<td>3.933</td>
</tr>
<tr>
<td></td>
<td>49.5</td>
<td>11.52</td>
<td>39.04</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-1.9</td>
<td>0.959</td>
<td>0.393</td>
<td>0.702</td>
<td>2.054</td>
<td>2.376</td>
<td>4.430</td>
</tr>
<tr>
<td></td>
<td>46.69</td>
<td>19.13</td>
<td>34.18</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-2.2</td>
<td>1.275</td>
<td>0.548</td>
<td>0.781</td>
<td>2.604</td>
<td>2.765</td>
<td>5.369</td>
</tr>
<tr>
<td></td>
<td>48.96</td>
<td>21.04</td>
<td>29.99</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-2.7</td>
<td>1.430</td>
<td>0.650</td>
<td>0.795</td>
<td>2.875</td>
<td>2.531</td>
<td>5.405</td>
</tr>
<tr>
<td></td>
<td>49.74</td>
<td>22.61</td>
<td>27.65</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.4. Concentration of surface functional groups of air oxidised KAU carbons.

*% to total non carbonyl capacity

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Carboxylic groups, meq/g</th>
<th>Lactones, meq/g</th>
<th>Phenolic groups, meq/g</th>
<th>Total (non carbonyl), meq/g</th>
<th>Carbonyl groups, meq/g</th>
<th>Total capacity, meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU-0.8</td>
<td>0.130</td>
<td>0.320</td>
<td>0.362</td>
<td>0.811</td>
<td>1.030</td>
<td>1.841</td>
</tr>
<tr>
<td></td>
<td>16.03</td>
<td>39.46</td>
<td>44.64</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-1.2</td>
<td>0.370</td>
<td>0.479</td>
<td>0.457</td>
<td>1.306</td>
<td>1.138</td>
<td>2.443</td>
</tr>
<tr>
<td></td>
<td>28.43</td>
<td>36.68</td>
<td>34.99</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-1.8</td>
<td>0.540</td>
<td>0.560</td>
<td>0.680</td>
<td>1.779</td>
<td>0.664</td>
<td>2.433</td>
</tr>
<tr>
<td></td>
<td>30.35</td>
<td>31.48</td>
<td>38.22</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The titration results show that all the carbonaceous sorbents possess oxygen functionality in a form of non-carbonyl and carbonyl functionality. The number of
weakly acidic groups drastically increases after oxidation. Thus the number of acidic groups neutralised by NaHCO₃ (carboxylic groups) represents only about 17% of the total number of acidic non-carbonyl groups for untreated active carbon KAUini, whilst after oxidation it represents nearly 50% for KAU-2.7.

Phenolic groups are dominant at low degrees of surface oxidation. As the degree of surface oxidation is enhanced, the proportion of stronger (carboxylic) acidic groups over other acidic groups increases. For carbons oxidised with nitric acid the total acidity can be increased up to five times compared to the original carbon for KAU carbons and can even reach a twenty fold increase for F 400. In the case of air oxidised carbons the improvement is only about two and a half times. Progressive oxidation of carbon with nitric acid creates a greater quantity of relatively strong carboxylic surface groups. The results in Table 6.2 suggest that the concentration of phenolic type functional groups decreases throughout the range of carbons whereas carboxylic functionality is on the increase. Thermal treatment of carbons in an oxidising atmosphere (air) leads to a decrease of the concentration and strength of surface acidic groups. This is particularly the case for carboxylic groups titrated with NaHCO₃ as shown for air oxidised carbons in Table 6.3. Phenolic groups were found to be dominant in air oxidised samples.

Various treatments were applied in order to determine their effect on oxidised carbon properties. Table 6.5 presents the results of direct titration for carbons. KAU-1.6 (oxidised by nitric acid) was extensively washed with 0.1 N sodium hydroxide. After a week of alkaline washing a decrease in carboxylic group concentration was observed. The carbon coloured the alkaline washing solution. This was due to the extraction of the humic acid compounds from the carbon. These substances are formed during carbon oxidation in the liquid phase due to a partial digestion of carbonaceous material. These compounds are leached from the surface during the alkaline wash. It was shown by Kuzin and Strashko that the humic acid molecules and oxidised carbon surface are structurally similar. Humic acids consist of flat networks of carbon rings with side radicals. Functional groups of the same type and mutual influence as in oxidised carbons, are statistically distributed in these acids. The reduction of carbon capacity after alkaline treatment may be associated with the
removal of these compounds. Heat treatment of oxidised carbons appeared to influence the surface acidic group distribution. Thus F 400 was heated in the furnace in air atmosphere for 7 hours at different temperature settings (at 400 °C for 4 hours, 430 °C for 2 hours, and 450 °C for 1 hour).

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Carboxylic groups, meq/g</th>
<th>Lactones, meq/g</th>
<th>Phenolic groups, meq/g</th>
<th>Total (non carbonyl), meq/g</th>
<th>Carbonyl groups, meq/g</th>
<th>Total capacity, meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU-1.6</td>
<td>1.840</td>
<td>0.620</td>
<td>0.790</td>
<td>3.250</td>
<td>2.747</td>
<td>5.997</td>
</tr>
<tr>
<td></td>
<td>56.62</td>
<td>19.08</td>
<td>24.31</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAU-1.6</td>
<td>1.540</td>
<td>0.630</td>
<td>0.780</td>
<td>2.950</td>
<td>1.770</td>
<td>4.720</td>
</tr>
<tr>
<td></td>
<td>52.20</td>
<td>21.36</td>
<td>26.44</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F400ini</td>
<td>0.047</td>
<td>0.073</td>
<td>0.003</td>
<td>0.123</td>
<td>0.235</td>
<td>0.358</td>
</tr>
<tr>
<td></td>
<td>38.21</td>
<td>59.35</td>
<td>2.44</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F400ox</td>
<td>0.719</td>
<td>0.439</td>
<td>0.427</td>
<td>1.586</td>
<td>1.356</td>
<td>2.941</td>
</tr>
<tr>
<td></td>
<td>45.33</td>
<td>27.68</td>
<td>26.92</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F400a</td>
<td>1.270</td>
<td>0.500</td>
<td>0.490</td>
<td>2.250</td>
<td>1.350</td>
<td>3.600</td>
</tr>
<tr>
<td></td>
<td>56.44</td>
<td>22.22</td>
<td>21.78</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F400h</td>
<td>1.100</td>
<td>0.530</td>
<td>0.920</td>
<td>2.540</td>
<td>1.390</td>
<td>3.940</td>
</tr>
<tr>
<td></td>
<td>43.31</td>
<td>20.87</td>
<td>36.22</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CKC</td>
<td>1.149</td>
<td>0.585</td>
<td>0.462</td>
<td>2.160</td>
<td>1.056</td>
<td>3.216</td>
</tr>
<tr>
<td></td>
<td>53.19</td>
<td>27.08</td>
<td>21.39</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.5. Concentration of surface functional groups of various carbons.

* u- untreated; w- washed with sodium hydroxide; h- heat treated
† % to total non carbonyl capacity

The resulting material (F 400h) was washed with distilled water and 0.1 N NaOH. The colouring of the washing solution appeared to be much less than in the case of the initial F 400. The results of the direct titration indicate slight reduction in the amount of carboxylic groups and a drastic increase in the quantity of phenolic groups. It is obvious that heat treatment of the oxidised carbon introduces additional surface functional groups of relatively weaker phenolic type. This treatment however did not significantly affect the overall capacity of the carbon.
The capacity of unoxidised F 400 is very low when compared to the oxidised modifications. It is also significantly lower than that presented by Mazet et al. Table 6.6 presents the concentrations of surface functional groups for F 400 obtained by this author.

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Carboxylic</th>
<th>Lactone</th>
<th>Phenolic</th>
<th>Carbonyl</th>
<th>Total capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>F 400</td>
<td>0.33</td>
<td>0.23</td>
<td>0.10</td>
<td>0.49</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 6.6. Concentration of surface functional groups on F 400 (meq/g).

The difference between the results may be due to the different chemical composition of the F 400 titrated by Mazet. The material used by the researcher may have been exposed to an oxidising atmosphere (air) for a longer period than our carbon. This would obviously result in a greater amount of surface acidic groups.

### 6.4 Electrophoretic mobility

Figures 6.1-6.3 show the electrophoretic mobility (zeta potential) vs pH plots for KAU carbons oxidised by nitric acid and air as well as other carbons including F 400 (oxidised), CKC, PGP-P and carboxylic resin Purolite C 104 (for comparative reasons).

An important parameter used to characterise the electrokinetic behaviour of a solid-liquid interface is the condition where the zeta potential is zero. It is often called the isoelectric point (IEP) of the interface. Active carbons should be regarded as amphoteric solids because of the varying amounts and nature of surface oxygen. By analogy with amphoteric oxides the amphoteric nature of carbons, illustrated in Figure 6.4, indicates that at some pH (the isoelectric point, pH_{IEP}) the net overall surface charge will be zero. At pH > pH_{IEP}, the carbon surface (e.g. covered by deprotonated functional groups) will attract cations from solution. At pH < pH_{IEP}, it will attract anions (e.g. acting as a Lewis base).
Figure 6.1. Electrophoretic mobility curves for KAU carbons oxidised by air

Figure 6.2. Electrophoretic mobility curves for KAU carbons oxidised by nitric acid
Therefore the zeta potential of carbons is an important factor in controlling their behaviour as ion sorbents in aqueous solutions.

The reactions of carbon with modifying agents (oxidising agents, ammonia, etc.), heat treatment in an inert or hydrogen atmosphere, and the presence of heteroatoms (nitrogen, phosphorus, sulphur, etc.) usually alters the electrokinetic properties.

**Figure 6.3.** Electrophoretic mobility curves for miscellaneous sorptive materials

**Figure 6.4.** Amphoteric nature of the surfaces of carbon particles.
A shift of $pH_{\text{IEP}}$ for initial KAU carbon to much lower values is observed as the degree of surface oxidation (sorbent capacity) increases. After oxidation in nitric acid or in air a negatively charged surface is generated at $pH$ values above 2. The isoelectric point for some severely oxidised carbons can reach $pH$ values as low as 0.9. A rather low $pH$ value of isoelectric point for initial KAU carbon is detected. Since the carbon was not stored under nitrogen, or in air excluding conditions, an ageing effect is observed. The activated carbons pick up oxygen slowly from the air. Puri et al. 17 studied this effect and found that in pure oxygen this process is rapid and is complete in 12 hours; in air it took nearly three months to complete. It is well known that essentially all oxygen-containing groups are removed during the high temperature treatment in a nitrogen atmosphere 18. The resultant surface is very active and both elemental analysis and microcalorimetric studies showed significant oxygen adsorption on re-exposure to air (oxygen) at room temperature 19. The research also confirmed the acidic nature of the stabilised form of this carbon.

It can be inferred that a longer oxidation time only results in a small increase in negativity of the surface. Thus for oxidised carbons, regardless of the method of oxidation or origin, the zeta potential is around $-35$ to $-40 \text{ mV}$. The zeta potential curves for different acid oxidised carbons rise steeply until $pH \sim 5$ and then start to flatten. This suggests that the dissociation of relatively strong carboxylic surface groups is responsible for this effect. Indeed, the dissociation of this type of group occurs in the $pH$ range of $\sim 2$ to 6, therefore enhancing the negativity of the surface. As for the air oxidised carbons, weaker surface functional groups are predominant. Their dissociation begins at higher $pH$ values. Hence the zeta potential curves are flatter in comparison to nitric acid oxidised samples. As far as the phosphorus-containing carbon is concerned, the negativity of its surface is attributed to the dissociation of more acidic phosphorus-containing groups. The comparison of dissociation constants for phosphoric acid and 3-hydroxybenzoic acid (analouges of the surface functional groups in carbons) revealed that phosphoric groups are more acidic than carboxylic groups. Thus $pK_1$ for phosphoric acid is 1.96 whereas $pK_1$ for carboxylic groups is 4.05 20, 21. Consequently the phosphorus-containing carbon possesses more negative surface than oxidised carbons (Figure 6.3). The isoelectric point for carboxylic resin Purolite C 104, despite its high sorptive capacity ($\sim 10 \text{ meq/g for Na}^+$), occurs in comparatively less acidic $pH$ ($pH \sim 2$ vs $pH \sim 0.9$ for KAU-1.6).
The electrophoretic mobility curve indicates lower negativity of the surface when compared to carbon materials. It is possible to conclude that carbon based sorbents are more acidic than carboxylic resin.

Owing to the special electrophysical properties of carbons, (namely the presence of delocalised π-electrons relatively easily transferable in a conjugated systems of bonds) the carbonaceous sorbents possess significant electrical conductivity. The properties of functional groups attached to the carbon surface and non-conductive polymeric matrix (ion-exchange resins) should diverge considerably. The strengths of real protonogenic surface functional groups (primarily carboxylic groups) in carbons should increase since the negative charge builds up close to the surface of oxidised carbon. This is demonstrated by the fact that cation-exchange on oxidised carbons, contrary to carboxylic resins, begins at pH values around 1.22, i.e. the acidity of carboxylic groups on the oxidised carbon surface is 10 times stronger than that of carboxylic resin.

6.5 pH titration

pH titration (potentiometric titration) is recognised as a simple and convenient method to study acidic and basic properties of ion-exchangers. The quantity and type of different functional groups in ion-exchangers is often assessed by analysing pH titration curves. The shape of these curves (solution pH as a function of alkali or acid added; absolute or relative amount of ions removed vs solution pH) usually indicates the nature of the ion-exchanger (mono- or polyfunctional), the type of functional groups and their dissociation ability, the most appropriate working range for the particular ion-exchanger, etc. If the ion-exchanger is in hydrogen form (i.e. it dissociates releasing hydrogen ions and possesses acidic properties), the titration of electrolyte solution in the presence of this material will consume more alkali than without the ion-exchanger. As a consequence, the titration curve for a solution containing a cationite will be shifted towards the increase of alkali volume added. Typical pH titration curves in the presence of ion-exchanger (curve 2) and without (curve 1) are presented in Figure 6.5. The abscissa difference for two points located
on the curves at the same pH allows the determination of the amount of hydrogen-ions released from the ion-exchanger at a given pH.

