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REMOVAL OF ORGANIC MICROPOLLUTANTS AND TRACE METAL FROM WATER USING MODIFIED ACTIVATED CARBONS

by

Purazen Chingombe

Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

of

Loughborough University

March 2006
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Finally, I greatly appreciate the financial support that was given to me by The Association of Commonwealth Universities which is a branch of the Commonwealth Scholarship Commission
ABSTRACT

Pollution of water by herbicides and heavy metals has caused world wide concern because of the adverse effects of these pollutants on the environment, humans and wildlife. This has resulted in tighter legislation being imposed on the levels of these pollutants in drinking water. For example, the European Union (EU) has set the legislation in the drinking water Directive Admissible Concentration for a single herbicide to a maximum of 0.1 ppb. Despite the tight environmental pollution controls, isolated cases of pollutants exceeding their limits are still encountered. This would suggest that research towards the efficient and effective removal of these pollutants will be an on-going process.

In this study, sorption of copper and some selected herbicides e.g. atrazine, benazolin and 2,4-dichlorophenoxyacetic acid (2,4-D) was undertaken on a conventional activated carbon and its modified series. A low level detection method was developed using High Performance Liquid Chromatography (HPLC) and this system was used to quantify the sorption capacity of the herbicides. In order to understand the sorption mechanism of the targeted pollutants, physical and chemical characterisation of the adsorbents was undertaken using a variety of techniques. These include, Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FT-IR) method, pore size distribution and surface area measurements, elemental analysis, sodium capacity determination, zeta potential and pH titration. The sorption data were presented and analysed by conventional adsorption isotherms. Sorption of the herbicides was favoured on carbon samples with least oxygen content while the uptake of copper was strongest in oxidised carbons. Kinetic experimental data were analysed by a pseudo second order model and the Boyd kinetic model. Molecular structural configurations and the physico-chemical properties of the adsorbent played a crucial role in the sorption behaviour of the herbicides.

Keywords: herbicides, atrazine, benazolin 2,4-D, copper, adsorption, activated carbons, surface modification, characterisation, kinetics studies.
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1. INTRODUCTION

World population growth has triggered agricultural and industrial growth for the sustenance of the day to day demands of the population. However, the increase in agricultural and industrial growth has also led to a corresponding growth in pollution related to the two activities. The use of pesticides to boost food production has caused increased contamination of drinking water, thus putting pressure on Governments to invest in the provision of clean water. The same can also be said about the increase in industrial activities which has seen, among many other pollutants, an increase of heavy metals in water bodies. Since the installation of water pollution control schemes are non-profit generating activities, there is a lot of on-going research into finding efficient but inexpensive ways of separating pollutants from drinking water. Various research activities have focussed on the improved efficiency of different established unit operations designed for wastewater purification. These unit operations have been developed over the years due to the realisation of the toxic nature of different pollutants present in wastewater streams. There is a significant number of different separation methods that are being employed in the wastewater industry, and most of them are designed for targeted pollutants.

1.1 Chemical Precipitation

This unit operation involves the alteration of the physical state of the target pollutants so as to facilitate their removal through the process of sedimentation (Metcalf and Eddy, 1991). This can be achieved by creating a voluminous coagulant that ultimately ‘traps’ the dissolved or suspended pollutants. The method is applied widely for the removal of heavy metals. It is well known that at high pH ranges, most heavy metals form hydroxide precipitates, hence by altering the pH of the wastewater, a lot of the heavy metals can be removed by the aid of a coagulant. However, this method of wastewater treatment suffers from the fact that in some cases the addition of chemicals results in increased amounts of dissolved constituents. Also, chemical precipitation of heavy metals is generally effective at concentrations greater than 100 mg/L (Lloyd-Jones, 2003). Since different metal ions precipitate at different pHs, chemical precipitation does not guarantee removal of the metal ions to tolerated levels.
1.2 Chemical Oxidation

This method has been applied in the removal of ammonia, organic micro-pollutants and in the reduction of micro-organism content of the wastewater. The most common oxidants employed in this process are chlorine dioxide, ozone and chlorine. Chemical oxidation processes have an added advantage of disinfecting the wastewater and the use of ozone ultimately results in the removal of colour. Chemical oxidation however, has a disadvantage when applied to organic residues in that, sometimes the degradation products of oxidation can be equally harmful and in some cases a complimentary technique is required.

1.3 Reverse Osmosis

Reverse osmosis involves the removal of dissolved salts from water by filtration through a membrane. This method is known to be highly efficient in the removal of dissolved salts and also the removal of a wide variety of dissolved organics. Reverse osmosis has not been widely applied in wastewater treatment because it is an expensive process with a low product flux that also requires highly skilled manpower.

1.4 Electrodialysis

This technique uses a semi-permeable ion-selective membrane that effects the separation of the ionic components of the wastewater. The method is applied under an electrical potential, which ultimately effects the migration of anions towards the positive electrode, while the cations are driven towards the negative electrode. This method has the disadvantage of membrane clogging emanating from colloidal organic matter in the wastewater and also, precipitation of some salts on the membrane surface can also occur. Membrane fouling can be minimised by applying a separation process targeted at reducing colloidal organic matter. Metcalf and Eddy (1991) report that pre-treatment by chemical precipitation, activated carbon pre-treatment and filtration can drastically reduce incidence of membrane fouling.

1.5 Ion Exchange

Ion exchange is a unit operation that uses an insoluble exchange material with ions that can be displaced by ions from the incoming solution. This process works in two stages that involves;
1. passing the wastewater through a cationic exchanger which results in the exchange of the hydrogen ions from the exchanger by the cations from the solution.

2. passing the wastewater from stage one into an anionic exchanger and this subsequently leads to the replacement of the anions hydroxide ions.

Hence the results of the two stages are the replacement of the dissolved solutes by hydroxide and hydrogen ions which will ultimately form water molecules. Ion exchange process however would require wastewater streams of low metal concentration (<1000 ppm) and with small quantities of competing ions to make it successful.

1.6 Adsorption

Adsorption on activated carbon is one of the well established and effective techniques for the removal of organic micropollutants from water. The adsorptive efficiency of activated carbon is due to its well developed internal pore structure, surface area and surface reactivity. Typically, activated carbon consists of interwoven micropores, mesopores and macropores and these are responsible for the high surface area of the carbons. The existence of surface functional groups in an activated carbon matrix means that they can be manipulated by thermal or chemical treatments to produce adsorbents that are tailored for particular functions. Activated carbons have been proven to be effective adsorbent for the removal of organic compounds from water (Streat and Horner, 2000). Research has also shown that they have a potential to remove heavy metals, especially in their modified states. For example, a number of authors have oxidised activated carbons to enhance sorption of heavy metals (Biniak et al., 1999; Saha et al., 2001a; Strelko and Malik, 2002; Jia et al., 2002). The oxidation processes have mainly been by use of nitric acid, ozone and air. The three methods have always produced the same results, that of producing weakly acidic functionality on the surface of the carbon. Saha et al. (2001b) compared the metal sorption capacity of a conventional carbon and its oxidised form. Strelko and Malik (2002) also compared metal sorption capacity on F400 and its oxidised form. Their results showed that copper uptake capacity had been enhanced by a factor of 4 for the oxidised sample.
Since wastewater streams consist of a mixture of pollutants that can generally be classified as organic and inorganic pollutants, tailoring an adsorbent to remove both classes of pollutants would give a significant process advantage.

<table>
<thead>
<tr>
<th>Process</th>
<th>Removal application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated-carbon adsorption</td>
<td>Natural and synthetic organic Compounds Including volatile organic compounds (VOCs); pesticides; polychlorinated biphenyls (PCBs); Heavy metals</td>
</tr>
<tr>
<td>Activated-sludge-powdered activated carbon</td>
<td>Heavy metals; ammonia; selected refractory priority pollutants</td>
</tr>
<tr>
<td>Chemical coagulation, sedimentation and filtration</td>
<td>Heavy metals and PCBs</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>Ammonia; refractory and toxic halogenated aliphatic and aromatic compounds</td>
</tr>
</tbody>
</table>

Table 1.1 Applications of chemical unit processes in wastewater treatment

1.7 Herbicides

Herbicides have undoubtedly contributed to the growth of agricultural productivity. For example it has been reported that a $4 billion U.S. investment in herbicide control saved $16 billion U.S. in crops every year (The working party on the incidence of pesticides in water, 1996). However, the benefit realised from the use of herbicides does not factor in the negative effects they have on human health and the environment.