![Figure 6.5. pH-titration curves for KAU-1.2 and blank experiment.](image)

The relationship (A) between the amount of cation which exchanges with hydrogen ion and pH, is determined from the abscissa difference at different pH values:

\[
A = C \frac{(V_1 - V_0)}{m}
\]  \hspace{1cm} (1)

Where \( V_1 \) is the volume of titrated alkali solution corresponding to a given pH value and in the presence of ion-exchanger (ml); \( V_0 \) is the volume of titrated alkali solution corresponding to a given pH value and in the absence of ion-exchanger (ml); \( C \) is the concentration of a titrant (M); \( m \) is the amount of dry ion-exchanger (g).

It is well known that active carbon is an amphoteric sorbent i.e. it can adsorb acids or bases depending on pH. The acidic surface properties are due to the presence of acidic surface groups. Such carbons have cation exchange properties. Carbons with low oxygen content show basic surface properties and anion-exchange behaviour.
Hence it is necessary to titrate carbonaceous adsorbents with both acid and alkali solutions in order to determine their ion-exchange nature.

The differential pH-titration (proton-binding) curves for the carbons studied are presented in Figures 6.6 – 6.8.

![Figure 6.6. Proton-binding curves for KAU carbons oxidised by nitric acid.](image-url)
Figure 6.7. Proton-binding curves for KAU carbons oxidised by air.

Figure 6.8. Proton-binding curves for miscellaneous sorptive materials.
The curves for all carbons are smooth and do not have very distinctive inflection points. However there is a distinguishing difference between the carbon samples oxidised in hot air and nitric acid. As seen from the titration curves for the former set of samples, pH titration curves rise rather steeply between the crossover point and pH ~ 6. The latter array of curves is shallower in this pH range indicating greater ion-exchange capacity. The results of Boehm's titration show that air oxidised carbon samples possess mostly weaker types of functional groups (phenolic) whereas the majority of functional groups in acid oxidised materials are carboxylic (stronger). Mironov and Taushkanov 23 suggested that carboxylic groups in carbons dissociate in the pH interval of 3 - 6 and phenolic groups dissociate above that. This can be seen from our pH titration results.

Figure 6.8 presents the pH titration curves for the phosphorus-containing carbon PGP-P and carboxylic ion-exchange resin Purolite C 104. By way of comparison the pH titration curves for KAU 1.8 and KAU 2.7 are also presented in this Figure. It can be seen that titration curves for carbon samples (whether the curves are smooth or have inflection points) are significantly different from the curve for the carboxylic resin. As inferred from the differential titration curves, the difference between carbons and resin is due to a difference in their relative acidic properties. The ion-exchange on Purolite C 104, despite its high exchange capacity, starts at pH ~3.2 i.e. dissociation pH of conventional carboxylic functional groups. The sorptive capacity of this material is used almost completely throughout the investigated range of the pH values. In contrast to the resin, the ion-exchange on carbon samples begins at lower pH values (pH 2 and lower) 24. As the pH increases, weaker functional groups begin to participate in ion exchange progressively. Phosphorus-containing carbon showed acidic properties throughout the pH range studied. The shape of the titration curve of this sample is similar to that of oxidised carbons indicating polyfunctional nature of this sorptive material.

The crossover point with the pH axis on the titration curves is the point where anion and cation exchange are in equilibrium. This point is considered to be a point of zero charge (PZC). As the degree of carbon oxidation increases, the crossover point occurs
at lower pH values. Thus the crossover point for unoxidised KAU is located at pH ~ 10 whereas that for the KAU 2.7 (high degree of surface oxidation) is at pH ~ 2.

The chemical properties of the carbon surface in contact with an aqueous environment are complex. Electrochemical techniques have been widely used to characterise carbon solids in aqueous solutions\textsuperscript{19,2}. It has been suggested that the isoelectric point (IEP) values are only representative of the external surface charges of carbon particles in aqueous solutions whereas the point of zero charge (PZC) varies in response to the net total (external and internal) surface charge of the particles\textsuperscript{25,26}. Therefore, the difference between PZC and IEP can be interpreted as a measure of surface charge distribution of porous carbon solids\textsuperscript{25}. Greater differential values indicate more negatively charged external than internal particle surfaces. Lower values correspond to a more homogeneous distribution of the surface charges. Table 6.7 presents the PZC and IEP values for the samples studied.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>PZC</th>
<th>IEP</th>
<th>PZC - IEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td>10</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>KAU 0.8</td>
<td>6.2</td>
<td>2.3</td>
<td>3.9</td>
</tr>
<tr>
<td>KAU 1.2</td>
<td>3.7</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>3</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>KAU 1.5</td>
<td>3.1</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>2.8</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>2.5</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>2.1</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>PGP-P</td>
<td>1.6</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>CKC</td>
<td>2.1</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>Purolite C104</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.7. Electrochemical properties of the sorptive materials studied.

The large difference between PZC and IEP was detected for KAUini (unoxidised sample). Since this carbon was not kept in an air tight container, ageing (slow
oxidation by air) of the sample occurred. The high value of PZC for this sample indicates that the internal surface preserves its basic character. The oxidation of the surface preferentially occurs on the external surface and this is indicated by low IEP value for this carbon. The difference between PZC and IEP decreases as the degree of oxidation increases. At low degrees of surface oxidation, functional groups are preferentially introduced onto the external surface, therefore the difference between PZC and IEP is large. As the degree of oxidation progressively increases, more oxygen-containing groups are added to the internal surface of carbon thus narrowing the PZC-IEP difference. The close values of PZC and IEP for the carbons with a high degree of surface oxidation indicate that the oxidation treatment affects the whole surface to a similar extent i.e. concentrations of functional groups on external and internal surfaces approach equal values. During the course of synthesis acidic functional groups are uniformly distributed between external and internal surface in both phosphorus-containing carbon and carboxylic resin. The PZC and IEP values in both specimens are low and closely matched thus indicating more homogeneous surface than in oxidised carbons.

The determination of true ionisation constants for polymeric acids (bases), even for monofunctional ones, is complicated by the progressive change of their values with the change in degree of neutralisation. This is related to the fact that the separation of every subsequent proton from the polymeric carcass is resisted by the electric field created by functional groups which are already ionised. According to Gregor et al 27, 28 the dissociation constant (K_{dis}) for polymeric acid (ionite) can be presented by the following equation:

$$K_{dis} = \frac{[H^+][A^-]}{[HA]} f(z)$$  \hspace{1cm} (2)

where \([A^-]\) and \([HA]\) are the concentration of ionised and respectively non-ionised functional groups in the ionite, and \(z\) is the ratio between the charged and uncharged groups:

$$z = [A^-] / ([A_{tot}] - [A^-])$$  \hspace{1cm} (3)
[A_\text{tot}] is the total concentration of the functional groups. If \( f(z) \) is presented in an empirical form \( f(z)=z^m \), where \( m \) is a constant, then the equation for \( K_{\text{dis}} \) can be written in a following way:

\[
K_{\text{dis}} = [H^+] \left( \frac{[A^-]}{[HA]} \right)^n
\] (4)

or

\[
pK_{\text{dis}} = pH - n \log \left( \frac{[HA]}{[A^-]} \right)
\] (5)

where \( n=m+1 \),

or:

\[
pK_{\text{dis}} = pH - n \log \left( \frac{1-\alpha}{\alpha} \right)
\] (6)

where \( \alpha \) is the degree of ionite neutralisation.

Although equation (6) is used for the determination of ionisation constants of many ionites, more accurate results are obtained when \( \alpha \) equals 0.5. In this case the pH of the supernatant solution is equal to \( pK_{\text{dis}} \) of the functional groups. By this method the average apparent \( K_{\text{dis}} \) for the ionite can be estimated.

The determination of ionisation constants for polyfunctional cationites is more complicated. In addition to the dependence of \( K_{\text{dis}} \) on the surface coverage, it is expected that a series of dissociation constants will be observed which are related to the dissociation of different types of functional groups. These will be dependent on equilibrium pH values. Naturally, for a polyfunctional ion-exchanger it is not meaningful to determine the average dissociation constant corresponding to its total capacity. It is instead necessary to determine the neutralisation points where \( \alpha \) is equal to 0.5 for each type of functional group. It is possible to determine \( pK_{\text{dis}} \) in a similar way to monofunctional cationites under the following conditions: there are only two or three group types, they significantly differ in their dissociation ability and there are corresponding inflection points on the pH titration curve. The titration curves are relatively smooth and usually do not have distinctive inflection points if there are many different types of functional groups and they are close in their dissociation ability. Therefore, the determination of dissociation constants for polyfunctional cationites is a difficult task particularly when the exact number of types
of functional groups is not known. However, this task can be performed reasonably accurately if the pH titration curve is arbitrarily divided into small sections. The average dissociation constants are then determined for each section according to Griessbach \(^{29}\), whereby is assumed that pH is equal to pK at the point corresponding to 50% of the group type represented by the curve section under inspection.

This approach may also be applied in the field of carbonaceous materials. It is well known that there is a wide variety of functional groups on carbon surfaces and that the inflection points on the pH titration curves for these materials are not well defined. The above approach allows assessment of the acid-base properties of carbons as well as determination of the apparent dissociation constants for these materials. Obviously this method is rather approximate. The division of the curve is carried out in an arbitrary manner due to the absence of well defined inflections on pH titration curves for carbonaceous materials.

Seki and Suzuki \(^{30}\) proposed a slightly different way of fitting potentiometric titration data and extracting acid-dissociation constants for the acidic sites on the cationite between pH \(-2\) and \(-10\). Assuming that the major acidic sites on carbons are carboxylic and phenolic groups, the acid-dissociation reactions can be written as:

\[
\begin{align*}
R\text{-}COOH & \leftrightarrow R\text{-}COO^- + H^+ ; K_1 \\
R\text{-}OH & \leftrightarrow R\text{-}O^- + H^+ ; K_2
\end{align*}
\]

The acid-dissociation constant \(K\) for a particular type of functional groups is defined as:

\[
K_{1,2} = \frac{a[H^+]}{1-a}
\]

where \(\alpha\) is the degree of dissociation of functional groups. The number of deprotonated acidic groups on carbon (dry wt. basis, g), \(X_o\), can be expressed as:

\[
X_o = N\alpha = \frac{NK_{1,2}}{K + [H^+]}
\]
where, \( N \) represents the number of acidic groups on carbon. Equation (10) may be fitted to potentiometric data (deprotonated acidic groups, mmol/g vs. equilibrium pH) to extract values for the two unknown parameters, \( N \) and \( K_{1,2} \).

The dissociation constants for the sorbents, presented in Table 6.8, were calculated by the method described above.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( pK_a) 1</th>
<th>( pK_a) 2</th>
<th>( pK_a) 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAUini</td>
<td>--</td>
<td>--</td>
<td>9.97</td>
</tr>
<tr>
<td>KAU 0.8</td>
<td>--</td>
<td>9</td>
<td>10.7</td>
</tr>
<tr>
<td>KAU 1.2</td>
<td>6</td>
<td>8.5</td>
<td>10.85</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>3.6</td>
<td>7.00</td>
<td>10.69</td>
</tr>
<tr>
<td>KAU 1.5</td>
<td>3.6</td>
<td>6.50</td>
<td>9.7</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>4</td>
<td>6.90</td>
<td>10.2</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>3</td>
<td>6.75</td>
<td>9.5</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>3.6</td>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>PGP-P</td>
<td>2.85</td>
<td>5</td>
<td>9.85</td>
</tr>
<tr>
<td>CKC</td>
<td>2.8</td>
<td>6.9</td>
<td>9.8</td>
</tr>
<tr>
<td>Purolite C 104</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.8. Dissociation constants for the materials studied

The obtained results show that all the carbons studied contain surface protonogenic groups with rather different dissociation constants. The dissociation constants vary between \( 10^{-3} \) and \( 10^{-11} \). It can also be concluded that the functional groups in carbons are more acidic than those of carboxylic resin Purolite C 104. It follows that these changes in surface acidity suggest that cation exchange on active carbons begins at lower pH values when compared to a polymeric weakly acidic resin.
6.6 FT-IR, $^{31}$P MAS-NMR and X-ray photoelectron spectroscopy.

The removal of ions from aqueous solutions is influenced by the functional groups present on the surface of the adsorbent. Functional groups may directly interact with ions by an ion exchange mechanism or by forming donor-acceptor type bonds. A wide variety of techniques can be applied to the determination of functional groups on the surface of carbons. Early studies used indirect methods of surface analysis i.e. titration, elemental analysis, etc. In recent years active carbons have been studied directly by a number of spectroscopic techniques such as Fourier Transform Infra Red (FT-IR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, X-ray Photoelectron spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA), etc. Numerous other techniques are available. The following discussion however is restricted to methods which have been applied in the characterisation of sorbents used in this study.

FT-IR spectra of KAUini, KAU-2.7 and PGP-P carbons can be seen in Figure 6.9. Transmission infrared spectra of carbon solids are generally poor quality because of the strong scattering and absorption exhibited by carbonaceous materials. The IR spectrum for the samples studied shows continuously increasing absorption at higher wave numbers, which can be attributed to adsorption of the conjugated aromatic ring structures. On the top of this continuous absorption spectrum, the absorption of surface groups can be observed. After baseline correction using a curved baseline suitable for strongly scattering samples, these absorptions appear as peaks. The peak at 1600 cm$^{-1}$ has been the subject of discussion for a long time. The most likely explanation was provided by Morterra and Low, who attributed this peak to the interaction of polyaromatic C=C bonds which are polarised by the binding of oxygen near to one end. This peak is present in all three samples. A new peak at 1700 cm$^{-1}$ appears in the spectrum of nitric acid oxidised KAU-2.7 carbon. This peak is specific for carboxylic acid groups and is observed only after prolonged oxidation. This peak can also be assigned to C=O stretching in lactone and/or acid anhydride.
Figure 6.9. FT-IR spectra of KAUini, KAU 2.7 and PGP-P.
The broad peak at a maximum near 1280 cm\(^{-1}\) may include adsorption bands characteristic of oxygen containing groups: Ph-O-R (1240 and 1030 cm\(^{-1}\)) and R-O-R (1150 cm\(^{-1}\)) ether groups, C-OH in carboxylic and phenolic groups (1250 cm\(^{-1}\)), C-OH in secondary (about 1070 cm\(^{-1}\)), primary (about 1030 cm\(^{-1}\)) and tertiary (about 1180 cm\(^{-1}\)) alcohols.\(^{34,36}\) The adsorption bands at about 1450 cm\(^{-1}\) and 1380 cm\(^{-1}\) indicate the presence of \(-\text{CH}_2-\) and \(-\text{CH}_3\) aliphatic groups, the contents of which decrease with increase in the degree of carbon oxidation.\(^{36}\) The increase of the 1600 cm\(^{-1}\) peak in the oxidised carbon sample is caused by formation of a quinone structure.

Similar experiments with surface oxidation of carbon materials were performed by Vinke et al\(^{33}\), Sellitti et al\(^{37}\) and Hontoria-Lucas et al\(^{38}\). These researchers associated an absorption peak at 1700 cm\(^{-1}\) with the surface carboxylic type groups formed during carbon oxidation. The relative increase in the 1600 cm\(^{-1}\) peak, attributed to surface quinones highly conjugated with the polyaromatic matrix, is also reported. There is an interesting similarity between our results and the results obtained by these researchers. The carbonaceous materials used in these studies are completely different in origin and structure. The materials they compared are peat-based carbons, carbon fibres and graphitic carbons whereas our carbons are based on carbonised apricot stones. Apparently, the types of surface groups formed upon surface oxidation are not dependent on the precursor material.

The transmission infrared spectrum for the phosphorus-containing carbon indicates the presence of adsorbed water (O–H stretch, 3450 cm\(^{-1}\)) together with adsorption bands at about 1600 cm\(^{-1}\) (aromatic C=C). Carbonisation of the precursor resin modified by a phosphorylating agent does not eliminate phosphorus from the surface of the resulting carbon. A strong absorption band at approx. 1050 cm\(^{-1}\) can be attributed to the O–P stretching mode and a second band at 550 cm\(^{-1}\) may arise from O–P–O bending vibrations.\(^{39,40}\) The absorption at 1040 - 1120 cm\(^{-1}\) may be assigned to C–P bonds.\(^{42}\) There is also a distinctive band at about 900 cm\(^{-1}\) which may be attributed to P–O–P vibrations. A broad band of pronounced absorption in the range 1100 - 1300 cm\(^{-1}\) also appears in the spectrum of the PGP-P carbon. This
band is probably due to P–O–C asymmetric stretching vibration and P=O stretching vibration\textsuperscript{40}.

These FT-IR results confirm the variety of functional groups on the surface of the PGP-P carbon. The carbonisation of the phosphorus-modified resin-precursor does not eliminate strongly hydrophilic phosphorus-containing groups from the surface. These groups apparently inhibit subsequent oxidation at high temperatures by blocking surface sites on the carbon surface.

Figure 6.10 shows a MAS NMR-\textsuperscript{31}P spectrum for the PGP-P carbon. It is thought that the broad line at 30 ppm is a consequence of contributions from various functional groups with a C–P bond. The carbon atom in this structure is part of the amorphous carbon material with non-uniform energetics (see Figure 4.5 in Chapter 4). The narrow line at –5 ppm represents phosphorus atoms surrounded by oxygen atoms belonging to phosphate and pyrophosphate functional groups. These atoms attached to graphite-like crystallites with more uniform energetics. The suggested surface groups are similar to those suggested by McKee et al\textsuperscript{40}.

![Figure 6.10. \textsuperscript{31}P MAS NMR spectrum for PGP-P carbon.](image-url)
Imamura et al.\textsuperscript{41, 42} have carried out similar investigations on the carbonisation of a phosphorus-containing phenolic resin which was heat treated at different temperatures (1000°C, 1500°C and 2000°C respectively). The $^{31}$P-NMR spectrum for the carbonised material treated at 1000°C possessed a set of peaks similar to the results presented in Figure 6.10. These researchers attributed the peaks in the NMR spectrum to chemically bound aromatic phosphorus compounds (Ph$_3$PO, Ph$_3$P, (PhO)$_3$PO, and Ph$_2$PO(OH)) as well as to red phosphorus (above 2000°C) and phosphorus incorporated in the cyclic ring systems of the graphene sheet.

XPS was carried out on KAU and PGP-P carbons to determine the chemical state of heteroatoms (oxygen and phosphorus) on the surface, identified by IR and NMR analysis. The spectra confirmed that the heteroatoms studied are chemically bound to the carbon surface and not just physically adsorbed onto it. PGP-P was also preloaded with lead to study the interaction between the metal and the surface functional groups of the carbon.

Figure 6.11 shows P 2p and Pb 4f$_{7/2}$ XPS narrow scans for the PGP-P and PGP-P loaded with lead.

The peak centered at 133 eV can be identified as the phosphorus sites which are bonded by –OPh, –Ph, =O, or –OH (e.g. Ph$_3$PO at 132.5 eV; (PhO)$_3$PO at 133.6eV, and Ph$_2$PO(OH) at 133.3 eV)\textsuperscript{42, 43}. There is a possibility that reduced phosphorus is present in this carbon (130-132 eV)\textsuperscript{41}.

The broad peak centered at 139 eV is attributed to the presence of lead. Lead is thought to be present in several forms i.e. as Pb(NO$_3$)$_2$ (adsorbate used to modify the carbon) at ~139.3 eV, PbPO$_4$ at ~138.9 eV, Pb(OH)$_2$ at ~138.6 eV\textsuperscript{44}. 
6.7 General Discussion

The carbonaceous materials used in this study are derived from both natural and synthetic polymeric precursors. The carbons obtained were further modified by oxidising agents (hot air and nitric acid) thereby introducing weakly acidic surface functional groups. As far as the PGP-P carbon is concerned, the groups were introduced during the course of material synthesis. Spectroscopic techniques confirmed the presence of a wide variety of functional groups on the surface of the carbon studied.

Oxidation with air yielded carbons with less acidic surface and consequently greater amphoteric properties than oxidation with nitric acid. This is confirmed by zeta potential measurements and pH-titration studies. The pH values of isoelectric point and point of zero charge for these materials are at a higher pH range than those for acid oxidised samples. The greater difference between IEP and PZC also indicates
that the surface of air oxidised carbons is more heterogeneous than that of nitric acid oxidised materials with respect to the surface acidity distribution. It appears that oxidation occurs preferentially on the outer surface of the carbons. The IEP-PZC difference decreases with the increase of carbon oxidation. This suggests that oxidation is a diffusion dependent process.

The titration of carbons with different strength bases also suggests that the samples oxidised by air and by acid differ in the distribution of acidic surface groups. Apparently, the relatively weaker type functionality is preferentially formed on the surface of air oxidised samples whereas nitric acid oxidation forms relatively stronger types of surface groups.

A possible mechanism for the formation of different types of acidic groups during progressive oxidation of the carbon may be suggested. Weakly phenolic type groups are formed on the surface of carbons with low degree of surface oxidation (especially for those oxidised by air). This process is likely to occur, via an intermediate step, by formation of the $O_2^-$ radical anion \(^{45}\). The formation of weakly acidic type surface groups can be represented by the following scheme \(^{46}\):

\[
\begin{align*}
\text{Carboxylic groups are likely to form as a result of further oxidation of the carbon already possessing phenolic surface groups. The following scheme shows a possible mechanism for formation of carboxylic groups} \quad &^{46} \quad \text{shows a possible mechanism for formation of carboxylic groups.}
\end{align*}
\]

Carboxylic groups are likely to form as a result of further oxidation of the carbon already possessing phenolic surface groups. The following scheme shows a possible mechanism for formation of carboxylic groups \(^{46}\)}:
The formation of carboxylic groups probably occurs directly at phenolic sites by cleaving of the π-conjugated bonds of the edge \( \text{C}=\text{C} \) atoms in the graphite-like plane. It is likely that alcohol hydroxyls are also formed in the surface layer. The decomposition of carboxylic groups during heat treatment of carbons may be another reason for the predominance of phenolic functional groups on the surface of air oxidised carbons. During air oxidation, various types of groups begin to form on the carbon surface and it is known that carboxylic groups are less stable than phenols upon heat treatment \(^{47, 48}\). It was illustrated that \( \text{CO}, \text{CO}_2, \text{H}_2\text{O} \) are released upon heating of active carbon. The amount of water released during heat treatment corresponds with the condensation and decomposition of primarily carboxylic groups. Some phenolic and carbonyl groups remained stable up to \( 800^\circ\text{C} \).

Oxidation of carbon with nitric acid may be analogous to the oxidation of aromatic hydrocarbons. The aliphatic side chains of the molecules are susceptible to oxidation and in many cases the final product will be an arylocarboxylic acid. If side chains of more than one \( \text{C} \) atom are present, the splitting of the \( \text{C}-\text{C} \) bond may occur at the \( \alpha \)-position of the benzylic carbon atom \(^{33}\). For example, the oxidation of 9,10-dihydrophenantrrene yields the corresponding dicarboxylic acid:
When one methylene group is present between two aromatic systems the oxidation is expected to stop at the ketone stage. This process can be illustrated by the oxidation of diphenylmethane:

\[
\begin{array}{c}
\text{CH}_2 \\
\text{Oxidation with nitric acid can be compared with the work performed by Papirer et al}^{47} \\
\text{and Otake and Jenkins}^{48}. \text{ In these studies, the formation of surface carboxylic groups was observed. The formation of hydroxyl groups and carbonyl groups upon nitric acid oxidation was suggested by Donnet and Ehrburger}^{49} \text{ and by Donnet}^{50}. \text{ Our investigation also indicates that the same oxygen functionalities are present on the carbon surface.}
\end{array}
\]

The surface functional groups (i.e. carboxylic, phenolic, etc) in oxidised carbons are analogous to the aromatic carboxylic acids and phenols. It is reasonable to expect that aromatic type acids, similar to phthalic or salicylic acids, would be formed upon oxidation of the edges of the ring structure because of the ring structure of the carbon basal planes.

The acid-base titration studies carried out using Boehm’s method\(^8,9\) suggested the presence of carboxylic acids on oxidised carbons. Hydrogen carbonate and carbonate anions were used as titrants for acidic carbon surface oxides. To observe an end point, the acid being titrated should be at least two orders of magnitude stronger than the conjugate acid of the base employed since the \(pK_a\) values of the conjugated acids \(\text{H}_2\text{CO}_3\) and \(\text{HCO}_3^-\) are 6.4 and 10.3 respectively\(^51\). The \(pK_a\) values of the surface acids titrated using Boehm’s method must be in the ranges \((a) \ pK_a < 4.4 \ \text{and} \ (b) \ 4.4 < pK_a < 8.3\). Several aromatic carboxylic acids possess dissociation constants which fit these ranges. Examples are presented in Table 6.9.
Surface oxidation generates a variety of randomly distributed surface functional groups. The positioning of these groups in close proximity may influence their acidity. For example, the acidity increases by more than an order of magnitude from benzoic to m-phthalic and salicilic acids (Table 6.9). The surface carboxyl groups of oxidised carbons exhibit even lower dissociation constants. This can be related to the fact that the surface groups are connected to π-conjugated condensed system of graphite-like planes. The number of the conjugated benzene rings and the positioning of the groups will also influence the acidity. For example, carboxylic acids derived from naphthalene and anthracene possess different dissociation constants depending on the location of carboxylic functional group on the aromatic ring (Table 6.10).

The delocalisation of 2p electrons of the oxygen in functional groups into the π-conjugated system results in a decrease in the effective negative charge on the oxygen. Consequently the mobility of the proton will increase, resulting in lower pKₐ values.

The state of the carbon surface cannot be considered as certain. It is not possible to identify any structural formations in carbons similar to a unit of structure in synthetic ion-exchange resins. The presence of delocalised electrons easily transferable in the conjugated system of condensed rings, random distribution and variations in the

<table>
<thead>
<tr>
<th>Acid</th>
<th>pK$_a$1</th>
<th>pK$_a$2</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Phthalic</td>
<td>2.89</td>
<td>5.51</td>
</tr>
<tr>
<td>m-Phthalic</td>
<td>3.54</td>
<td>4.60</td>
</tr>
<tr>
<td>p-Phthalic</td>
<td>3.51</td>
<td>4.82</td>
</tr>
<tr>
<td>Benzoic</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>Salicilic</td>
<td>2.93</td>
<td>12.37</td>
</tr>
<tr>
<td>m-Oxy-Benzoic</td>
<td>4.08</td>
<td>9.78</td>
</tr>
<tr>
<td>p-Oxy-Benzoic</td>
<td>4.61</td>
<td>9.31</td>
</tr>
<tr>
<td>2,4-Dioxy-Benzoic</td>
<td>3.22</td>
<td>-</td>
</tr>
<tr>
<td>2,6-Dioxy-Benzoic</td>
<td>1.22</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.9. Dissociation constants for the selected aromatic acids in water $^{52,53}$. 
mutual arrangement of functional groups, has a significant effect on the dissociation ability of surface functional groups in carbons \(^9\).

<table>
<thead>
<tr>
<th>Acid</th>
<th>(pK_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene-2-carboxylic acid</td>
<td>4.16</td>
</tr>
<tr>
<td>Naphthalene-1-carboxylic acid</td>
<td>3.69</td>
</tr>
<tr>
<td>Anthracene-9-carboxylic acid</td>
<td>3.65</td>
</tr>
<tr>
<td>Anthracene-1-carboxylic acid</td>
<td>3.68</td>
</tr>
<tr>
<td>Anthracene-2-carboxylic acid</td>
<td>4.17</td>
</tr>
</tbody>
</table>

Table 6.10. Dissociation constants in water \(^{54,53}\).

Significant increase in strength of individual protonogenic groups (for example carboxylic groups) can happen as a result of negative charge build-up close to the carbon surface. This is similar to the strength increase of carbonic acids with electron-attracting substituents e.g. halogens. Another reason for the enhanced strength of carbon functional groups can be a mutual influence of closely positioned functional groups (so-called "orto-effect"). Obviously, the individual functional groups of any particular type will exhibit a spread of their dissociation constants.