Because of their negative impact on human health and the environment, stringent legislation has been imposed on the purity of drinking water. The European Union (EU) agreed to have the drinking water Directive Admissible Concentration for single herbicide or pesticide at a maximum of 0.1 µg/L (EU drinking water directives, 1998).
Regardless of the strict legislation on herbicides, in isolated cases herbicides exceeding their limits have been reported. For example in Great Britain the National Rivers Authority (1998) showed that eulan and permethrin (mainly in effluents from the textile industry) had exceeded their Environmental Quality Standard (EQS) limits. Also diazinon, a sheep dip insecticide, had also exceeded its EQS limits. One major concern was that the most commonly used herbicides atrazine, diuron, bentazone, isoproturon and mecoprop exceeded the standard 0.1 μg/L in surface waters. This has and is always a major concern simply because most ground water sources used for drinking water have no treatment facilities designed to remove herbicides. Also the most common water treatment processes such as sedimentation, disinfection, coagulation and filtration can remove effectively only selected herbicides, especially those that have low solubility in water. On the other hand, advanced water treatment processes (mainly utilising adsorption onto activated carbon) have proved to be the most efficient and reliable method for the removal of aqueous dissolved organic herbicides. Hence a lot of studies have gone into trying to improve the removal efficiency of the existing adsorbents. In improving the adsorption capacity of adsorbents, attention has been turned on to the number of variables that affect the adsorption capacity of the activated carbons. Some of the variables are as stated by Radovic et al. (1997) a) the nature of the adsorbent (e.g. functional groups present, surface area and pore size distribution, ash content); b) the nature of the adsorbate (e.g. functional groups present, polarity, hydrophobicity, molecular weight and size, solubility and pKₐ or pKₐ for weak electrolytes); and c) solution conditions e.g. pH, temperature and adsorbate concentration, presence of competitive solutes, polarity of solvents.

1.8 Water Pollution by Metal Ions

Coupled with herbicides, heavy metals are a group of pollutants that require special monitoring because of their potential danger to humans. Heavy metals is the classification that is generally applied to those metals of particular concern in the treatment of industrial water wastes: copper, silver, zinc, cadmium, mercury, lead, chromium, iron and nickel. Other metals that may be considered part of this category are tin, arsenic, selenium, molybdenum, cobalt, manganese and aluminium. Most of these metals appear in the inorganic form in industrial wastewater, except in textiles and dyeing where they are found in the organic form. As a result of the potential
hazards of heavy metals to human health, the EU Drinking Water Directives (80/778/EEC) have set the limits on the admissible concentrations of heavy metals shown in Table 1.2.

The most common method of treatment for the above pollutants in the inorganic form is by chemical precipitation. However, the achievable concentration through the method of precipitation falls short of the permissible levels in drinking water. For example, the achievable concentration for copper is 0.5 mg/L while the permissible concentration in drinking water is 0.1-3 mg/L (Strelko, 1999). In addition, the precipitation process produces sludge that requires further treatment. Thus a lot of research has gone into looking for alternative methods for heavy metal removal. Other methods that are already in use include ion exchange and reverse osmosis.

Activated carbon is a potentially attractive adsorbent for heavy metal removal. It has received considerable attention for the removal of organic compounds from water in recent years, however its potential for adsorption of inorganic compounds has received little publicity in the water field. Until around 1970, the use of activated carbon for metal removal was only applied to improve the efficiency of metallurgical recovery. However, the concept of adsorption of metals on activated carbon had already been demonstrated by Wanatabe and Ogawa (1929).

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Achievable concentration precipitation (µg/L)</th>
<th>Regulatory limits (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>300</td>
<td>5</td>
</tr>
<tr>
<td>Chromium</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>Copper</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td>Nickel</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>Zinc</td>
<td>1000</td>
<td>4000</td>
</tr>
</tbody>
</table>

Table 1.2 Comparison of the achievable concentration through chemical precipitation with the EU regulatory limits.
1.9 Target Pollutants of Study

Since wastewater pollutants come from a variety of sources, it is impossible to make a comprehensive study of all the pollutants in a single research study. However, study of individual or a few targeted pollutants is feasible and the results can be extended further in interpreting the behaviour of similar pollutants. In this investigation, the selected pollutants of interest are atrazine, benazolin, 2,4-dichlorophenoxyacetic acid (2,4-D), and copper. The first 3 pollutants can be classified as herbicides while copper fall under the heavy metals classification. Some selected properties of the herbicides are given in Table 1.3. Atrazine has been chosen because it has a long history of polluting water bodies due to its widespread use as a total weed control in non-crop areas. It is also regarded as one of the most difficult pesticides to remove (Streat and Sweetland, 1998). Ever since atrazine was prohibited for use in non-agricultural activities, benazolin is one of a group of four pesticides that has been identified as an alternative (Homer and Streat, 2000). Benazolin is highly soluble in water (600 mg/L) when compared to atrazine. Also, very little research has been published regarding its sorption behaviour. The herbicide 2,4-D was also chosen in this study because of its close similarity with benazolin and the similarity is interesting especially when investigating the effect of the small functional variability on the uptake of the two herbicides. Copper has been selected as a representative of heavy metals since its presence can easily be quantified and its chemistry in aqueous solution is well documented.

1.9.1 Atrazine

Atrazine is widely used as a pre-emergent herbicide and is used mainly on corn, sorghum and sugar cane. Atrazine operates by disrupting the photosynthesis routes in broad-leaf plants, and this subsequently leads to ‘starvation’ which ultimately results in the death of the plant. Atrazine is known to have low volatility and low solubility in water which makes it relatively mobile in aquatic bodies and in soil (Murphy et al., 2005). Atrazine is also known to breakdown through microbiological degradation of the parent compound to the hydroxylated species or by hydrolysis of the triazine ring (Chung et al., 1996). The half life of atrazine has been reported to be in the region of 224 days which makes it a relatively persistent herbicide in the environment. Its high persistence in the environment makes it more hazardous because it is classified under a group of toxic chemicals called endocrine disrupting compounds (ECD). Such compounds are known to affect the physiological processes
that are controlled by hormones (Tanaka et al., 2004, Friedmann, 2002). Hence these molecules are able to affect sexual behavioural activity and the reproductive system development.

**1.9.2 Benazolin and 2,4-D**

Benazolin and 2,4-D are classified under acidic herbicides and as atrazine, they are also used to control broadleaved weeds in gardens and farming. The herbicide 2,4-D in particular, has been widely employed because of its low cost and good selectivity and also it is considered to be moderately toxic (Akcay et al., 2005). Because of their moderately high solubility, the likelihood of runoff from land to rivers and leaching to groundwater can be much of a concern when applying the two herbicides. Also, 2,4-D is a poorly degradable compound which makes it a highly persistent herbicide in aqueous environments. It has been claimed that excessive exposure to 2,4-D has a negative effect on the brain, liver, kidney, heart, digestive system, muscle and the unborn child.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Chemical formula</th>
<th>Structural formula</th>
<th>Solubility in water (mg/l)</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>C₈H₁₂ClN₃</td>
<td><img src="" alt="Atrazine Structure" /></td>
<td>33</td>
<td>1.7</td>
</tr>
<tr>
<td>Benazolin</td>
<td>C₆H₇ClNO₃S</td>
<td><img src="" alt="Benazolin Structure" /></td>
<td>600</td>
<td>3.04</td>
</tr>
<tr>
<td>2,4-D</td>
<td>C₈H₆Cl₂O₃</td>
<td><img src="" alt="2,4-D Structure" /></td>
<td>890</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Table 1.3 Chemical properties of the target herbicides.

**1.9.3 Copper**

Copper is a metal that can be broadly classified as a transition metal or a heavy metal. The major man-made copper releases are from coal-fired power stations and metal producing industries. Other sources include incinerators and sewage treatment plants. The environmental agency published data on the release of copper into controlled waters and sewer for England and Wales, and the data is shown in the
form of a graph in Figure 1.1. The agency cited the principal sources of copper transfer as the chemical industries which involve activities such as the manufacture and use of organic and inorganic chemicals. They also cited the fuel and power sector, petroleum processes and the chemicals sector as the principal sources of pollution in controlled waters.

Small amounts of copper are essential to mammals and many living organisms. However it can be toxic to mammals and the environment at high concentrations. It is well established that copper is toxic to soil micro-organisms and can affect nutrient recycling and mineralization of nitrogen and phosphorus. In humans, excessive exposure to copper can affect the digestive system, kidneys, lungs and the liver.

![Graph showing releases of copper to sewer and controlled waters](image)

**Figure 1.1** Releases of copper to controlled waters and sewer between 1998 and 2001 (Environment Agency, 2002).

**1.10 Research Objectives**

Activated carbon remains the most attractive adsorbent for the removal of herbicides; research has also shown that it has a potential to remove heavy metals from water. Its potential is enhanced through its well developed internal pores and a variety of surface functional groups. Since pollution in wastewater is due to a cocktail of pollutants varying in chemical and physical properties, the use of activated carbon especially in its modified form could be an attractive way of enhancing the removal
of toxic chemicals from drinking water. Hence the overall objective of this research is to evaluate the performance of a conventional activated carbon and its modified series for the removal of herbicides and a metal ion from water. The sorption performances of the samples can also lead to the elucidation of the adsorption mechanisms of the targeted pollutants, and such information is essential in the preparation of adsorbents fashioned for different purposes. The adsorbate-adsorbent interactions will be closely studied and the experimental data will be correlated using conventional theoretical methods.