Study of the phosphorus-containing carbon suggested that on heat treatment of the phosphorus-modified resin an array of strongly hydrophilic groups is formed on the surface of the resulting carbon. These groups apparently inhibit subsequent oxidation at higher temperatures by blocking active sites on the carbon surface. A possible reaction mechanism, involving the formation of monomeric and dimeric surface complexes from a phosphorylating agent adsorbate, is represented by the following scheme \(^{59,40,41,55}\):
The NMR, pH-titration and electrophoretic mobility results suggested that the PGP-P material was inhomogenous in nature. The carbon matrix appeared to consist of crystalline and amorphous components. The chemical properties of functional groups attached to graphite crystallites will be different to similar functional groups attached to amorphous carbon (incompletely carbonised parts of the precursor). In the former case the interaction between surface functional groups will be facilitated by easily transferable π-electrons. These groups are likely to be more acidic, i.e. they may dissociate at lower pH values since the negative charge builds up close to the carbon surface. The surface groups in the latter case will be more isolated because of the hindrance of π-electron transfer in the partially carbonised material. The properties of this set of functional groups will resemble functional groups of synthetic ion-exchange resins situated on a non-conductive matrix. Hence, these functional groups will be comparatively weaker and will dissociate at relatively higher pH values.

6.8 Conclusions

Chemical surface modification of active carbons yields great differences in the properties of these materials. The modifications described can be used to prepare a carbon with "tailor-made" properties. By choosing a suitable modification technique,
it is possible to control the quantities of heteroatoms (functional groups) on the surface of the material modified.

Direct titration techniques and spectroscopic measurements revealed a number of different surface functional groups containing heteroatoms such as oxygen and phosphorus. The pH-titration results demonstrate that oxidised carbons and the phosphorus-containing carbon, despite their relatively lower sorptive capacity (amount of ion-exchange groups), appear to be more acidic than those of weakly carboxylic resin. Electrophoretic mobility measurements detected that the carbon surface is negatively charged within the range of pH values studied. The relatively high amount and distribution of surface acidic groups present on the carbons is expected to affect the capacity and selectivity of sorption of different ionic species.

6.9 References

35. Morterra, C. and Low, M.J.D. Spectrosc. Lett. 1982, 15, p. 689


Chapter 7: Sorption Studies

7.1 Introduction

Water intended for human consumption in the UK must comply with the relevant requirements outlined by European Council Directive 80/778/EEC. The concentration of any individual heavy metal in drinking water must be in the low μg/l range. The low limits for heavy metals set by the current legislation present a serious challenge for water supply companies and also prompt new research in applying sorptive materials (active carbons) already used for the removal of organic contaminants.

Carbonaceous materials have not been utilised for the removal of heavy metals from water on an industrial scale. However, a considerable amount of the relevant bench-scale research has been carried out upon the subject (Chapter 3). Heavy metal sorption by active carbons is a complex process since it is dependent on the chemistry of water, the heavy metal species distribution and the chemistry of the carbon surface. These three areas are interrelated, for as each one changes it directly affects the other.

The objective of this study is to demonstrate the efficiency of carbonaceous materials in treating heavy metal-bearing solutions. Lead and copper were chosen as the subject of this study because of their likely presence in the water distribution system as a result of corrosion and leaching from lead pipes and lead/tin-soldered joints associated with copper pipes commonly used in household plumbing.

Waste waters generated by electroplating and metal finishing industries may contain nickel and cadmium as well as lead and copper. Precipitation processes are the most economical for these high metal concentration wastes. However, many metal-bearing streams contain complexing agents which decrease the effectiveness of precipitation leading to relatively high metal content in the effluent. In addition, the current regulatory levels for heavy metals discharge limits are approaching those of drinking water standards. Hence additional treatment processes downstream from the
precipitation process may be necessary to remove metal residuals prior to discharge.

Active carbons containing heteroatoms (oxygen and phosphorus) were selected for this investigation. It was shown previously that active carbons with heteroatoms on their surface have fairly high metal sorptive capacity, a rigid structure, and exhibit selective properties towards a number of heavy metals. However there is scarce information in the available literature concerning the influence of the degree of carbon oxidation on metal sorption as well as on competitive interactions between various metal species (lead and copper in particular) for surface active sites. As far as the phosphorus-containing carbon is concerned, the selectivity of this material towards some heavy metals may be analogous to phosphorus-containing synthetic resins and inorganic ion exchangers.

7.2 Effect of Carbon Surface Oxidation

The carbonaceous sorptive materials used in this project are oxidised using nitric acid and hot air. After oxidation the surface characteristics of the carbon are changed. Generally, a reduction in surface area and a slight increase in pore volume are observed and are reported in Chapter 5. However, these altered physical properties do not adversely affect metals sorption. On the contrary, a dramatic increase in the uptake of heavy metal ions from aqueous solutions is observed and this is shown in Figure 7.1. Modification of the carbon surface by oxidation introduces a variety of acidic functional groups. These functional groups dissociate in aqueous solutions and bind metal species. Oxidation also changes the nature of the carbon samples from hydrophobic to hydrophilic. The improved hydrophilicity of the oxidised carbon surface enables better accessibility of metal ions to surface active sites. The sorptive capacity of the oxidised samples is also significantly enhanced. The metal uptake capacity increases by a factor of up to 10 for air oxidised carbon and up to 20 for the nitric acid oxidised sample.
7.3 Metal Sorption from Buffered Solution

Oxidised carbon may be considered as a weakly acidic cation exchanger containing various surface functional groups. One of the possible pathways of metal sorption by active carbons can be described by the following reaction scheme:

\[
\text{Me}^{z+} + nRI \rightleftharpoons Rn\text{Me}^{(z-n)} + n\text{H}^+
\]

where Me is a metal ion, R-H is an acidic functional group, n is a number of functional groups (ligands) interacting with one metal ion, and z is the charge on the metal ion. The solution pH becomes acidic because of the hydrogen ions released into solution as a result of metal sorption. Since metal sorption is a pH dependent process, the decrease of solution pH has an adverse effect on metal uptake. Figure 7.2 presents pH variations during equilibrium metal sorption for different carbons as a function of
the amount of carbon introduced.

Figure 7.2. Equilibrium solution pH vs amount of carbon introduced during metal sorption.

The pH of the supernatant solution decreases as the amount of carbon increases. It was shown in a previous Chapter that the dissociation of surface functional groups in carbons strongly depends on pH of solution i.e. the sorptive capacity of carbon falls as the pH decreases. This phenomenon is sometimes overlooked when metal sorption isotherms are being determined and therefore yields incorrect adsorptive capacity results. In order to eliminate this source of error, metal sorption isotherms are often performed in buffered solutions. Thus, Abbasi 2 and Nair 3 investigated heavy metals removal from citrate, acetate and borate buffer solutions using conventional and oxidised active carbons. These authors found that metal sorption is considerably enhanced in the presence of buffers. It was furthermore suggested that metal ions are removed by active carbon as complex compounds.

Similar equilibrium sorption tests were performed in this project. pH in lead-containing solutions was controlled by an acetate buffer and by adjustment with alkali.
The results clearly indicate that sorptive capacity of carbon for lead increases two fold when the experiment is performed in the buffered solution. Multivalent metal ions in solutions tend to react with buffers, which can act as good complexing agents. It is known that lead forms the complex ions PbAc\(^+\), PbAc\(_2\), [PbAc\(_3\)]\(^-\), and [PbAc\(_4\)]\(^2-\) in acetate solutions. Apart from metal ions being removed by conventional ion-exchange, the buffer-metal complexes are adsorbed as neutral molecules. This can lead to incorrect conclusions regarding the equilibrium ion exchange capacity of active carbons.

7.4 The Influence of pH on Metals Removal by Active Carbons

The surface of carbonaceous sorbents in aqueous solutions can be either positively or negatively charged. The surface charge largely depends on the pH of the external solution. It was shown previously that the pH of aqueous solutions is an important variable which controls the metal sorption at carbon-water interfaces. House and Shergold found that metal sorption capacity of active carbon depends on the pH value at the point of zero charge (PZC). These researchers observed an abrupt reduction in metal sorption near to this pH value. The removal of cations is favoured at pH values above PZC and vice versa for anions. Acidic functional groups on the surface of carbons act as ion-exchange sites for metals. In order to enable the sorption of cations, the feed solution pH has to be close to that of the pK values of functional groups.

The effect of the external solution pH on the extent of the metal sorption for various sorbents can be seen in Figures 7.3 and 7.4. These experiments were performed in both batch and mini-column mode.

The amount of metal removed by carbons increases sharply between pH 1.5 and 3. The adsorption experiments were not conducted at pH above 5 due to the formation of metal precipitates. All carbons show a similar trend.
Figure 7.3. Effect of solution pH on the extent of metal sorption by carbons (batch mode).

Figure 7.4. Lead uptake on oxidised carbon at different pH values (column mode).
However the carbons with higher degrees of surface oxidation, oxidised by nitric acid (KAU 2.7 and CKC), begin to sorb metal ions at lower pH values. Adsorption at very low pH values (pH ~ 1-2) (Figure 7.4) may be attributed to certain relatively strong acidic functional groups. Surface functional groups with electronegative atoms e.g. oxygen which possess a lone pair of electrons can form coordinate covalent bonds with metal ions in solution. Delocalised π-electrons will enhance the electronegative nature of these atoms, thereby facilitating complexation of metal ions to the carbon surface. This is of course in addition to parallel ion exchange reactions where protons of weakly acidic surface functional groups are exchanged for metal ions. Although acidic groups stronger than carboxylic are not generally thought to exist on carbons, the experimental results published by Strazhesko and Tarkovskaya\textsuperscript{11,12} indicated the existence of some relatively strong acidic groups on oxidised carbons which participate in metal sorption reactions at pH 1-2 and even lower.

7.5 Metal Sorption from Aqueous Solutions

Adsorption isotherms and sorptive capacities of lead and copper for different sorbent samples are shown in Figures 7.5-7.10 and Table 7.1 respectively. All adsorption isotherms were carried out in mg/l range of concentrations without addition of any buffer to control the equilibrium pH of the feed solution. The solution pH was adjusted by careful addition of sodium hydroxide or hydrochloric acid and was kept constant at 4.8 ± 0.1. This pH value was selected in order to avoid precipitation of metal hydroxides\textsuperscript{7,13}.
Figure 7.5. Equilibrium sorption of lead by air oxidised KAU carbons.

Figure 7.6. Equilibrium sorption of lead by nitric acid oxidised KAU carbons.
Figure 7.7. Equilibrium sorption of lead by miscellaneous sorbents.

Figure 7.8. Equilibrium sorption of copper by air oxidised KAU carbons.
Figure 7.9. Equilibrium sorption of copper by nitric acid oxidised KAU carbons.

Figure 7.10. Equilibrium sorption of copper by miscellaneous sorbents.
Table 7.1. Equilibrium metal sorptive capacities of the sorbents studied (mmol/l range).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Lead</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 0.8</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>KAU 1.2</td>
<td>0.09</td>
<td>0.15</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>KAU 1.5</td>
<td>0.18</td>
<td>0.22</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>0.23</td>
<td>0.30</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>0.44</td>
<td>0.47</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>0.56</td>
<td>0.51</td>
</tr>
<tr>
<td>F 400 (ox)</td>
<td>0.22</td>
<td>0.29</td>
</tr>
<tr>
<td>PGP-P</td>
<td>0.76</td>
<td>0.61</td>
</tr>
<tr>
<td>CKC</td>
<td>0.54</td>
<td>0.47</td>
</tr>
<tr>
<td>KAU 1.6</td>
<td>1.74</td>
<td>2.5</td>
</tr>
<tr>
<td>Purolite C 104</td>
<td>3.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The results clearly show that sorption capacity of carbons strongly depends on the degree of surface oxidation i.e. concentration of surface functional groups capable of metal binding. The carbons oxidised by nitric acid possess greater sorptive capacity than those oxidised by air. It is also evident that the sorptive capacity of copper is greater than that of lead for carbons with low concentration of the acidic surface groups. However, as the degree of surface oxidation increases, the sorptive capacity of lead approaches that for copper (Table 7.1 and Figures 7.5, 7.6, 7.8 and 7.9). The results of metal uptake are in agreement with those discussed in the available literature (Chapter 3). However, the variation of copper and lead sorptive capacities with respect to the degree of surface oxidation has not been reported before.
The phosphorus-containing carbon PGP-P displays a relatively greater sorptive capacity for lead than for copper when compared with oxidised carbons (Table 7.1 and Figures 7.7 and 7.10). This material was prepared with the aim of improving the selectivity towards heavy metals and these results show sorptive behaviour similar to that of other phosphorus-containing adsorbents.14, 15

The experiments performed with weakly acidic ion-exchange resin Purolite C 104 indicated that this material did not reach its saturation capacity within the range of sorbent concentration studied (no isotherm plateau was achieved). Sorptive capacity of this material for both copper and lead is significantly higher than the metal sorption capacity of active carbons.

Heavy metals can be present at very low concentrations (usually in μg/l range) in water intended for human consumption. It is evident from the available literature (Chapter 3) that these low levels, even at the current maximum admissible concentration, may adversely affect human health. Therefore it was necessary to assess the sorptive performance of carbonaceous materials towards heavy metals at trace concentrations.

Sorption isotherms for the metals studied were determined in the μg/l range of concentrations. The trends in metal removal were similar to those for mg/l range. Table 7.2 lists the equilibrium sorptive capacities of the materials investigated.

The data presented in Table 7.2 indicate that it is difficult to observe any specific trends in metal removal at trace concentrations. The shape of equilibrium sorption isotherms suggests that the adsorbents were not saturated in the working range of carbon concentrations. Hence the sorptive capacities for lead and copper are similar. When the sorption tests were conducted with a solution containing both metals it appeared that the sorptive capacity for each individual metal is similar and is approximately a half of that for the single metal. Both metals apparently use the same surface sorption sites. Since the equilibrium metal concentration was very low, there was no competition between these two cations for the surface sites. It is likely that at higher concentrations the surface-metal interactions will be different.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Lead (µmol/g)</th>
<th>Copper (µmol/g)</th>
<th>Lead (µmol/g)</th>
<th>Copper (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 0.8</td>
<td>1.380</td>
<td>3.030</td>
<td>0.945</td>
<td>0.341</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>28.125</td>
<td>25.353</td>
<td>15.797</td>
<td>15.844</td>
</tr>
<tr>
<td>KAU 1.5</td>
<td>31.278</td>
<td>30.857</td>
<td>18.557</td>
<td>24.273</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>57.325</td>
<td>55.100</td>
<td>20.611</td>
<td>24.223</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>56.516</td>
<td>59.236</td>
<td>20.383</td>
<td>23.869</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>60.488</td>
<td>60.003</td>
<td>24.392</td>
<td>27.969</td>
</tr>
</tbody>
</table>

Table 7.2. Metal sorptive capacities of the sorbents studied (µmol/l range).

### 7.6 Removal of Radionuclides by Active Carbons

Ion-exchange and sorption have been widely used for many years throughout the nuclear industry to decontaminate aqueous waste streams. Standard formulations of sorbents are used worldwide to process nuclear industry liquid wastes. However, as new materials are developed and discharge limits are lowered, it becomes increasingly difficult for operators to comply with the governing principles of ALARP (as low as reasonably practicable) and BATNEEC (best available technology not entailing excessive cost)\(^\text{16}\).

Oxidised carbons and phosphorus-containing carbon are novel materials for the removal of nuclear fission products. These sorbents possess obvious advantages over other more conventional sorptive materials (ion-exchange resins, inorganic ion-exchangers, zeolites, etc.) because of their high mechanical strength, chemical and radiation stability, high sorption selectivity, cheap and simple manufacturing process. Carbonaceous materials have also been used in medical applications to decontaminate...
the human body from radionuclides due to their inertness and biological compatibility\textsuperscript{17}. Hence it was thought appropriate to examine carbonaceous adsorbents for the removal of various radioactive isotopes.

A number of active carbons were tested for the removal of radionuclides from several reference waste streams (Chapter 4). The composition of these streams is similar to those discharged from nuclear power plants. Tables 7.3-7.9 show the sorption results obtained with the reference waste streams.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Feed, Bq/ml (pH 9)</th>
<th>Equilibrium concentration, Bq/ml ((\gamma)-activity)</th>
<th>DF (24 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>Cd-109</td>
<td>83.5</td>
<td>4.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Hg-203</td>
<td>77.1</td>
<td>9.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Cr-51</td>
<td>31.6</td>
<td>3.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Ru-106</td>
<td>57.6</td>
<td>13.7</td>
<td>5.8</td>
</tr>
<tr>
<td>Cs-137</td>
<td>96.3</td>
<td>7.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Mn-54</td>
<td>84.3</td>
<td>12.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Ag-110m</td>
<td>62.4</td>
<td>5.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe-59</td>
<td>84.4</td>
<td>40.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Zn-65</td>
<td>85</td>
<td>4.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Co-60</td>
<td>104.4</td>
<td>7.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 7.3. Removal of radionuclides by F400(ox) in II\textsuperscript{+}-form from NAEC S1 reference waste stream (\(\gamma\)-activity).
Table 7.4. Removal of radionuclides by F400(ox) in Na⁺-form from NAEC S1 reference waste stream (γ-activity).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Feed, Bq/ml</th>
<th>Equilibrium concentration, Bq/ml</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(pH 9)</td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>Cd-109</td>
<td>83.5</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Hg-203</td>
<td>77.1</td>
<td>9.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Cr-51</td>
<td>31.6</td>
<td>6.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Ru-106</td>
<td>57.6</td>
<td>19.8</td>
<td>8.7</td>
</tr>
<tr>
<td>Cs-137</td>
<td>96.3</td>
<td>35.9</td>
<td>59.5</td>
</tr>
<tr>
<td>Mn-54</td>
<td>84.3</td>
<td>4.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Ag-110m</td>
<td>62.4</td>
<td>9.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe-59</td>
<td>84.4</td>
<td>45.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Zn-65</td>
<td>85</td>
<td>3.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Co-60</td>
<td>104.4</td>
<td>2.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 7.5. Removal of radionuclides by KAU 1.9 in Na⁺-form from NAEC S1 reference waste stream (γ-activity).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Feed, Bq/ml</th>
<th>Equilibrium concentration, Bq/ml</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(pH 9)</td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>Cd-109</td>
<td>83.5</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Hg-203</td>
<td>77.1</td>
<td>9.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Cr-51</td>
<td>31.6</td>
<td>6.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Ru-106</td>
<td>57.6</td>
<td>19.8</td>
<td>8.7</td>
</tr>
<tr>
<td>Cs-137</td>
<td>96.3</td>
<td>35.9</td>
<td>59.5</td>
</tr>
<tr>
<td>Mn-54</td>
<td>84.3</td>
<td>4.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Ag-110m</td>
<td>62.4</td>
<td>9.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe-59</td>
<td>84.4</td>
<td>45.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Zn-65</td>
<td>85</td>
<td>3.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Co-60</td>
<td>104.4</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Isotope</td>
<td>Feed, Bq/ml</td>
<td>Equilibrium concentration, Bq/ml</td>
<td>DF</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>----------------------------------</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>(pH 9)</td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>Cd-109</td>
<td>75</td>
<td>4.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Hg-203</td>
<td>64</td>
<td>4.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Cr-51</td>
<td>67</td>
<td>2.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Ru-106</td>
<td>98</td>
<td>4.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Cs-137</td>
<td>139</td>
<td>68</td>
<td>80</td>
</tr>
<tr>
<td>Mn-54</td>
<td>45</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Ag-110m</td>
<td>66</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe-59</td>
<td>97</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn-65</td>
<td>85</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Co-60</td>
<td>132</td>
<td>13</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**Table 7.6. Removal of radionuclides by PGP-P in II*-form from NAEC S1 reference waste stream (γ-activity).**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Feed, Bq/ml</th>
<th>Equilibrium conc., Bq/ml (α-activity)</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(pH 9)</td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>KAU 1.9 (Na⁺)</td>
<td>9.60</td>
<td>1.00</td>
<td>0.05</td>
</tr>
<tr>
<td>F 400 (ox) (H⁺)</td>
<td>9.60</td>
<td>1.15</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Table 7.7. Batch contact test with selected carbons using NAEC S3 reference waste stream (α-activity).**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Feed, Bq/ml</th>
<th>Equilibrium conc., Bq/ml (β-activity)</th>
<th>DF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(pH 9)</td>
<td>1 hour</td>
<td>6 hours</td>
</tr>
<tr>
<td>KAU 1.9 (Na⁺)</td>
<td>7.70</td>
<td>0.92</td>
<td>0.60</td>
</tr>
<tr>
<td>F 400 (ox) (H⁺)</td>
<td>7.70</td>
<td>2.95</td>
<td>2.00</td>
</tr>
</tbody>
</table>

**Table 7.8. Batch contact test with selected carbons using NAEC S3 reference waste stream (β-activity).**
Table 7.9. Batch contact test with selected carbons at different pH values using NAEC S5 reference waste stream (α-activity).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Feed, Bq/ml</th>
<th>Equilibrium conc., Bq/ml (α-activity)</th>
<th>DF (24 hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 hour</td>
<td>6 hours</td>
<td>24 hours</td>
</tr>
<tr>
<td>KAU 1.9 (Na⁺) pH 7</td>
<td>8.10</td>
<td>0.62</td>
<td>0.20</td>
</tr>
<tr>
<td>F 400 (ox) (H⁺) pH 7</td>
<td>8.10</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td>KAU 1.9 (Na⁺) pH 9</td>
<td>8.10</td>
<td>0.56</td>
<td>0.19</td>
</tr>
<tr>
<td>F 400 (ox) (H⁺) pH 9</td>
<td>8.10</td>
<td>0.41</td>
<td>0.20</td>
</tr>
<tr>
<td>KAU 1.9 (Na⁺) pH 11</td>
<td>8.10</td>
<td>1.78</td>
<td>0.48</td>
</tr>
<tr>
<td>F 400 (ox) (H⁺) pH 11</td>
<td>8.10</td>
<td>1.72</td>
<td>0.42</td>
</tr>
</tbody>
</table>

The data presented in Tables 7.3-7.9 show that carbonaceous adsorbents exhibit exceptionally high decontamination factors (DF) for the radionuclides. The performance of the materials tested is comparable to or exceeds that of some commercially manufactured sorptive materials specifically designed to remove heavy metals and radioisotopes. Thus it can be seen that F 400 (ox) in protonated and cationic (Na⁺) forms shows similar results for the removal of the isotopes studied. The protonated form of F 400 (ox) unexpectedly shows a very high decontamination factor for Cs-137 removal. This is a very unusual finding since carbons do not normally possess selectivity towards this metal. Relatively low decontamination factors were detected for Fe-59. This is also rather surprising since oxidised carbons normally exhibit higher selectivity towards iron over other metals (Chapter 3). On the contrary, PGP-P carbon is found to have a very good decontamination factor for iron.

The uptake rate of radionuclides by carbons from NAEC S1 stream is found to be fast (Tables 7.3-7.6). Within one hour 85-95 % of metals are removed from the solution. However there are some exceptions. Fe-59, Ru-106 and Cs-137 are removed by oxidised carbons relatively slowly compared with the rest of the metal ions. Thus, within one hour only 45-55 % of iron, 60-70 % of ruthenium and 60-65% of cesium are removed by oxidised carbons. PGP-P shows an opposite trend in uptake rate of these metals except for Cs-137 where the uptake rate is similar to oxidised carbons.
Generally, after 24 hours 95-99.5% of γ-emitters are removed from the feed solution.

KAU 1.9 (Na⁺) and F 400 (ox) (H⁺) were also studied for the removal of α- and β-emitters (Pu, Am, Sr and Np) from NAEC S3 and NAEC S5 reference streams (Tables 7.7-7.9). The results for NAEC S3 indicate that KAU 1.9 give much higher decontamination factors than F 400 (ox). The pH dependence of DF for KAU 1.9 (Na⁺) and F 400 (ox) (H⁺) is reflected in Table 7.9. The removal of radioactive metals was carried out from NAEC S5 which also contains 1 g/l of NaHCO₃. It can be seen that DF increases with pH for KAU carbon whereas DF decreases in inverse proportion to pH for F 400 (ox). Similar to the uptake of γ-emitters, α- and β-emitting isotopes are also rapidly removed from the feed solution. The results of metal sorption rate indicate that 90-95% of radionuclides are taken up during the first hour.

7.7 Kinetics of Metal Sorption

The use of adsorbents such as hydrous oxides and active carbons is an effective treatment process for the removal of metal species. The study of metal ion sorption can provide information useful in the research of metal ion transport in surface and sub-surface systems. Equilibrium and kinetic studies are both important in gaining a better understanding of metal sorption mechanisms.

Kinetic studies were carried out in order to determine the rate of cation removal by different carbonaceous sorbents. These materials are rather complex systems with respect to their surface chemistry. It was shown in previous chapters that these sorbents contain a variety of acidic and basic functional groups. These groups, as well as the virgin carbon surface, can interact with metal species resulting in several simultaneous processes i.e. ion exchange, surface precipitation, redox reactions, complex formation, etc. These processes complicate the interpretation and modeling of metal uptake by carbons.

The results of kinetic experiments are shown in Figure 7.11. The experiments were performed with the lead ion since it is a prime metal in this study.
It can be seen that the rate of metal removal by the carbons derived from different precursors (i.e. natural products and synthetic polymers) and modified in different ways (i.e. oxidation by air and acid) is fast. During the first thirty minutes of the experiment approximately 75 - 90 % of metal is removed by the adsorbents (except for PGP-P). CKC carbon is particularly remarkable removing approximately 94 - 96 % within the first 30 min. of the experiment. The rapid phase of metal sorption is followed by a much slower phase. The kinetic curves usually reach an equilibrium plateau within 24 hours. In contrast to KAU and CKC carbons, the phosphorus-containing carbon exhibits a much slower metal sorption rate. The effect of sorbent particle size on metal sorption rate can be seen in Figure 7.12.
Chapter 7

Figure 7.12. Lead sorption rate for CKC at different particle size.

Earlier work performed by Ivanova et al.\textsuperscript{18, 19, 20} also suggests that metal sorption by active carbons occurs in two stages. During the initial stage (first few minutes of the experiment) approx. 70 - 90\% of metal is rapidly removed by carbon. The following stage of metal uptake is slow and prolonged and may take up to several days to complete\textsuperscript{21}. These researchers related this phenomenon to non-homogeneity of the carbon surface which contains a variety of functional groups. These surface groups which act as sorption sites may differ both with respect to strength of the metal sorptive bond and the rate of sorption onto the sites\textsuperscript{21}. Peel et al.\textsuperscript{22} related these two phases to the macropore and micropore regions. Relatively quick sorption occurs in the macropores and large mesopores where the controlling step is external mass transfer. The following slow adsorption approaching equilibrium occurs in the micropores where intraparticle diffusion is important.

A different approach to explain two-phase metal sorption by carbons was used by Matskevich et al.\textsuperscript{23} and Ivanova et al.\textsuperscript{19, 20}. Their explanation of fast metal sorption
was based on the electrochemical theory of Frumkin (Chapter 2). The researchers attributed the rapid uptake to the exchange of metal ions with protons in the electrical double layer of the carbon. The rate of metal removal slows down substantially with the presence of chemical interactions between surface groups and metal ions. Moreover, the slower the kinetics of sorption, the higher the ability of a particular ion to be specifically adsorbed onto the surface of carbon. Reactions between simple, easily dissociated aqueous ions are usually very fast and therefore not rate controlling. However some published data suggest that chemical reaction rate controls the exchange of transition metal ions or complex ions capable of strong chelate type complex formation with surface functional groups (e.g. iminodiacetate or phosphonate groups).