The adsorbents chosen for this work are:
1. F400: supplied by Chemviron, USA
2. AC1: F400 sample oxidised with HNO₃ and water washed.
3. AC2: F400 sample oxidised with HNO₃ and washed with sodium hydroxide.
4. AC3: F400 sample oxidised with HNO₃ and heat treated at 580 K
5. AC4: F400 annealed at 1173 K in the presence of hydrogen
6. AC5: Aminated AC4 sample.

The complete description of the preparation of the samples is given in Chapter 6.

The objectives of this investigation are as summarised as:
- Development of a quantification procedure for the herbicides using High Pressure Liquid Chromatography (HPLC).
- Development of a Solid Phase Extraction (SPE) technique for the concentration of the herbicides to values that can be detected on the HPLC. This process was necessary because sorption experiments were performed at low concentrations i.e. ppb levels.
- Surface modification of the conventional activated carbon through thermal and chemical methods. This process was performed in order to alter the surface functional groups that are usually associated with the sorption performance of activated carbons.
- Characterisation of the adsorbent samples for the purposes of establishing the physical and chemical properties the adsorbents. The properties are essential in establishing the sorption behaviour and the association between the adsorbent and adsorbate.
• Evaluation and correlation of equilibrium and kinetic data by conventional theoretical methods.
• Propose a possible adsorption mechanism of the targeted pollutants. This information is invaluable when fashioning adsorbents for different functions.

1.11 References


2. ACTIVATED CARBON
Activated carbon is the generic name given to amorphous carbonaceous materials with an extensively developed internal pore structure. The characteristics of activated carbons depend upon the carbonaceous precursor and the technique of activation used in their production. Activated carbon is obtained by thermal decomposition, combustion and partial combustion of different carbonaceous substances. The carbonaceous substances are usually cheap vegetable materials with high carbon content and low ash content. The raw material can be wood, peat, fruit stones, nutshell, sawdust etc (Bansal et al., 1988). Non-vegetable sources include blood, bones, leather waste, fish, petroleum products and by-products (Hassler, 1967). Currently the bulk of the activated carbon comes from natural coal, because of its low cost and availability.

Activated carbons have proven versatile adsorbents mainly due to their large surface area and surface reactivity. Activated carbons also possess "favourable pore size, which makes the internal surface accessible, enhances the adsorption rate, and enhances mechanical strength" (Bansal et al., 1988). According to the International Union of Pure and Applied Chemistry (IUPAC) system, the pore structures are divided into 3 categories. These are namely micropores (< 2 nm in diameter), mesopores (between 2 and 50 nm in diameter) and macropore (> 50 nm). The pores exist in different shapes which can be v-shaped pores, tapered pores, capillary shaped with one end closed or open at both ends, contracted entrance pores, etc.

Micropores constitute the bulk of the area and their sizes are usually comparable with the adsorbate molecules. The mechanism of adsorption in micropores is due to micropore filling and it comes as a result of the adsorption force field that encompasses the whole volume of micropores. This type of mechanism leads to higher heat of adsorption energy as compared to the adsorption energy on surface or mesopore regions. For example, Dubinin (1966) reported that the adsorption of n-hexane on activated carbon as 15 kcal/mole compared to 10 kcal/mole on non-porous carbon black at a loading of 0.25 mmole/g.

Mesopores have a dual function that involves adsorption and channels for the adsorbate to access the interior of the adsorbent. The mechanism of adsorption is via
capillary condensation. Macropores serve as passages for the adsorbate to access the interior of the adsorbent and they do not contribute significantly to the adsorption capacity.

2.1 Physical Structure
It is now generally accepted that the structure of activated carbon to be like stacks of flat aromatic sheets crosslinked in a random manner. The recent acceptable model of the structure emanates from a model that was proposed by Oberlin et al. (1980) when investigating the pyrolysis of kerosene shale and kuckersite. It was proposed that the microtexture of the carbonaceous particle consisted of individual wrinkled layers of polyaromatic molecular stacks separated by tilt and twists. The authors likened the microstructures to “crumbled sheets of paper” as shown in Figure 2.1 (a). The modernised version of the earlier image is shown in Figure 2.1 (b). It is believed that the microporous slit-shaped spaces lie between the twisted aromatic sheets. Transmission Electron Microscope (TEM) of other carbons have revealed the same observations (Fryer, 1981: Marsh and Crawford, 1982).

![Figure 2.1](image1.png)

**Figure 2.1** (a) Model of porous microtexture (crumbled sheets of paper) of a carbonaceous particle (Oberlin *et al.*, 1980). b) Modern representation of the microstructure of active carbons (Bansal *et al.*, 1988).

2.2 Chemical Properties
The surface properties of activated carbon are mostly influenced by functional groups that are lodged on the edges and corners of the graphene layers of the carbon. These heteroatoms are basically derived from the precursor and they arise as a result of imperfect carbonisation or they can arise through activation. Hydrogen and oxygen are among the chief components in the activated carbon surface. Other elements that usually exist but in minute quantities include sulphur, phosphorus and nitrogen. These elements are also derived from the precursor. "Impurities" in the
form of ash, are also found but these impurities are normally found occluded in the pores of the carbon and they may not be chemically combined with the carbon. The ash content originates from chemicals added during the activation process or they may be part of the precursor. It has been reported that activated carbon from plastics or saccharose contains ash that ranges from 0.5-1% while that from wood ranges in the region between 3-8 percent, with fossil coal producing ash that can exceed 20% (Dubinin, 1966).

Among the variety of surface groups that may exist on the carbon surface, carbon-oxygen groups have received a lot of attention compared to other groups. The carbon oxygen groups are classified under a broad category of acids and bases.

2.2.1 Acidic Surface Groups
The majority of the carbon-oxygen groups have been investigated and positively identified as acid groups. For the review of the identification studies by a number of researchers the author refers the reader to the excellent review paper by Donnet (1968). A review article by Boehm (1994) gives a list of the groups as shown in Figure 2.2 The group marked (a) is a carboxylic group that is thought to form a carboxylic anhydride, (b), if two carboxylic acids are in close proximity. The lactone group, (c) is believed to be a product of condensation reaction of a hydroxyl with a carboxyl or carbonyl group. Lactols (d) are also formed in the same manner. A single hydroxyl group of a phenolic character is shown in (e). Structures (f) and (g) are carbonyl groups in different environments while (h) is an ether type functional group. The different acidic groups have been differentiated by Boehm (1966). His method involved selective neutralisation techniques using bases of different strengths. He postulated that carboxyl groups could be neutralised by NaHCO₃ while lactones were believed to be neutralised by Na₂CO₃. He further postulated that phenolic groups could be neutralised by NaOH while sodium ethoxide was considered to react with carbonyl groups. However, the validity of the Boehm neutralisation has been questioned by Puri (1970) who maintained that an individual acid group could neutralise different amounts of alkali of varying strengths. They supported their argument by performing titration curves of sugar charcoal using sodium bicarbonate, sodium carbonate, ammonium hydroxide and barium hydroxide.
2.2.2 Basic Functional Groups

The existence of basic functional groups on activated carbon has always been acknowledged, but there has not been in depth studies on the elucidation of the structures that cause basicity in carbon. Voll and Boehm (1971) were among the first to realise the basic nature of carbon. They prepared a carbon with basic properties by heating carbon at 1273 K under vacuum. The carbon was then exposed to dry oxygen and the quantity chemisorbed was observed. It was noted that when the carbon was contacted with aqueous acids, an amount of the acid was taken up, implying that the carbon had some basic functionality. Earlier, Garten and Weiss (1957) had also conducted some studies on the basic properties to chromene structures that were thought to oxidise easily in the presence of hydrochloric acid to form carbonium ion. The carbonium ion is the one that was thought to be responsible for the weakly basic character of the carbon. However, Voll and Boehm (1971) later put forward the idea of the existence of some pyrone structures to explain the adsorption of acids. This process has been widely accepted and is as shown in Figure 2.3 with the full structures shown in Figure 2.4.

Figure 2.2 Possible structures of surface oxygen groups (Boehm, 1994).
Contrary to the experimental observations of Voll and Boehm (1971), Puri (1970) observed that carbon that was outgassed at 1473 K in vacuum and cooled out of contact with oxygen was a better adsorber of acids. This implied that the basic character of carbon could not be attributed to oxygen containing surface structures alone. This led to the oxygen free Lewis-base concept and it was thought that the Lewis bases were lodged on carbon surfaces in the same way as they exist on polycondensed aromatic hydrocarbons. Because of the unclear nature of the Lewis base sites, Fabish and Schleifer (1984) used the work function concept for correlating the functional groups on carbon black material. This concept involved measurement of the contact potential difference between the carbon black sample surface and a gold reference surface. From a variety of modified carbon black samples, the authors were able to obtain a relationship between the carbon surface
functional groups and the change in the work function of the carbon samples. The change in the work function was assumed to be strongly related to the dipole strengths of the functional groups and it was also noted that the dipole moments associated with the surface groups were directed outwards from the surface of the carbon. It was noted that small additions of localised functional groups resulted in a significant change in work function. The authors attributed also the change in the work function between pH of 10 and 6 for the modified samples to the "lessening of the Lewis basal plane response due to progressive localisation of itinerant basal plane electrons by the oxides chemisorbed onto the fundamental carbon platelet structures located at the particle surface". This observation was compared to the process of increasing or decreasing acidity in Bronsted acids. Hence this led to the \( C_\pi \) concept where \( C_\pi \) was defined as graphitised carbon surface portion having some \( \pi \) electrons that were thought to be responsible for Lewis basicity.