7.8 Mini-Column Experiments

The majority of commercial and laboratory applications of adsorption and ion-exchange involve operations where the solution to be treated is passed downflow through a fixed bed of sorptive material contained within a cylindrical vessel. Full scale studies of carbon-packed adsorbers are time consuming and require large quantities of feed solution. Therefore small scale studies were conducted on an accelerated basis using carbon materials with a reduced particle size (45 - 90 μm) and mini-columns (total column volume 3 cm³ and sorbent bed volume approx. 0.6 cm³)

Mini-column experiments were conducted to evaluate the selectivity and sorptive capacity of the studied materials towards heavy metals such as lead, copper, nickel and cadmium. Although the majority of previous studies on metal removal by carbon were concentrated on batch equilibrium and metal sorption rate, several studies on the use of active carbon-packed columns have been reported in the literature. The use of granular activated carbon (GAC) columns for lead and cadmium removal was studied by Reed et al. Synthetic waste waters containing the target metals, organic contaminants and chelating agents were used in this study. For metal only tests significant quantities (up to 325 BV) of feed solution were treated prior to breakthrough. Metal uptake values of 30 mg/g were achieved.
Activated carbon-packed mini-columns were used by Kuennen et al.\(^{26}\) and Taylor and Kuennen\(^{27}\) to evaluate the removal of lead from aqueous solutions with the prospect of using activated carbon in a point-of-use fixed-bed adsorber for the extraction of soluble and insoluble lead from drinking water. Capacity of carbon for lead was found to be a function of pH. It was also demonstrated that under dynamic conditions zinc and cadmium are not as well retained as lead and copper.

Arunachalam et al.\(^{28}\) carried out column investigations on waste water containing 200 mg/l of lead (influent pH 5) using a coconut-shell-based carbon and a commercial activated carbon. Breakthrough occurred after 160 BV for the coconut carbon. The metal uptake capacities for the coconut shell carbon and commercial carbon were 93.3 mg/g and 5 mg/g, respectively.

There is no literature information, however, on the use of active carbons with surface heteroatoms in column mode for competitive removal of copper, lead, nickel and cadmium. If modified active carbons are to be considered as feasible materials for the removal of heavy metal ions from aqueous solutions, additional information on their efficiency in the column mode must be gathered.

All metal sorption tests using mini-columns were carried out at pH 4.8 in order to avoid the precipitation of the metals on the surface of carbons. The concentration of each metal in the feed solution was 0.15 ± 0.01 mmol/l (unless otherwise stated). Mini-column experiments were performed using mixed-metal feed solutions. Normalised mini-column breakthrough curves for lead and copper in the presence of nickel and cadmium (not shown) for the sorbents studied can be seen in Figures 7.13 - 7.25. Figures 7.17 and 7.22 show representative normalised breakthrough curves for all four metals on KAU 1.5 and PGP-P. These show a typical behavior pattern for nickel and cadmium. Tables 7.10-7.12 summarise copper and lead uptake results in mini-columns for the sorptive materials studied. Table 7.13 provides information concerning copper - lead % ratio on the adsorbent.
Figure 7.13. Lead and copper normalised breakthrough curves for KAUini.

Figure 7.14. Lead and copper normalised breakthrough curves for KAU 0.8.
Figure 7.15. Lead and copper normalised breakthrough curves for KAU 1.2.

Figure 7.16. Lead and copper normalised breakthrough curves for KAU 1.8.
Figure 7.17. Lead, copper, nickel and cadmium normalised breakthrough curves for KAU 1.5.

Figure 7.18. Lead and copper normalised breakthrough curves for KAU 1.9.
Figure 7.19. Lead and copper normalised breakthrough curves for KAU 2.2.

Figure 7.20. Lead and copper normalised breakthrough curves for KAU 2.7.
Figure 7.21. Lead and copper normalised breakthrough curves for KAU 1.6.

Figure 7.22. Lead, copper, nickel and cadmium normalised breakthrough curves for PGP-P.
Figure 7.23. Lead and copper normalised breakthrough curves for Purolite C 104.

Figure 7.24. Lead and copper normalised breakthrough curves and effluent pH profile for F400 (ox).
Figure 7.25. Lead and copper normalised breakthrough curves and effluent pH profile for CKC.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Cu sorbed, mmol/g</th>
<th>Pb sorbed, mmol/g</th>
<th>Cu sorbed as 10% of total capacity, mmol/g</th>
<th>Pb sorbed as 10% of total capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 1.5</td>
<td>0.153</td>
<td>0.081</td>
<td>0.091</td>
<td>0.048</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>0.209</td>
<td>0.117</td>
<td>0.137</td>
<td>0.088</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>0.267</td>
<td>0.189</td>
<td>0.176</td>
<td>0.148</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>0.299</td>
<td>0.248</td>
<td>0.209</td>
<td>0.185</td>
</tr>
</tbody>
</table>

Table 7.10. Metal uptake results in mini-columns for acid oxidised KAU carbons.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Cu sorbed, mmol/g</th>
<th>Pb sorbed, mmol/g</th>
<th>Cu sorbed @ 10% of total capacity, mmol/g</th>
<th>Pb sorbed @ 10% of total capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 0.8</td>
<td>0.095</td>
<td>0.004</td>
<td>0.018</td>
<td>0.006</td>
</tr>
<tr>
<td>KAU 1.2</td>
<td>0.218</td>
<td>0.014</td>
<td>0.073</td>
<td>0.007</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>0.273</td>
<td>0.042</td>
<td>0.169</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Table 7.11. Metal uptake results in mini-columns for air oxidised KAU carbons.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Cu sorbed, mmol/g</th>
<th>Pb sorbed, mmol/g</th>
<th>Cu sorbed @ 10% of total capacity, mmol/g</th>
<th>Pb sorbed @ 10% of total capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 1.6</td>
<td>0.181</td>
<td>0.434</td>
<td>0.248</td>
<td>0.318</td>
</tr>
<tr>
<td>PGP-P</td>
<td>0.044</td>
<td>0.270</td>
<td>0.004</td>
<td>0.189</td>
</tr>
<tr>
<td>CKC</td>
<td>0.186</td>
<td>0.156</td>
<td>0.134</td>
<td>0.119</td>
</tr>
<tr>
<td>F400 (ox)</td>
<td>0.129</td>
<td>0.087</td>
<td>0.109</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 7.12. Metal uptake results in mini-columns for miscellaneous sorbent.
Results in Tables 7.10 and 7.11 show a direct relationship between metal uptake and the degree of surface oxidation. The duration of carbon exposure to the oxidising agent (air, nitric acid, etc.) correlates with the amount of surface groups generated.

Flow rate through the mini-column affects the efficiency of removal of metal ions. Lower flow rates allow treatment of greater volumes of the metal-bearing solution. Higher flow rates result in deterioration of local equilibrium conditions and consequently an increase of mass transfer zone height. This yields flatter breakthrough curve profiles and ultimately reduces metal removal efficiency of the adsorbent. An example is given in Figure 7.26 where lead ion is removed by F 400 (ox) at two different flow rates, namely 1 ml/min and 3.5 ml/min. Removal efficiency in the latter case falls by 25 %.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Cu sorbed, % to total</th>
<th>Pb sorbed, % to total</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAU 0.8</td>
<td>95.68</td>
<td>4.31</td>
</tr>
<tr>
<td>KAU 1.2</td>
<td>93.86</td>
<td>6.14</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>86.72</td>
<td>13.28</td>
</tr>
<tr>
<td>KAU 1.5</td>
<td>65.31</td>
<td>34.69</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>64.21</td>
<td>35.78</td>
</tr>
<tr>
<td>KAU 2.2</td>
<td>58.63</td>
<td>41.37</td>
</tr>
<tr>
<td>KAU 2.7</td>
<td>54.71</td>
<td>45.29</td>
</tr>
<tr>
<td>KAU 1.6</td>
<td>29.40</td>
<td>70.60</td>
</tr>
<tr>
<td>PGP-P</td>
<td>14.01</td>
<td>85.99</td>
</tr>
<tr>
<td>CKC</td>
<td>54.28</td>
<td>45.72</td>
</tr>
<tr>
<td>F 400 (ox)</td>
<td>59.76</td>
<td>40.24</td>
</tr>
</tbody>
</table>

Table 7.13. % ratio of copper and lead on adsorbent.
The pH of the mini-column effluent provides useful information regarding metal-carbon surface interactions. The pH of the effluent was significantly lower than the influent pH throughout the duration of the breakthrough experiment. The influent solution pH was kept constant at 4.8 during the entire test. Figures 7.24 and 7.25 show that pH in the effluent is initially low, i.e. 3 - 3.5. The effluent pH gradually increases as the metal concentration within the mini-column approaches breakthrough. The reduced pH of the effluent solution during the metal sorption experiments suggests that metal removal by active carbons is of an ion exchange nature whereby cations replace protons in acidic surface functional groups. The effluent pH rises as less hydrogen ions are released at the exhaustion of the mini-column.

The breakthrough curves for the carbons show a preference for lead and copper over nickel and cadmium. During metal ion sorption in mini-columns the effluent concentrations of cadmium and nickel exceed the influent concentrations (Figures 7.17 and 7.22). This phenomenon is typical of frontal elution chromatography. As
the feed solution passes down the sorbent bed, leading edge adsorption sites saturate with all metal ions present in the feed solution. Subsequently, the metal ions with low sorption affinity (nickel and cadmium) are displaced by more preferred ions (lead and copper) competing for the same adsorption sites. The less preferred metals are eluted from the bed and attain an effluent concentration which is higher than the influent concentration.

Closer examination of breakthrough curves also reveals that the selectivity of oxidised carbons towards lead and copper is variable. Although both ions are removed, sorptive materials do not exhibit 100% selectivity towards any of these particular metals. The data provided in Table 7.13 indicates that the ratio between copper and lead removed by carbons apparently depends on the extent of surface oxidation and the method of carbon surface oxidation. Thus air-oxidised samples exhibit higher copper selectivity, particularly for carbons with a lower degree of oxidation (Figures 7.14 and 7.15). The amount of lead taken up by carbon progressively increases, i.e., the copper-lead ratio changes with an increase in the extent of carbon oxidation (Tables 7.11 and 7.13). A similar trend is observed for the nitric acid oxidised series of carbon samples (Table 7.10). The ratio of lead - copper removal gradually switches in favour of lead as the degree of carbon oxidation increases. For a high surface oxidation sample, KAU 2.7 (total sorptive capacity 2.8 mmol/g), the copper-lead ratio almost reaches 50:50 and for the sample with an even greater degree of oxidation, KAU 1.6 (total sorptive capacity 3.25 mmol/g), (Table 7.12), lead is preferred over copper (copper-lead ratio is approx. 30:70).

The method of carbon oxidation strongly influences the selectivity of the adsorbent towards copper and lead. The results of mini-column experiments show that the copper-lead ratio is different for carbon samples with approximately the same sorptive capacity but oxidised with different oxidising agents. For example, the copper-lead ratios for air-oxidised KAU 1.8 (total sorptive capacity 1.8 mmol/g) and acid-oxidised KAU 1.5 (total sorptive capacity 1.7 mmol/g) are 87:13 and 65:35 respectively (Table 7.13).

PGP-P displays higher lead uptake compared with copper in dynamic sorption experiments from mixed metal-bearing solutions (Figure 7.22). Copper ions were detected in the mini-column outlet almost immediately whereas lead breakthrough
was observed after approximately 400 bed volumes of feed solution had passed through. The ratio between copper and lead on the carbon was found to be 14 : 86.

Purolite C 104 (Figure 7.23) carboxylic resin showed remarkable selectivity towards lead. Copper breakthrough occurred after approximately 500 bed volumes whereas lead was not detected in the effluent even after 6000 bed volumes. The high sorptive capacity of this material is attributed to a large concentration of carboxylic groups (~10 mmol/g compared with about 2-3 mmol/g for active carbons).

The copper and lead breakthrough profiles for CKC lie between those of highly oxidised KAU 2.7 and KAU 1.6 (Figures 7.25, 7.20 and 7.21 respectively). The breakthrough curves for both lead and copper almost overlap and the copper-lead % ratio on the adsorbent is about 50 : 50 (Table 7.13). This material has a total sorptive capacity of only 2.16 mmol/g and should remove the metals similarly to KAU 1.9 (nitric acid oxidised). However it exhibits a copper and lead removal pattern resembling that of the carbons with greater surface oxidation e.g. KAU 2.7 and KAU 1.6. This phenomenon suggests that selective removal of metals does not depend solely on the carbon oxidation method and the degree of surface oxidation. The variable selectivity of oxidised carbons towards heavy metals apparently depends on the distribution of surface functional groups and this might be related to the origin of carbon.

7.9 Metal Recovery

Successful column operations strongly depend on how easily the sorptive material can be regenerated after the loading cycle. If active carbon-packed columns are to be considered as a feasible treatment option for metal-bearing streams, effective regeneration methods must be identified. The most obvious regeneration scheme is one that takes advantage of the pH dependence of metal sorption. In the present study lead ion is selected as the target metal in the desorption experiments and 0.5 M nitric acid is used as a regenerant.
Three sorbents, namely KAU 1.8, KAU 1.9 and PGP-P were chosen for regeneration studies. The former two materials possess different surface functional group distribution. The latter material has phosphorus-containing surface functionality. However all these materials are similar in their total sorptive capacities determined by sodium hydroxide titration.

The specific objective of this study was to assess the regeneration efficiency of carbons after saturation with the target metal ion. Desorption efficiency was determined using the amount of lead extracted from solution during the run in question as a benchmark. The amount of lead bound to the carbon (determined from mass balance and acid elution) was used to calculate metal desorption efficiency. A summary of mini-column regeneration experiments is presented in Table 7.11.

Lead desorption from the mini-columns using an excessive amount (250 ml) of nitric acid appears to be incomplete. After the first cycle PGP-P carbon shows comparatively better recovery than the oxidised carbons KAU 1.9 and KAU 1.8 (87 %, 66 % and 68 %, respectively). Metal desorption efficiency in the following cycles shows improvement particularly in the case of oxidised carbons. However the metal sorptive capacity of all sorptive materials decreases. When the metal-loading values, obtained from mass balance and acid elution, are compared for different runs, it becomes apparent that a certain amount of metal remains on the carbon from run to run. Reed and Arunachalam 25 and Reed et al 29 reported similar findings. The authors studied lead and cadmium removal using GAC-packed columns. It was shown that after first cycle only 70 - 80 % of lead ion was recovered from the column. Subsequent regeneration runs after column saturation showed progressive improvement in metal recovery.

Desorption of metals from the active carbon-packed mini-columns previously loaded with copper, zinc or nickel was investigated by Tai et al 30. Mini-column regeneration was performed with 10 bed volumes of 0.1 M hydrochloric acid. The authors showed that a maximum of 90 % metal ions were recovered from carbon after the first run.
<table>
<thead>
<tr>
<th>Run/Carbon</th>
<th>Pb loading, mmol /g</th>
<th>Pb recovered, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from elution</td>
<td>from mass balance</td>
</tr>
<tr>
<td>1st run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGP-P</td>
<td>0.327</td>
<td>0.375</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>0.166</td>
<td>0.252</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>0.119</td>
<td>0.163</td>
</tr>
<tr>
<td>2nd run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGP-P</td>
<td>0.334</td>
<td>0.364</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>0.226</td>
<td>0.236</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>0.134</td>
<td>0.158</td>
</tr>
<tr>
<td>4th run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGP-P</td>
<td>0.343</td>
<td>0.346</td>
</tr>
<tr>
<td>KAU 1.9</td>
<td>0.205</td>
<td>0.210</td>
</tr>
<tr>
<td>KAU 1.8</td>
<td>0.159</td>
<td>0.167</td>
</tr>
</tbody>
</table>

Table 7.14. Results of metal recovery experiments.

Results of column regeneration experiments suggest that metal sorption by active carbons is not entirely ion exchange but also involves more complex processes. Metal sorption by active carbons may be related to the composition of aqueous solution, metal species distribution and the physico-chemical properties of the carbon surface. Thus, Reed and Arunachalam \(^{25}\) concluded that surface or pore liquid precipitation, which are considered to be non-specific in nature, may be the dominant metal removal mechanism. This was inferred from the fact that column effluent pH was initially high (pH 11) followed by slow decrease to the influent pH (pH 5). Tai et al. \(^{40}\) attributed metal extraction from water to the presence of different oxygen complexes on the carbon surface. Metal uptake by active carbon involves not only simple ion exchange but also the formation of strong metal complexes with oxygen functional groups in carbons.

It was shown that the sorptive materials used in the metal recovery experiments are
acidic in nature (Chapter 6). Moreover the experiments with mini-columns were conducted under slightly acidic conditions. Therefore the precipitation of lead as a possible removal mechanism can be ruled out. Incomplete metal recovery can be associated with the formation of very strong complexes between functional groups and metal ions. These complex compounds are not decomposed by 0.5 M nitric acid and thus prevent complete metal recovery. This phenomenon may indicate that metal ions are attached to the surface by a complexation mechanism as well as by ion exchange.

Very sharp metal elution profiles were observed during mini-column regeneration experiments (Figures 7.27 and 7.28). Desorption was nearly complete after about 8 bed volumes (4.8 ml) of regenerant. Further passing of approx. 100 ml of nitric acid through the mini-columns additionally recovered only ~ 1% of the metals. This suggests that the regeneration of carbonaceous materials with acids is an efficient process.

![Figure 7.27. Lead and copper elution profiles for CKC](image_url)
7.10 General Discussion

Introduction of heteroatoms onto the surface of carbonaceous materials radically changes their ability to bind metal ions from aqueous solutions. Thus, it has been shown that metal sorption capacity of active carbons can be enhanced substantially by modifying them by either heat treatment in an oxidising atmosphere or interaction with hot nitric acid. On the other hand, introduction of heteroatoms (phosphorus) via a carbon precursor followed by carbonisation also yields carbonaceous material with significantly improved metal sorptive properties.

Metal uptake capacity of oxidised carbons is strongly dependent on the degree of carbon surface oxidation. Longer exposure of carbon to the oxidising agent (during modification) results in a greater amount of surface groups capable of binding metal ions. The materials studied show exceptional selectivity towards copper and lead over nickel and cadmium. The latter two metal ions are not taken up in the presence of copper and lead.

Figure 7.28. Lead and copper elution profiles for F 400 (ox)
Further analysis of the results for metal sorption from multi-metal bearing solutions revealed that copper-lead distribution on the sorbent is different for the materials modified by hot air and nitric acid. Air oxidised samples tend to prefer copper over lead. Acid oxidised materials with a low degree of surface oxidation show a similar trend. However, the amount of lead ion removed by the carbon gradually increases comparatively to copper with the enhancement of carbon surface oxidation. Highly oxidised carbon samples, e.g. KAU 2.7 and KAU 1.6, display a reverse selectivity pattern showing a preference towards lead over copper. The observed metal uptake pattern for these carbons resembles that of Purolite C 104 carboxylic resin and algal biomass which display much higher selectivity towards lead.

The use of different oxidation methods results in the synthesis of carbons possessing varying surface functional group distribution (Chapter 6). Oxidation with nitric acid generates a higher concentration of carboxylic groups on the surface. Other weakly acidic functional groups (phenolic type) represent a lower proportion of the overall sorptive sites in nitric acid modified carbons. In contrast, hot air oxidation produces materials with dominant weaker types of acidic functional groups, e.g. phenolic. Examination of Boehm's titration data and metal sorption results suggests that the selectivity of the oxidised carbons correlates with the quantity and proportion of carboxylic groups amongst other acidic surface groups. This suggestion is illustrated in Figure 7.29. It can be seen that the increase in the amount of lead removed coincides with the gradual increase in carboxylic groups on the surface of carbons.

Earlier studies support the suggestion that sorptive properties of oxidised carbons strongly depend on the degree of surface oxidation. Kovyrshin et al showed that selective removal of a particular metal is related to the distribution of surface functional groups. These researchers studied the removal of thallium by oxidised carbon and found that selective sorption is due to phenolic surface functional groups. Strashko et al carried out a series of experiments to determine the influence of the degree of carbon oxidation on the separation of potassium and caesium. The chromatographic separation of these metals is found to be related to the extent of carbon oxidation.
Figure 7.29. Correlation of metal uptake and surface functional groups development for the oxidised carbons.

Acid-base titration and spectroscopic studies (Chapter 6) suggested the presence of organic acid ligands attached to the surface of oxidised carbon. These ligands can be loosely considered as derivatives of aromatic compounds. A comparison of the stability constants for the complexes between metal ions and organic ligands derived from aromatic compounds indicates that lead and copper usually form more stable complexes than nickel and cadmium. The stability constants of these complexes coincides with the selectivity series for oxidised carbons. Stability constants for the selected aromatic acids are presented in Table 7.15. The formation of relatively strong surface complexes between surface functional groups and copper and lead compared to nickel and cadmium may result in better retention of the former ions.
Table 7.15. Stability constants of metal-organic ligand complexes.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$\text{Cd}^{2+}$</th>
<th>$\text{Cu}^{2+}$</th>
<th>$\text{Ni}^{2+}$</th>
<th>$\text{Pb}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic</td>
<td>1.4</td>
<td>1.6</td>
<td>0.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Phenoxyacetic</td>
<td>1</td>
<td>1.3</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Salicylic</td>
<td>5.55</td>
<td>10.00</td>
<td>4.52</td>
<td>-</td>
</tr>
<tr>
<td>$m$-Methoxybenzoic</td>
<td>1.3</td>
<td>1.6</td>
<td>0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Phthalic</td>
<td>2.5</td>
<td>3.10</td>
<td>2.14</td>
<td>-</td>
</tr>
</tbody>
</table>

Oxidation of carbons with different oxidising agents generates some undesirable by-products such as humic compounds. This is particularly pronounced for nitric acid modified carbon samples with a high degree of surface oxidation. Humic acids are readily soluble in alkaline solutions and may leach from carbons if sorption experiments are carried out at higher pH. Therefore, exhaustive alkaline washing may be necessary to get rid of these undesired substances after the preparation. However if the sorption operations are performed under near neutral or slightly acidic conditions, humic substances remain on the carbon. The exact nature of the humic substances is ill-defined. However it has been shown earlier by Kuzin and Strashko that functional groups of humic compounds are very similar to those of oxidised carbons and are capable of binding heavy metals strongly and selectively. They found that the humic compounds extracted from the carbon surface were similar to those obtained from other sources i.e. naturally occurring humic substances. The authors also suggested structural similarity between the carbon surface and the humic acid molecules.

The large complex structure of humic acid macromolecules (Figure 7.30) results in the possibility of them becoming entangled or bound to the carbon surface through a variety of complex interactions (i.e. hydrogen bonding, anion exchange etc.).

The flexibility of humic macromolecules may allow rotation of surface functional
groups thereby facilitating the interaction of several neighbouring functional groups with a heavy metal ion resulting in formation of chelates (relatively stronger complexes). This is in sharp contrast to the rigid structure of active carbons, where the possibility of metal ion interaction with multiple functional groups is statistically restricted. Consequently humic acids may contribute to the overall metal sorptive capacity and selectivity of oxidised carbons.

Figure 7.30. Postulated structure of humic compound with complexed iron 17

(Adapted from the original paper).

Active carbons show a preference for different metals not only according to the different groups present on the surface, but also on the metal properties. Metals can be described as being Class (a) (hard) and Class (b) (soft) 38, 39. Ligands (i.e. functional groups) which form stronger complexes with Class (a) metals are described
as hard and those which form stronger complexes with Class (b) metals are called soft. Hard metals form more stable complexes with hard ligands and soft metals form more stable complexes with soft ligands. Hard metal ions are either highly charged and/or relatively small with a high charge to radius ratio. This results in the valence shell electrons being strongly bound to the metal and less available for covalent bonding with a ligand. Consequently, interaction with ligand donor atoms having high electronegativities is favoured. Hard-hard interactions are more electrostatic in nature. In contrast, soft metal centres have low charge to radius ratios and interact with less electronegative donor atoms. Soft-soft interactions are frequently more covalent in character.

It is well known from the electronic configuration of copper that the electron cloud is held strongly to the nucleus and copper is a hard metal compared to lead. Low concentrations of dissociated carboxylic groups may prefer the harder copper ions. As the degree of carbon oxidation (i.e. the concentration of carboxylic groups) progressively increases, the preference for copper is diminished and breakthrough curves for lead and copper begin to coincide. Purolite C 104 resin is a monofunctional cationite containing carboxylic groups only. The high concentration of these groups in Purolite C 104 may result in a larger amount of undissociated groups in similar conditions (e.g. solution pH). Electrostatic interactions and the carbonyl-oxygen atom may be responsible for the greater selectivity displayed by the carboxylic resin.

The selectivity of the phosphorus-containing carbon towards lead can be attributed to soft-soft interactions. Lead is a soft metal which interacts readily with the soft ligands such as R₃P, (RO)₃P etc. PGP-P however does not display 100 % selectivity towards lead. The experimental results show that copper is also taken up to a lesser extent. The removal of this metal ion can be attributed to hard-hard interactions with phosphoric groups (PO₄)³⁻.

Phosphonic groups present on the PGP-P carbon are very good hydrogen ion acceptors and according to Helfferich rank above water in the polarisation sequence. As a result of stronger polarisation, PGP-P prefers larger, more strongly hydrated, and more polarisable cations i.e. lead. Purolite C 104 with carboxylic
groups behaves in a similar way though here the effect is less pronounced 41.

Another reason for the enhanced selectivity of PGP-P carbon towards lead over other metals may be related to the formation of stronger ion pairs or bonds with the fixed ionic groups. This can be readily explained with the Le Châtelier principle: in the ion-exchange equilibrium

\[ \Delta + B \rightleftharpoons B + \Lambda \]

the reverse process (right to left, uptake of \( \Lambda \) in exchange for \( B \)) is favoured if \( \Lambda \) is removed in the ion exchanger by the fixed ionic groups. The situation is similar to that in other reversible chemical systems in which a reaction is favoured if one of the products is removed by some other process e.g. evaporation or precipitation. Interactions of this sort are likely to occur if the surface functional groups are similar in structure to precipitating or complexing agents which react with the sorbed metal ion 40. To a first approximation a carbon surface containing metal-phosphate species can be compared with water insoluble metal phosphates. The corresponding solubility product value (\( K_{sp} \)) for lead phosphate is -42.10 whereas the solubility products for copper, cadmium and nickel phosphate are -36.9, -32.6 and -30.3 respectively 42-44. This coincides with the selectivity series for PGP-P: \( \text{Pb} > \text{Cu} > \text{Cd} \geq \text{Ni} \). This stability series also corresponds to the stability constants of metal-pyrophosphate complexes (\( pK_1 \) for lead is 10.1 against 6.4 for copper, 5.6 for cadmium and 5.82 for nickel). The formation of more stable lead surface compounds results in greater retention of this metal on the surface of the phosphorus-containing carbon (as inferred from the measured breakthrough curves).

Fast metal uptake by oxidised carbons may be due to a number of reasons. One reason is the extent of development of the porous structure of these materials. The results presented in Chapter 5 indicate that oxidised carbons derived from agricultural by-products (KAU carbons) possess a wide range of pores. Well developed small mesopores (30 Å) act as transport channels to allow better access of metal ions to the functional groups situated within the microporous structure of carbon particles. The porous structure of synthetic carbons derived from polymeric resins may be controlled during the manufacture of the resin-precursor. After carbonisation of the resin, the
resulting carbonaceous materials usually retain the pore structure of the resin-precursor. For example, CKC carbon possesses excellent mesopores with a well-defined peak at 400 Å as well as micropores at around 7 - 9 Å. These pores were prefabricated by introduction of pore-forming additives during the manufacture of the styrene-DVB resin-precursor. Consequently, the highly developed mesopore structure of this material has a positive effect on the rate of metal removal. On the other hand, the phosphorus-containing carbon contains only micropores, below 10 Å. This structural feature is attributed to the fact that phosphorus-containing functional groups introduced onto the surface of resin restrict catalytic gasification during thermal treatment of the precursor. This yields carbon with a low surface area and mostly microporous structure, thus providing increased tortuosity and consequently a slower metal sorption rate.