Leon et al. (1992) made an intensive study of the nature of surface basicity of two series of highly pure, chemically and/or thermally pre-treated carbons. They carefully observed the uptake of HCl on the modified carbon series. They presented evidence of electron donor-acceptor interactions of the type \( C_\pi + H_3O^+ \leftrightarrow C_\pi - H_3O^+ \) for carbons with low oxygen content. It was postulated that the \( C_\pi \) sites were located at the \( \pi \) electron rich regions of the basal planes of the carbon situated far from the edges. The interaction of \( C_\pi \) with \( H_3O^+ \) ions resulted in the localisation of the \( \pi \) electron pair associated with the donor-acceptor complex. They also concluded that the donor-acceptor interaction was limited by electrical, electronic and geometric effects. An increase in basal plane diameter and density of the benzenoid rings favoured the formation of the electron-donor complex. Uptake of HCl on carbons with fairly high oxygen content made them conclude that only the pyrone type group was responsible for the basicity in carbon as had been proposed by Voll and Boehm (1971). They proposed that "the basicity of carbon surfaces arises from a combination of electron donor acceptor and pyrone type interactions."

2.3 Surface Modification of Carbons

2.3.1 Surface Modification by Oxidation
It is now acknowledged that activated carbons are relatively unstable in the presence of air. The process leads to a more stable form of an oxidised carbon with an
increased ratio of oxygen to carbon. In recent years, several methods of deliberately oxidising carbon have been reported. These methods have been classified under gaseous oxidation or chemical oxidation. Puri (1970) made an excellent review of the chemical modification of carbons. The oxidation process is known to fix an amount of oxygen surface complexes in the form of carbonyls, ketones, lactones, phenols, quinones, alcohols and ethers (Saha et al., 2001b). Effectively the oxidation process makes the carbon more hydrophilic and more prone to wetting. In many cases the oxygen containing groups behave as weak acids or bases, which possess ion exchange properties. This property has been observed by a number of authors. Strelko and Malik (2002) observed that nitric acid oxidised carbon samples acquired an acidic character, with the carboxylic group being the dominant surface functional group. They further observed that the modified sample displayed cation exchange properties when used to adsorb Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\). Saha et al. (2001b) also reported that the ion exchange performance of activated carbon samples is enhanced by oxidation. They investigated sorption capacity of modified activated carbon for Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\). Bautista-Toledo et al. (1994) adsorbed Cr\(^{3+}\) and Cr\(^{6+}\) on conventional carbon and nitric acid modified carbons. The superiority of oxidised carbon over the conventional carbon on the uptake of the two ions was observed. The enhanced capacity was attributed to increased surface oxygen complexes due to the oxidation process. They actually concluded that metal uptake was a function of surface oxygen complexes rather than the porosity and surface area of the carbons. Saha et al. (2001) also reported that the enhancement of metal sorption by oxidised carbons was also due partly to the presence of humic acids, which are by-products of acid oxidation.

Barton et al. (1997) investigated the effect of oxidation on the basic and acidic nature of the carbon. They used a series of oxidised carbons made by treating with nitric acid at various temperatures and/or by anodically oxidising the carbon in K\(_2\)SO\(_4\) for various times. They also used a carbon sample that was heated for 2 hours under N\(_2\) at 1173 K. It was realised that for the most extensive oxidised sample the number of basic sites was approximately zero while for a heat treated sample the number of acidic sites was very small.
Vinke et al. (1994) looked at the mechanism of the nitric acid oxidation process. They assumed that nitric acid oxidation of carbon was similar to the oxidation of aromatic hydrocarbons; these reactions are well documented in literature. For example, the authors illustrated the oxidation process by using the oxidation of 9,10-dihydrophenanthrene and diphenylmethane.

The authors postulated that the oxygen surface groups could be incorporated in the carbon basal planes through a radical mechanism as shown in the illustrated reaction sequence. The reaction sequence involves the formation of a nitrous acid radical that 'knocks out' a hydrogen atom in the aliphatic side chain of the activated carbon. The resultant radical that is formed then reacts with a nitrogen dioxide radical to form a stable compound, shown in scheme (d). A hydrolysis reaction then leads to the formation of an alcohol, given in scheme (e). They further proposed that there was the possibility of splitting a C-C bond with an α-substituent like a keto-group, followed by oxidation towards carboxylic acid groups as shown in equation (f).

\[
\begin{align*}
\text{HNO}_3 + \text{HNO}_2 &\iff 2 \cdot \text{NO}_2 + \text{H}_2\text{O} \\
\cdot\text{NO}_2 + \text{H} + &\iff \text{HNO}_2^+ \\
\text{Ar-CH}_2\text{-CH}_2\text{Ar} + \text{HNO}_2^+ &\rightarrow \cdot\text{Ar-CH-CH}_2\text{-Ar} + \text{H}_2\text{NO}_2^+ \\
\cdot\text{Ar-CH-CH}_2\text{-Ar} + \cdot\text{NO}_2 &\rightarrow \text{Ar-CHONO-CH}_2\text{-Ar} \\
\text{Ar-CHONO-CH}_2\text{-Ar} + \text{H}_2\text{O} &\rightarrow \text{Ar-CHOH-CH}_2\text{-Ar} + \text{HNO}_2 \\
\text{Ar-CO-CH}_2\text{-Ar} + \cdot\text{NO}_2 &\rightarrow \text{Ar-CO}_- + \text{ONO-CH}_2\text{-Ar} \\
\end{align*}
\]

N.B. Ar in these reactions represents the carbon aromatic basal plane.

### 2.3.2 Modification by Fixation of Nitrogen Containing Functional Groups

In comparison to surface modification by oxidation, nitrogen functional groups on an activated carbon have not been studied extensively. However some authors have been successful in fixing nitrogen functionality on activated carbon. Recently Jia et al. (2002) reported the fixation of nitrogen to be as much as 9.4% as was shown from their elemental analysis results. The nitrogen was thought to exist in pyridinic, pyrrolic and pyridonic functional groups. They also reported that these functional groups are predominantly basic and enhance the adsorption of copper, cadmium and nickel ions. It was presumed that co-ordination bonding was responsible for the observed enhanced uptake, since calcium ion uptake was not affected by the change in surface groups. Jansen and Bekkum (1994) had earlier proposed the existence of
amide, nitriles and tertiary amine groups. They proposed the following structures as shown in Figure 2.5

![Fig 2.5](image)

**Figure 2.5** Types of chemical nitrogen fixation by activated carbons: a) N-alkylamide, b) tertiary amine, c) lactam, d) amide, e) pyridine f) nitrile functional groups (Jansen and Bekkum, 1994).

Vinke *et al.* (1994) proposed that nitrogen fixation in carbon by ammonia would give the same results as in reactions with organic compounds containing similar functional groups. The classical reactions are summed up as:

\[
\begin{align*}
\text{Ar-OH} + \text{NH}_3 & \rightarrow \text{Ar-NH}_2 + \text{H}_2\text{O} \\
\text{Ar-CH}_2\text{OH} + \text{NH}_3 & \rightarrow \text{Ar-CH}_2\text{-NH}_2 + \text{H}_2\text{O} \\
\text{R-COOH} + \text{NH}_3 & \rightarrow \text{R-CNH}_2 + \text{H}_2\text{O} \\
\text{R-CO-R} + \text{NH}_3 & \rightarrow \text{R-CN-R} + \text{H}_2\text{O} \\
\text{R-CH=CH-R} + \text{NH}_3 & \rightarrow \text{R-CH}_2\text{-CHNH}_2\text{-R}
\end{align*}
\]

Radovic *et al.* (1997) also compared nitrogen-containing carbons with other carbons of a varying nature for the removal of aniline and nitrobenzene. They noted that the presence of nitrogeneous functionality had an adverse effect on the adsorption of
nitrobenzene (that was considered to be adsorbed through a donor-acceptor mechanism) when compared to heat-treated carbon that contained graphene layers unperturbed by electron withdrawing functional groups. It was felt that the incorporation of nitrogen in carbon caused a decrease in the \( \pi \)-electron density in the basal planes (graphene layers) due to \( \pi \)-electron localisation or withdrawal (caused by nitrogen functional groups). This would then imply that incorporation of nitrogen decreases \( \pi \) electron density on the graphene layers of the carbon. However, this statement is not necessarily accurate because most authors who have tried to incorporate nitrogen functionality have not had much success in controlling the nature of the nitrogen functional groups. In most of the cases it is probable that the nitrogen is attached to the carbon in the pyridinic and pyrrolic forms and such nitrogen is electron withdrawing. Other forms like lactam and imides make much contribution to the \( \pi \) system since they are normally bonded to non aromatic regions of the carbon. However, it is well known that when nitrogen in the form of amine group is attached to an aromatic species, it tends to enhance the \( \pi \) electron cloud of the aromatic system. This is achieved through the lone pair of electrons from the nitrogen which is believed to be delocalised and hence it would contribute to the \( \pi \) electron cloud of the aromatic system. Hence, a carbon with amine functionality would then be expected to have increased \( \pi \) electron cloud than a conventional carbon.