Chemical reactions between surface groups of carbons and metal ions are possibly another rate determining step. It is reported in the literature that the activation energies for particle diffusion are generally higher for chelating resins (60 - 100 kJ/eq) compared with intraparticle diffusion of simple ions in conventional resins (about 25 - 40 kJ/eq). Similar phenomena may be expected for the carbonaceous materials, particularly for the phosphorus-containing carbon. Since this is a mostly microporous material, it is likely that functional groups located on the walls of micropores in close proximity may form chelate-type surface compounds with lead. Oxidised carbons may contain humic acids on the surface as well as oxygen-containing functional groups. These acids (by-products of carbon oxidation) contain functional groups similar to oxidised carbons. These humic acids as well as oxidised carbons may contain some nitrogen probably in a form of functional groups (as inferred from elemental analysis). Oxygen- and nitrogen-containing functionalities of both carbons and humics can interact with heavy metals forming strong surface complexes thus contributing to a slow phase of the metal sorption rate.

The excellent removal of radionuclides by active carbons can be attributed to the presence of inorganic impurities and humic compounds in the carbon structure, conditioning of adsorbents prior to the sorption experiments, chemistry of the feed solutions, etc. Thus it was shown in Chapter 6 that F 400, derived from coal may
contain substantial quantities of foreign components (up to 7.4 % of ash). These components include the oxides of Si, Al, Ti, Fe, etc. These oxides themselves are known to be very good adsorbents for heavy metals and radionuclides. Since the feed concentration of the radioisotope feed solution studied was very low (~ 100 Bq/ml), these metal oxide admixtures may act as selective adsorbents within the carbon and remove radionuclides selectively.

Another reason for the enhanced selectivity of oxidised carbons towards radioisotopes may be related to the presence of humic substances. An earlier investigation carried out by Chuvela et al 45, 46, 47, 48 revealed that natural humic compounds (which are similar to those in oxidised carbons) are capable of binding radionuclides selectively. Like oxidised carbons, humic acids possess two major types of functional groups: carboxylic and phenolic. The distribution of these groups in the humic acids present on the carbon surface is likely to be responsible for the improved selectivity towards radioactive metal species.

Prior to sorption experiments the materials were conditioned to attain the required pH (alkaline). This conditioning may be very important for the enhancement of the selectivity of active carbons. It was shown in earlier studies that the stability of carbon-metal surface complexes increases with pH (as inferred from stability constants) 11, 49, 50. Stability constants tend to characterise interactions of cations with relatively stronger carboxylic groups of carbon at slightly acidic and near-neutral pH values. At higher pH values relatively weaker surface groups (i.e. phenolic), together with relatively stronger groups (i.e. carboxylic), begin to dissociate and participate in complexation of metal ions. Therefore the metal-carbon bond will be stronger at higher pH values (stability constants decrease).

Conditioning of the adsorbents at high pH values with sodium hydroxide effectively converts them into a cationic form. Cationic forms of carbonaceous materials may exhibit somewhat different sorptive properties compared to adsorbents in the hydrogen form. Thus Mironov and Taushkanov 51 determined the exchange constants for a variety of systems such as nickel-sodium, nickel-hydrogen, zinc-sodium and zinc-hydrogen on oxidised carbons. These researchers reported low values of apparent exchange constants for Ni$^{2+}$- II$^+$, Zn$^{2+}$- II$^+$ and particularly for Na$^+$- II$^+$. They suggested that these low values are due to a high affinity of surface functional
groups in active carbons towards hydrogen ions resulting in poor metals uptake. On the other hand, the exchange constants between the divalent cations and sodium ions attained high values i.e. good cations uptake.

7.11 Conclusions

The results of this study have shown that modified active carbons can be developed for the selective removal of heavy metals from aqueous solutions. Various surface functional groups containing heteroatoms i.e. oxygen or phosphorus are responsible for the improved selectivity towards lead and copper over nickel and cadmium. Furthermore, the selectivity of carbons towards copper and lead can be controlled by varying the oxidation treatment conditions as well as employing different oxidising agents. Oxidised carbons can remove metal ions from solutions with relatively high acidity. This property is related to the relatively low pK values of carboxylic type groups present on the surface. The electron-donating carbon matrix enhances the negative charge residing on the oxygen thereby promoting dissociation of acidic groups at reduced pH values compared to carboxylic resin Purolite C 101.

Active carbons can be successfully applied for the removal of a number of radionuclides from aqueous solutions. The results confirm that carbons exhibit remarkable selectivity and fast uptake of radioisotopes. The presence of mineral admixtures, humic substances and a variety of surface functional groups in carbons as well as experimental conditions (solution pH, sorbent conditioning, etc.) are likely to influence the removal of radionuclides.

Kinetic studies have shown that metal sorption rates are rapid for oxidised carbons and slow for the phosphorus-containing carbon and this is related to the porous structure of the materials studied. Metal sorption in kinetic experiments is also found to proceed in two phases (fast and slow). Oxidised carbons remove up to 95% of metal during the fast phase.
Mini-column studies for the multi-metal solutions revealed a variable selectivity of carbons towards copper and lead. It is suggested that selectivity towards heavy metals is dependent on the distribution of surface functional groups. Flow rate of influent solution strongly influences the shape of the breakthrough profile and sorptive capacity of adsorbent.

Repeated cycles of lead sorption/elution indicate reduction in the service capacity of the carbon-packed mini-column. This reduction in mini-column capacity is most pronounced after the first sorption/elution cycle. Some of the metal sorption sites within the carbon may covalently bind heavy metal ions to the surface. These binding sites may resist regeneration during the elution cycle and therefore lower the capacity of the sorbent bed.

### 7.12 References

Chapter 8: Conclusions and Future Work

8.1 Conclusions

The objective of this investigation was to evaluate the selective removal of heavy metals from aqueous solutions using porous carbonaceous adsorbents containing heteroatoms on the surface. These carbons were based on agricultural by-products (KAU carbons) and synthetic polymeric precursors (styrene/DVI resin-based CKC and phenol-formaldehyde resin-based PGP-P). The physical and chemical properties of the sorptive materials were studied to determine the important parameters in selective metal sorption. The properties of these materials were compared to those of commercially available carboxylic resin Purolite C 104 and oxidised active carbon Chemviron Filtrasorb 400 (F 400).

The literature survey revealed that very little fundamental work has been published in the West on the selective sorption of heavy metals by active carbons containing heteroatoms (oxygen, phosphorus, etc.) on their surface. Almost no data was available on the use of active carbons derived from synthetic polymeric materials.

Oxygen-containing weakly acidic functional groups were introduced onto the surface of the carbons by oxidation using hot air or nitric acid. Variation of exposure to the oxidising agent yielded samples with different degrees of surface oxidation. Phosphorus was introduced onto the carbon surface by phosphorilation of phenol-formaldehyde resin followed by pyrolysis. This treatment resulted in a relatively large concentration of various phosphorus-containing functional groups. These modifications were carried out to enhance the metal sorptive properties of active carbons.

A study of the pore size distributions of the sorptive materials (determined from nitrogen adsorption isotherms) showed that oxidation did not significantly affect pore
size distributions. However surface area and pore volume decreased as the degree of carbon oxidation increased.

Synthetic carbons derived from polymeric materials have several advantages over carbons based on natural precursors. The porous structure of synthetic carbons may be tailored during the manufacture of polymeric resin-precursor. Analysis of the pore size distribution of styrene/DVB resin-derived CKC carbon suggested that this sample is biporous. This material possesses a large proportion of mesopores at 400 Å and some micropores at 5-10 Å. Phosphorus-containing carbon PGP-P was found to be mostly microporous with a low pore volume, due to the presence of phosphorus-containing functional groups which protect the surface from excessive burn-off. Synthetic carbons also possess exceptional mechanical strength, uniform shape (spheres), smooth ('glazed') outer surface, absence of dust and a very low ash content.

The functional groups on the sorptive materials were characterised by numerous techniques including FT-IR spectroscopy, solid state NMR spectroscopy, X-ray photoelectron spectroscopy, elemental analysis, acid-base titration techniques and zeta potential analysis. Modification of carbons significantly increased oxygen content from an initial 5 % wt to as much as 16 % wt. Phosphorus content of the PGP-P carbon was found to be 6.5 % wt.

Titration with bases of different strengths (Boehm's titration) revealed significant differences in surface functional group distributions for materials oxidised by hot air and nitric acid. Relatively weaker phenolic groups are dominant on the air oxidised materials. Progressive oxidation of carbon with nitric acid introduced a greater quantity of relatively strong carboxylic surface groups. As the degree of surface oxidation is enhanced, the proportion of carboxylic (stronger) groups increases. By inference, the surface functional group distributions were dependent on the method of carbon oxidation, duration of carbon exposure to the oxidising agent and the type of carbon.

Acid-base titration experiments and spectroscopic measurements confirmed the polyfunctional nature of carbonaceous adsorbents. The pH-titration data also demonstrated that oxidised carbons and phosphorus-containing carbon, despite their lower sorptive capacity (concentration of ion-exchange groups), appeared to be more acidic than carboxylic resin Purolite C 104. Zeta potential results showed that the
carbon surface was negatively charged within the range of pH values studied. The differences between pH of point of zero charge and pH of isoelectric point suggested that the surfaces of carbons with a higher degree of oxidation were more homogeneous than those of carbons with lower degrees of surface oxidation.

Heavy metal sorptive characteristics of carbons were determined in both batch and mini-column experiments (in mmol/l and μmol/g concentrations range). Metal sorptive capacity of carbons increased proportionally with the degree of surface oxidation. Removal of metals was shown to be a pH-dependent process. It was also observed that carbons with high degree of surface oxidation were capable of metal uptake at pH values as low as 1.5. This was related to the presence of π-electrons in the carbon matrix which reduce the effective negative charge on the oxygen of functional groups resulting in an increased proton mobility (lower pKₐ values). Metal sorption rate was found to be dependent on porous structure of the materials studied. Oxidised carbons with better developed mesopore structure exhibited faster sorption rate than microporous phosphorus-containing carbon. Metal sorption in kinetic experiments was also found to proceed in two phases (fast and slow). Oxidised carbons remove up to 95 % of metal during the fast phase.

Excellent removal of a variety of radioactive isotopes from aqueous solutions was observed. The carbons displayed exceptionally high decontamination factors for α-, β- and γ-emitters. The kinetics of radionuclide removal was rapid. Within the first hour up to 90 % of metals were extracted. Selective removal of radionuclides was attributed to the presence of mineral admixtures and humic acids in carbons as well as the surface functional groups and solution pH.

Mini-column studies for the multi-metal solutions showed a preference of oxidised carbons towards lead and copper over nickel and cadmium and a variable selectivity towards copper and lead. Air oxidised samples tended to prefer copper to lead. Nitric acid oxidised materials with a low degree of surface oxidation showed a similar trend. However the amount of lead ion removed by the carbon progressively increased compared to copper with the enhancement of carbon surface oxidation. Highly oxidised carbon samples exhibited a reverse selectivity pattern showing a preference towards lead over copper. The observed metal uptake pattern resembled that for
carboxylic resin and algal biomass which possess much higher selectivity towards lead. Enhanced selectivity of PGP-P towards lead over the rest of the metals studied was detected. The selectivity of carbons towards metals was explained by the differences in the distribution of surface functional groups, soft and hard metal-ligand interactions, presence of humic acids and various functional groups on the carbon surface.

Repeated cycles of lead sorption/elution indicated reduction in the service capacity of the carbon-packed mini-columns which was most pronounced after the first cycle. Sorption capacity reached a steady level after 3-4 cycles. Metal elution profiles were very sharp showing almost complete metal elution after passing 8 bed volumes of regenerant through the mini-column.

8.2 Future Work

The present study has provided an insight into the potential of carbonaceous adsorbents for the selective removal of heavy metals from aqueous solutions. However, further investigation is necessary to completely assess their potential.

Results presented in this study were based on carbonaceous materials oxidised by hot air and nitric acid with different degrees of surface oxidation. Variable selectivity of these carbons towards lead and copper was observed depending on the surface functional group distributions. Oxidation of active carbons can be performed using a number of oxidising agents e.g. potassium permanganate, hydrogen peroxide, sodium hypochlorite etc. as well as by electrochemical means. It is likely that the distributions of surface functional groups as well as the degree of surface oxidation of the materials produced by these agents will be different to those oxidised by air and nitric acid. As a consequence the selectivity of such materials can be different and this will provide a better control in preparation of materials with specific metal selectivity.

Metal sorption experiments were performed using distilled water containing only ionic species. However these experiments are not completely realistic in that water in the real environment may also contain organic impurities (e.g. pesticides, natural
Conventional unfunctionalised active carbon is widely used in the purification of drinking water from organic contaminants. It is expected that oxidised carbon with acidic surface functional groups will be capable of simultaneous removal of both organic and inorganic species. This effect might be particularly pronounced in the case of hydrophilic or polar organic molecules due to high hydrophilicity of the oxidised carbon surface. The use of oxidised carbons would substantially simplify the technological scheme of drinking water purification.

Sorption of radioactive metals from aqueous solutions yielded very encouraging results. The selectivity of carbons towards radionuclides was attributed to several factors, one of them was the presence of mineral admixtures. The selectivity of carbons can be further enhanced by introduction of metal oxides or phosphates capable of ion-exchange into the carbon matrix (carbomineral adsorbents). Of particular interest are the oxides/phosphates of titanium, zirconium, tin, iron, etc., which are known to be selective sorptive materials towards a variety of heavy metals. Introduction of these oxides can be carried out by either precipitation of metals into the pores of carbonaceous material or by introduction of metal oxide/phosphate during the synthesis of polymeric resin followed by pyrolysis. Carbomineral adsorbents will possess high mechanical, chemical and ionising radiation stability and still have a developed porous structure.

The presence of heteroatoms on the surface of carbons was found to be responsible for the selective removal of certain heavy metals. Phosphorus, in particular, significantly enhanced the selectivity of carbon towards lead over copper, nickel and cadmium. Introduction of other heteroatoms i.e. sulphur, nitrogen, etc. will probably change the selectivity pattern. The presence of sulphur is expected to improve carbon selectivity towards mercury. On the other hand, nitrogen should enhance anion-exchanging and complexing properties of carbons. The combination of heteroatoms (i.e. phosphorus, nitrogen and sulphur) on the carbon surface might also have an effect on the selectivity pattern.
Appendix 1: List of Publications