There is a potential of incorporating amino functional groups to the carbon basal planes if classical organic chemistry reactions are applied. The process is normally performed by nitrating the aromatic carbon through electrophilic substitution and then aminating through reduction. One example of such reactions is the two stage amination of phenanthrene as shown in Figure 2.6 (a) and (b). The first stage involves nitration of phenanthrene by a combination of nitric acid and sulphuric acid to give five products that differ in the nitro position as shown in the Figure 2.6 (a). Sulphuric acid in this reaction is used for the formation of the nitronium cation which later attaches itself to one of the available positions on the phenanthrene molecule. The first stage of the reaction as shown in Figure 2.6 (a) is the electrophilic substitution stage where an \( \text{H}^+ \) is substituted by \( \text{NO}_2^+ \) ions. Reduction of the nitrated products is then performed using a suitable reducing agent usually sodium dithionite in the presence of a catalyst.
2.3.3 Other modification processes

Donnet (1968) gave a review of the chemical reactivity of carbons and he was able to document reactions that have been performed on individual functional groups. Some of the reactions are as listed in Figure 2.7. From the listed reactions, it is interesting to note that the reactions of the activated carbons are analogous to the reactions that occur to similarly functionalised aromatic molecules. The symbol R in this instance represents the basal plane of the carbon.

Figure 2.6 Amination of penanthrene a) Nitration stage b) Amination stage (Gutsche and Pasto, 1975).
Selected reactions on carboxyl functions

\[ R-COOH + CH_2N_2 \rightarrow RCOOCH_3 + N_2 \]
\[ R-COOH + SOCl_2 \rightarrow R-COCl + SO_2 + HCl \]
\[ R-COOH \xrightarrow{\text{Heating above 973K}} R-H + CO_2 \]

Selected reactions on hydroxyl functions

\[ R-OH + CH_2N_2 \rightarrow R-OCH_3 + N_2 \]
\[ R-OH + O_2N/COCl \rightarrow R-O-NO_2 + HCl \]
\[ R-OH + SO_2/OMe \rightarrow R-OCH_3 + SO_2/OMe \]

Selected reactions on quinonic functions

\[ \text{Figure 2.7 Examples of reactions that can occur on various functional groups of the carbon.} \]

2.4 Conclusions

The literature shows that activated carbon is derived from ‘fused’ aromatic rings with severe structural defects. Its behaviour in terms of chemical reactivity, is expected to match those of organic aromatic molecules as is observed from the various surface modifications that can be achieved. Also, the various surface functional groups makes activated carbon a versatile adsorbent with the potential to remove organic and inorganic adsorbates.
2.5 References


Barton S.S., Evans M.J.B., Haliop E., MacDonald J.A.F., 1997, Acidic and basic sites on the surface of porous carbon, Carbon, 35 (9), 1361-1366.


3. ADSORPTION OF ORGANIC AROMATIC MOLECULES AND COPPER IONS FROM WATER

3.1 Introduction
This chapter covers some theoretical aspects of adsorption and surveys the literature relating to the adsorption of the target adsorbates. Since the herbicides under this study are aromatic, a general discussion on the postulated adsorption mechanisms of aromatic molecules is also taken into account.

3.2 Adsorption Theory
3.2.1 Introduction to Adsorption
Adsorption is the accumulation of material on two interfaces. Tien (1994) mentioned that the term was first used in connection with the condensation of gases on free surfaces and gaseous absorption. The adsorbed species is called the adsorbate and the material on which adsorption is taking place is called the adsorbent. Adsorption can take place on a number of combinations of phases and these are gas-solid, gas-liquid, liquid-solid, and liquid-liquid phases. It is widely believed that adsorption is caused by adsorbent surface atoms that are usually subjected to unbalanced forces of attraction normal to the surface plane.

There are two ways through which molecules can attach to the surface of an adsorbent. These are namely physisorption and chemisorption. Physisorption occurs through van der Waals forces that are weak and non-specific while in contrast, chemisorption occurs through the formation of chemical bonds. Comparison of the two processes is shown in Table 3.1.

3.2.2 Physisorption
Physical adsorption is as a result of weak van der Waals forces that can induce dipole-dipole interaction and it can involve polar and non-polar molecules. In a case in which non-polar molecules are involved, the attractive forces are due to instantaneous dipoles caused by a momentary distortion of the distribution of charge on one of the molecules. It is postulated that the electron motion in a molecule or an atom would lead to a rapidly oscillating dipole moment. At any instant the lack of symmetry of the electron distribution about the nuclei imparts a transient dipole moment to an atom or molecule that averages zero over a longer time interval. Also, when in close proximity
to a solid surface, each instantaneous dipole of an approaching molecule induces an oriented dipole moment in a surface molecule. The moments then interact to produce an instantaneous attraction. This involves the attraction between the positive end of one polar molecule to the negative end of a neighbouring polar molecule.

<table>
<thead>
<tr>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption is through van der Waals interactions</td>
<td>Adsorption is through the formation of chemical bonds</td>
</tr>
<tr>
<td>Typical values of enthalpy of adsorption are in the region of 20 kJ/mol (Atkins, 1986)</td>
<td>Typical values of enthalpy of adsorption are in the region of 200 kJ/mol (Atkins, 1986)</td>
</tr>
<tr>
<td>The adsorbate retains its identity since enthalpy of adsorption is not enough to lead to bond breakage and formation</td>
<td>The adsorbate is altered in its identity due to bond formation and breakage</td>
</tr>
</tbody>
</table>

Table 3.1 Comparison of physisorption and chemisorption.

3.2.3 Hydrogen Bonding

Hydrogen bonding is a unique case of a dipole-dipole interaction. Hydrogen bonding occurs when hydrogen is bonded to a highly electronegative atom, usually oxygen, fluorine or nitrogen. "When hydrogen is bonded to one of these atoms its electron cloud is distorted towards the highly electronegative atom, thus exposing the positively charged hydrogen nucleus" (Sweetland, 1997). The hydrogen so bonded is then capable of forming electrostatic forces of attraction with adjacent electronegative atom and the resultant bond is stronger than the dipole-dipole interaction. Examples of hydrogen bonding cases are shown in Figure 3.1.
3.2.4 Adsorption through Complex Formation

Adsorption can occur through complex formation with metals that are bound on the surface of the adsorbent. However, the organic molecule that is adsorbed must possess a ligand, and the ligand enables the formation of a co-ordination bond with the metal. An excellent example of adsorption through complex formation is the removal of phenol and s-triazine by complexation as shown in Figure 3.2.

![Figure 3.2 Binding of phenol and s-triazine by complexation (Sweetland, 1997).](image)

3.3 Adsorption Mechanism

The design of an adsorber requires background knowledge of the mechanism of adsorption coupled with the adsorption capacity of the adsorbent. The kinetics can be
described by 3 stages that include external diffusion, movement through the boundary layer, followed by internal diffusion. External diffusion involves the movement of adsorbate molecules from the bulk of the solution towards the surface of the adsorbent. This is followed by movement of molecules through the boundary layer while internal diffusion involves the movement of molecules in the interior of the particles. Movement of molecules at this stage can be by surface and/or pore diffusion mechanism as shown in Figure 3.3. Al-Duri and McKay (1992) have reported that surface diffusion is very important in the adsorption process and that it contributes to 90% of the intraparticle diffusion.

![Figure 3.3 Adsorption process mechanism.](image)

External diffusion involves the transfer of the adsorbate from the bulk of the solution to the surface of the adsorbent through a stagnant film surrounding the adsorbent particles. An equation describing external mass transfer is as given by Al-Duri and McKay (1992):

\[
N_i = \frac{VdC_i}{dt} = k_f A(C_i - C_s)
\]  

(3.1)

where \(N_i\) is the external mass transfer rate, \(C_i\) and \(C_s\) are fluid phase concentration at time \(t\) and equilibrium fluid phase concentration respectively and \(k_f\) is an external film mass transfer coefficient while \(V\) is the solution volume.
The external mass transfer is characterised by the external film mass transfer coefficient $k_f$. According to Baup et al. (2000), $k_f$ is mainly a function of the adsorbent particle size and not the nature or porosity of the adsorbent. In non-ideal stirred vessels the $k_f$ value depends on the flow conditions around the adsorbents. For a completely mixed batch reactor the following equation can be applied (Hand et al., 1982):

$$\frac{2k_f R}{D_t} = 2 + 0.64 \text{Re}^{1.182} \text{Sc}^{0.333}$$  \hspace{1cm} (3.2)

in which Re is the Reynolds number and Sc is the Schmidt number. These numbers are represented by the following expressions respectively:

$$\text{Sc} = \frac{\mu}{\rho_l D_t}$$  \hspace{1cm} (3.3)

$$\text{Re} = \left(\frac{2R}{\mu}\right)^{\frac{1}{2}} \left(\frac{P}{\rho_l V}\right)^{\frac{1}{2}}$$  \hspace{1cm} (3.4)

$D_t$ = diffusivity of the adsorbate in water, $\mu$ = viscosity of water, $\rho_l$ = density of water, $P$ = power dissipated in reactor, $R$ = radius of adsorbent, $V$ = volume of solution

McKay and Al-Duri (1990) have used the following equation to describe $k_f$ in batch adsorption systems:

$$k_f = -\frac{V}{A C_o} \left(\frac{dC}{dt}\right)_{t \to 0}$$  \hspace{1cm} (3.5)

where $C_o$ is the initial concentration, $V$ is the volume of solution, and $A$ is the total surface area of the adsorbent particles. The above equation is based on the unreacted shrinking core mass transfer model.

The second mass transfer process is internal diffusion. This process can involve one of two different phenomena, namely, pore diffusion and surface diffusion. In some cases
the phenomena can occur simultaneously. In pore diffusion the adsorbate molecules diffuse in the fluid filling the pores before adsorption, while in surface diffusion the adsorbate molecules migrate along the surface of the adsorbent.

In pore diffusion for single species adsorption, kinetic data can be correlated in terms of Fick’s first law of diffusion:

\[ N_A = D \frac{\partial C_p}{\partial r} \]  

(3.6)

where \( D \) is the intraparticle diffusivity and \( C_p \) is the concentration in the pore space. Pore diffusion is affected by a number of parameters but prime among them are the adsorbent pore size and adsorbate concentration. For large pores and fairly concentrated solutions a molecular diffusion mechanism dominates in the mass transfer process, since collisions are predominantly from adsorbate molecules. If the adsorbent pores are smaller than the mean free path of the adsorbate the mass transfer process becomes Knudsen diffusion, and in this mechanism the collision between the fluid molecules and the walls are significant and must be factored into the intraparticle diffusion process.

3.4 Adsorption Isotherms

The capacity of an adsorbent to adsorb sorbates from water is best described graphically in the form of adsorption isotherms. An adsorption isotherm can be defined as the relationship between the amount of sorbate per unit mass of adsorbent \( (q_e) \) and the equilibrium concentration \( (C_e) \) of adsorbate in solution. A wide variety of adsorption isotherms have been proposed to model different types of adsorption systems, but Freundlich and Langmuir isotherms have been used widely.

3.4.1. Freundlich Isotherm

Equilibrium relationships can often be described by a Freundlich equation which is given in the form:

\[ q_e = K C_e^{\frac{1}{n}} \]  

(3.7)

where \( q_e \) and \( C_e \) are the amount of sorbate per unit mass of adsorbent and the equilibrium concentration respectively while \( K \) and \( \frac{1}{n} \) are empirical constants that
are heavily dependent on the nature of solid and adsorbate and on the temperature. Low values of $\sqrt{n}$ imply strong bonding interaction between the adsorbate and the adsorbent and generally in such circumstance the isotherm is irreversible. $K$ is related to the capacity of the adsorbent for the adsorbate. The linear relationship of the above equation is given as:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

(3.8)

A plot of $\ln q_e$ versus $\ln C_e$ gives a straight line with a gradient of $\frac{1}{n}$ and an intercept of $\ln K$. However the Freundlich isotherm works only when the adsorbate does not change identity after adsorption, in other words there should be a complete absence of chemisorption.

### 3.4.2 Langmuir Adsorption Isotherm

The Langmuir isotherm is based on the kinetic theory, that at equilibrium the rate of adsorption is equal to the rate of desorption. There are a number of assumptions on which the Langmuir equation is based, and are stated as (Do, 1998):

1. the adsorption energy is constant over all the sites, in other words the sites are equivalent;
2. adsorption sites are localised;
3. one adsorbate molecule can only be accommodated by each site.

Langmuir adsorption isotherm equation can be represented as follows:

$$q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e}$$

(3.9)

where $b$ is a constant that gives an indication of the strength of bonding between the adsorbate and adsorbent. The higher the value of $b$ the stronger the adsorbate/adsorbent interaction.

### 3.4.3 Redlich-Peterson Equation

The Redlich-Peterson equation has been proposed to improve the fit by the Freundlich or Langmuir equations. The equation consists of a linear dependence of concentration in the numerator while an exponential concentration function is in the denominator, and can be represented as:
The parameters \( K_{\text{RP}}, a_{\text{RP}}, \) and \( \beta \) are the Redlich-Peterson parameters. When \( \beta = 1 \), the equation converts to the Langmuir form. Also, adsorption is favourable when the constant \( \beta \) is between 0 and 1.

### 3.5 Adsorption of Organic Aromatic Molecules by Activated Carbon

The adsorption of organic molecules from water by activated carbon is one of the most important processes in waste water and drinking water treatments. The process also finds application in hazardous waste treatment, pharmaceutical industries, food industries etc. Adsorption on activated carbon has also been recommended as the best available environmental technologies by the US Environmental Protection Agency (Moreno-Castilla, 2004).

Although activated carbon finds a wide application in environmental cleaning and industrial processes, the specific adsorption mechanism for organic aromatic molecules is not well understood. This is due to the complex heterogeneous nature of the activated carbon surface and a variety of molecular interactions involved in the adsorption systems. Despite the controversy in the adsorption mechanism of organic molecules, three important adsorption mechanisms have emerged from the literature. These are: the \( \pi-\pi \) dispersion interaction mechanism, the hydrogen bonding formation mechanism, and the electron donor-acceptor complex formation mechanism.

Coughlin and Ezra (1968) proposed the first two mechanisms and the third was proposed by Mattson et al. (1969). The adsorption mechanisms of aromatic molecules have been extensively investigated using phenol and its derivatives. The first mechanism based on the experimental work involving adsorption of phenol on active carbon and pelletised channel black assumed that adsorption was effected through association of the \( \pi \) electrons of the graphene layers of the carbon and \( \pi \) electrons of phenol. In this proposed mechanism, Coughlin and Ezra (1968) employed oxidised and reduced carbons to adsorb phenol and nitrobenzene from water. The authors observed that an increase in surface oxygen groups by oxidation resulted in inhibited adsorption of both phenol and nitrobenzene. They then proposed that \( \pi-\pi \) dispersion interaction was the key to organic molecules uptake. In this case, it was assumed that
the acidic functional groups located on the edges of the carbon basal planes would localise the $\pi$ electrons thereby removing them from the $\pi$ electron system of the basal planes. Such a system was thought to create 'positive holes in the conducting band of the $\pi$ electron system' thus weakening the association between $\pi$ electron of the phenol aromatic ring and the $\pi$ electrons of the basal planes resulting in reduced phenol uptake.

Earlier Dubinin (1966) had proposed that water molecules could form hydrogen bonds with the oxide functional groups of the activated carbon. Hence Dubinin (1966) suggested that water molecules adsorbed on the oxygen sites would become secondary adsorption sites which would retain other water molecules through hydrogen bonding. As a result complexes of associated water molecules would form inside the microporous carbon adsorbent, thus preventing the organic molecules from accessing a large portion of the active surface area within the adsorbent. However, based on observed experimental results, Coughlin and Ezra (1968) felt that such a mechanism was highly unlikely.

Pinto and Leng (1997) investigated the effects of surface properties of activated carbons on the adsorption behaviour of phenol. They used a conventional carbon F400 and its modified series. The modification involved air oxidation, deoxygenation at 1123 K in a stream of nitrogen, acid washing with hydrochloric acid and impregnation of iron. The authors observed that as the surface oxygen decreased, the amount of phenol adsorbed increased. The authors concurred with the idea of a $\pi$-$\pi$ interaction of phenol and the adsorbent. However, contrary to Coughlin and Ezra's explanation about water molecules not taking part in the mechanism of adsorption, Pinto and Leng (1997) concluded that increased carboxylic acid led to increased water adsorption resulting in reduced phenol uptake. They also showed that hydrochloric acid washed sample had increased capacity when compared to the conventional sample. The observation was attributed to the metal content of the carbon. The authors maintained that metals act as sites for water adsorption and as a result, acid washing results in the reduction of the ash content which subsequently leads to decreased water adsorption and hence an increased phenol capacity. Such an observation was in agreement with the notion of Matsumura et al. (1985) that metals on adsorbent surface act as sites for water adsorption.
Pinto et al. (2000) made further investigations on the adsorption of aromatics when they looked at the effect of chemical surface heterogeneity of activated carbon on the uptake of organic molecules. This time, Pinto et al. (2000) employed a petroleum pitch based activated carbon which they labelled LP-DI. They modified the carbon by oxidation and reduction using methods from their previous work. The oxygenated carbon was designated LP-Air while the deoxygenated carbon was given the symbol LP-N₂. To carefully investigate the effect of water molecules on the adsorption mechanism, the authors compared phenol uptake with water as the solvent and with hexane as solvent. When adsorption experiments were performed using water as solvent, the results showed a decrease in adsorption capacity as surface oxygen was increased. This is consistent with observations made by Coughlin and Ezra (1968). Also their previous studies (previously mentioned) had shown similar observations. The authors proposed that the decrease in the uptake of phenol as the oxygen content was increased was due to the interference by water molecules that adsorb on hydrophilic polar oxygen groups at the entrance of the carbon pores. The experimental observations by Pinto et al. (2000) disapproved the idea of the donor-acceptor mechanism that had been proposed by Mattson et al. Mattson et al. (1969) who had proposed that there was complex formation of a donor-acceptor in nature between the adsorbate and the carbonyl oxygen group of the carbon. According to this mechanism, the phenol aromatic ring would act as an acceptor while the carbonyl oxygen groups on the carbon would act as a donor. Hence according to Mattson's mechanism, sorption of phenol would be expected to increase with the corresponding increase of oxygen functional groups. However this mechanism was in contrast with the observation of Pinto et al. (2000) and Coughlin and Ezra (1968). To validate the notion of interference by water molecules in the sorption process, Pinto employed cyclohexane as the solvent. The results showed that the carbon sample LP-Air which had the highest carbon content and had the maximum capacity, while the conventional sample had the lowest capacity. Sample LP-Air which had the lowest capacity in water, had the highest uptake in cyclohexane solvent while sample LP-N₂ had a lower uptake capacity in cyclohexane as compared to sample LP-Air. The authors highlighted the importance of the solvent molecules, and hence the use of cyclohexane to enhance the uptake phenol in oxygenated sample by eliminating the water adsorption mechanism. However, the authors did not attempt to explain why phenol
uptake was higher in the sample LP-Air than in LP-N₂ when cyclohexane was used as solvent. The authors drew a general conclusion that water adsorption, dispersion-repulsion interactions and hydrogen bonding were the main mechanism while donor-acceptor was not significant. From their results, it can be seen that the process of hydrogen bonding and the competition between a solute and a solvent are important and cannot be neglected.

Haydar et al. (2003) drew similar conclusions when they adsorbed p-nitrophenol on activated carbons with different oxidations. They employed conventional and oxidised carbons as the adsorbents. They also monitored the oxygen functional groups on each carbon by performing temperature programmed experiments. In order to check for electron donor-acceptor mechanism, the authors checked for any relationship between CO-evolved (which has a direct bearing on the amount of carbonyl functional groups present) and the phenol uptake for each carbon sample. The authors found no relationship between the amounts of CO-evolving groups and the p-nitrophenol adsorption capacity. Hence it was concluded that the donor-acceptor mechanism was not involved in the adsorption process. However, Epstein et al. (1971) had earlier investigated the adsorption of p-phenol on isotropic pyrolytic carbon. They subjected their carbon samples to electrochemical oxidation at varying current densities to produce reproducible surface functionality. It was observed that the p-phenol adsorption was favoured on oxidised surfaces. The authors concluded that adsorption of p-phenol was through an electron donor-acceptor mechanism.

3.6 Sorption of atrazine, benazolin and 2,4-D

3.6.1 Introduction
This section reviews the adsorption of herbicides onto activated carbon, mainly focusing on atrazine and benazolin and 2,4-D. It also covers the adsorption of herbicides on polymeric resins, activated carbon, and other materials. The structures and properties of the selected herbicides are shown in Table 1.3 in the introduction section.

The increasing demand for food has driven the increase in agricultural productivity. This in turn has fuelled the demand and use of a variety of herbicides. A report by the National Rivers Authority (1992) shows that there are as much as 450 varieties of
herbicides and pesticides that are approved for use by the Department for Environment, Food and Rural affairs (DEFRA) and the Health and Safety Executive (HSE). The greatest users of herbicides are agriculture and horticulture. In England and Wales, the Environment Agency (EA) released data shown in Figure 3.4 on herbicide use for the period 1988-2000. Though the data seems to show a decrease in the use by weight over the period covered there has been an emergence of new herbicides that are more effective in smaller quantities. However, formulations treated areas have increased significantly over the years.

Figure 3.4 Pesticides use in agriculture and horticulture in England and Wales (Environment Agency, 2003).

Herbicides are potential polluters of water. Due to their physical and chemical nature, some herbicides are highly persistent in the environment while others are easily degradable but producing end products that are toxic to plants and animals. Herbicides can find their way into water supplies from several sources: the main source of herbicide contamination is leaching through the soils as a result of agricultural activities. Other sources include discharges from industry, sewage waste and urban run-off. Despite the stringent legislation from the EU, detection of some herbicides
exceeding the limit of <100 ng/L has been documented. Atrazine, one of the target pollutants in this study still features as one of the frequently detected pesticides in fresh water (see Figure 3.5.) Since the ban on atrazine on non-agricultural activities, there has been a downward trend in its detection over the years. However, the increased use of atrazine on maize may be increasing its frequency of detection, especially in ground water. A study in 2001 of over 600 ground water sites around the Thames and Anglian regions revealed that atrazine was the most frequently detected pesticide (De Lurio, 2002). Hence, there is a need for further research on the removal of atrazine since its existence in water bodies can be potential hazard to both plants and mammals. Figure 3.5 also shows that 2,4-D features prominently among the frequently detected herbicides because 2,4-D is widely used due to its low cost and good selectivity. Also, 2,4-D is frequently detected because of its poor biodegradability (Akçay et al., 2005).

![Figure 3.5 Trends in the pesticides occurring most frequently in freshwaters (Environment Agency, 2006).](image)

Adsorption of benazolin is one of the areas to be investigated in this report. Horner and Streat (2000) reported benazolin as one among many pesticides that can be an alternative for atrazine since its ban for non-agricultural use. A report compiled by the Environment Agency (2003) revealed for the first time in England and Wales that benazolin has become one of the 10 most frequently occurring herbicides in surface water. Therefore, it would be necessary to investigate benazolin removal from water since little information is available about its sorption characteristics.
3.6.2 Sorption of Atrazine, Benazolin and 2,4-D

A variety of adsorbents have been investigated to assess their performance on a number of water pollutants. Adsorption on activated carbon has always been superior in the removal of organic compounds as micro-pollutants from wastewater and natural water compared to other sorbent materials (Mazet et al., 1994). Their superiority is mainly due to a well developed and large internal surface structure that is comprised of hydrophobic graphene layers and hydrophilic surface functional groups (Jia et al., 2002). This physico-chemical nature of carbon makes it a versatile adsorbent that can be applied for gas and liquid phase applications. Despite its superiority, a number of adsorbents have been investigated and compared with activated carbon. One such group of adsorbents are polymeric resins that have high porous structures that compare very well with carbon. Streat and Horner (2000) compared the adsorption capacity of some highly soluble herbicides (benazolin, bentazone, imazapyr and trichlopyr) on activated carbon and a hypercrosslinked polymer MN-200. Batch adsorption isotherms at pH 3 and pH 10 showed that adsorption of herbicides was significantly higher on Chemviron F-400 than MN 200 with single component adsorption being greater than multi-component systems. A selective sequence of benazolin > triclopyr > bentazone > imazapyr was observed for F400. It was postulated that benazolin was involved in a donor-acceptor complex mechanism with carbonyl oxygen on carbon. They argued that the chloro group on the aromatic ring of benazolin could act as an electron withdrawing group thus reducing the electron density in the π ring system. It was then
assumed that benazolin could act as an acceptor in the donor-acceptor complex with F400.

The selectivity on MN-200 was found to be a function of pH. At pH 3 the selectivity was triclopyr > bentazone > benazolin > imazapyr, while at pH 10 the order was imazapyr > benazolin > triclopyr > bentazone. Also, mini-column adsorption studies of each herbicide on F400 and MN 200 confirmed that MN 200 was less effective in removing these herbicides. Streat and Sweetland, (1998 a, b) echoed similar sentiments when they investigated the removal of pesticides (atrazine, simazine, chlorotoluron, isoproturon diuron) on MN-100, MN-150, MN-200 and compared the sorption with published data on F 400. The capacity of Chemviron F-400 for atrazine in ultra pure water was shown to be higher than MN 200. Results on their mini column studies also confirmed that Chemviron F400 has a higher capacity for pesticides adsorption than polymeric adsorbents. But on the competitive adsorption of the pesticides with fulvic acid, the mini-column studies showed slightly reduced adsorptive capacity in polymeric sorbents in the presence of fulvic acid (20 mg/L) than in Chemviron F400. They attributed this to the physical and chemical properties of the materials. Suffet et al. (1978) compared the sorption performance of Amperlite XAD polymer with chemviron F-400. They concluded that F-400 was more effective in the adsorption of non-polar trace organic compounds.

Matsui et al. (1996) investigated the suitability of activated carbon to adsorb some organic pesticides. They used a micro-column technique with rapid small scale column test theory. The target pesticides in the study were simazine, diazinon napropamid, bentazone, asulam and hymexazol. The effect of humics on the adsorption of the pesticides was also studied. Their major results showed that adsorption capacity of diazinon was decreased by the competitive adsorption effect of humic acid and that the breakthrough curve for humic acid was not affected by the presence of diazinon. Humic acid was shown to be the dominant adsorbate and most of the compounds adsorbed consisted of humic acid. The hydrophobic pesticides simazine, diazinon and napropamid showed almost the same breakthrough curves and adsorption capacity. However, the hydrophilic adsorbents bentazone, asulam and hymexazol showed earlier breakthrough and smaller capacity than the hydrophobic pesticides. It was concluded that for hydrophilic pesticides the adsorption capacity was inversely related
to the water solubility of each pesticide (bentazone, asulam, hymexazol in the order of increasing water solubility and decreasing adsorptive capacity). This was shown further when they studied the relationship between adsorptive capacity at 20% breakthrough point and the water solubility of various pesticides in organic free water and humic acid background solution. Results showed that hydrophobic pesticides which had a water solubility of less than 100 mg/L had almost the same adsorptive capacity. The other hydrophilic pesticides showed decrease in capacity with increase in water solubility in humic acid background solution as well as in organic free water. It was then concluded that water solubility was the major property that characterised adsorption property because the pesticides used differed in chemical composition and molecular weight. However, water solubility effects alone cannot adequately address adsorption of pesticides on activated carbon. Other variables and properties also come into play. For example Baup et al. (2000) worked on the adsorption of atrazine, bromoxynil and diuron on GAC F400. Results showed that adsorptive capacity of the pesticides followed the order diuron > bromoxynil > atrazine even though bromoxynil is more soluble than atrazine that in turn is less soluble than diuron as shown in Table 3.2. Interestingly, they explained the results in terms of the structure of the molecules instead of their solubility in water. It was postulated that diuron is more adsorbed than atrazine because the diuron molecule appears to be more linear and flat than a molecule of atrazine because of the electron delocalisation that stiffens the urea part and consequently, keeps in the plane of the phenyl group. On the other hand, the ethyl and the isopropyl group of atrazine cannot be placed in the plane of the triazine because of steric hindrance. Hence, this gives atrazine more ‘volume’ than diuron. For bromoxynil the authors noted that it is a slightly larger molecule than diuron, but has a greater functional variability than atrazine and hence a broader range of possible sites.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>33</td>
</tr>
<tr>
<td>Diuron</td>
<td>42</td>
</tr>
<tr>
<td>Bromoxynil</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.2 Solubilities of selected herbicides.
Some authors (Ayele et al., 1996; Pelekani and Snoeyink, 1999 and 2000) have looked at the effect of pore size and pore size distribution on competitive adsorption between pesticides. Also the effect of competitive adsorption with other organic pollutants has also been investigated. Pelekani and Snoeyink (2000) performed experimental studies on the competitive adsorption between atrazine and methylene blue on activated carbon, and they also evaluated the importance of pore size distribution. Their studies revealed that when a narrow distribution of primary micropores (pore width < 8 Å) is present, simultaneous adsorption and dye preloading greatly impacted on atrazine adsorption. Increasing the pore volume and shifting the pore size distribution into the secondary micropore region (8 Å < pore width < 20 Å) reduced the degree of competition. It was further noted that the relative impact of preloading with methylene blue on atrazine adsorption decreased with increasing pore volume and pore size. The impact of pore size on the competition mechanism between natural organic matter and atrazine was also studied by Pelekani and Snoeyink (1999). They used two microporous activated carbon fibres with narrow and broad pore size distributions and they denoted them ACF-10 and ACF-25 with average pore sizes of 6 Å and 13.4 Å, respectively. Single solute, simultaneous and preloading experiments were performed. It was noted that atrazine adsorption was significantly reduced in the presence of natural organic matter on ACF-10. Also the uptake of atrazine by ACF-10 in the presence of natural organic matter (simultaneous adsorption) was comparable to the natural organic matter preloaded capacity. They observed also that during competitive adsorption of atrazine and natural organic matter, the reduction in capacity for atrazine was much less for ACF-25 which had primary micropores as well as a large volume of secondary micropores than for a carbon with a narrow pore size distribution. The above work seems to indicate that atrazine adsorbs more in secondary micropores than in primary micropores. Recently Patricia et al. (2002) have put forward the notion that
for an adsorbent to be effective, it should exhibit a large volume of micropores with width that are about 1.3 to 1.8 times larger than the kinetic diameter of the target adsorbate.

Mazet et al. (1994) looked at the influence of heat or chemical treatment of activated carbon onto the adsorption of organic compounds (humic acids, phenol, phthalic acid, salicylic acid, benzoic acid, atrazine, sodium dodecyl sulphate). Chemviron F400 powdered activated carbon (PAC) was used as the starting material and part of it was subjected to heat treatment in an inert nitrogen stream at different temperatures and the sample was denoted PAC(T) concentrated nitric acid treated sample was denoted CAP(OC). Some interesting results obtained are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Atrazine</th>
<th>Salicylic acid</th>
<th>Phthalic acid</th>
<th>Benzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>300</td>
<td>57</td>
<td>60</td>
<td>160</td>
</tr>
<tr>
<td>PAC(T)</td>
<td>477</td>
<td>63</td>
<td>75</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 3.3 Adsorption capacity values (mg/g) of activated carbon: heat treated and non-treated sample.

Their results showed that heat treatment had the effect of destroying acid groups and to increase the basic groups whereas acid treatment increased the carboxylic, lactonic, phenolic, and carbonyl groups and diminish the basic groups. Results in Table 3.3 shows that adsorptive capacity for the heat treated carbon was higher than for the untreated carbon. The above results and others made the authors to conclude that the presence of acidic functional groups retards the adsorption of organic solutes. However, the authors conceded that the total performance of powdered activated carbon is appraised not only by the parameters of specific surface area, pore volume and pore size distribution but also by the electric charge of PAC particles. But the general observation from the work was that the adsorption capacity followed the sequence PAC(T) > PAC > PAC(OC).
3.6.3 Effect of Pesticide Polarity and Surface Charges of the Adsorbent

Relatively little information is available pertaining to the effect of surface charge and ionic strength on the adsorption of atrazine, benazolin and 2,4-D. However, there is limited literature that deals with other pesticides and natural organic matter. Mastui et al. (2002) have looked at the adsorption of asulam and simazine (polar and non-polar, respectively) on thermally activated low polarity coal based granular activated carbon (GAC) and chemically active high polarity wood based GAC. They observed that the removal of simazine and asulam was higher in the adsorbers containing coal based GAC. This was attributed to the suitability of the pore volume and the lower polarity of the coal based GAC. They indicated that “the relatively high oxygen content and the greater polarity of the pore surfaces in chemically activated wood based GACs leads to enhanced adsorption of water. Water can adsorb by means of hydrogen bonds on oxygen containing functional groups, and clustering of additional water molecules occurs around water molecules adsorbed at these sites. Such clusters adversely affect the adsorption of trace targeted pollutants by (i) preventing pollutant access to non-polar regions on the activated carbon surface (ii) reducing the interaction energy between the pollutant and the adsorbent surface and/or (iii) effectively blocking pollutant access to micropores.” It was further noted that the adsorption of asulam was less than that for simazine, the reason being that asulam associates more with the solvent than simazine. Recently some work by the same authors on the pesticide adsorption by granular activated carbon adsorbers with a component of competitive adsorption using same target pollutants have partly revealed simazine and asulam removals were greater in the adsorbers containing coal based GAC. Similar observations were noted echoed by Patricia et al. (2002) when they adsorbed two drinking water contaminants, methyl tertiary-butyl ether (relatively polar), and trichloroethene (relatively non-polar) on activated carbon with three activation levels. They noted that hydrophobic adsorbents effectively removed both pollutants better than hydrophilic adsorbents. This was attributed to enhanced water adsorption on hydrophilic surfaces.

Few materials other than carbon have been tried as potential adsorbents. Clausen and Fabricius (2001) investigated adsorption capabilities of iron oxides for non-ionic and ionic pesticides and the adsorption was monitored as a function of pH, ionic strength, and pesticide concentration. Results showed that adsorption of non-ionic pesticides (atrazine and isoproturon) was insignificant, whereas the adsorption of the acidic
pesticides (mecoprop 2,4-D, and bentazone) was significant on all investigated iron oxides. The adsorption capacity increased with decreasing pH and it was noted that addition of CaCl₂ in concentrations from 0.0025 to 0.01M caused the adsorption capacity to diminish. However their work did not focus on the comparison between iron oxides and activated carbons.

Gonzalez-Pradas et al. (1997) evaluated the potential use of bentonite to remove atrazine from water. Bentonite dessicated at 383K untreated and acid treated with H₂SO₄ was used for the adsorption experiments. From batch experiments it was observed that acid treated bentonite was more effective than natural bentonite. The same authors (2000) also looked at the removal of paraquat and atrazine from water by montmorillonite (Ce or Zr) phosphate crosslinked compounds. The experiments were done at two different temperatures (288K and 308K), and a batch process was used. The results indicated that an increase in temperature did not have any clear effect on the adsorption of paraquat on both adsorbents. Conversely, adsorption of atrazine decreased slightly at the increase in temperature from 288K to 308K. This was attributed to some physical process. Ce montmorillonite adsorbent showed superiority in adsorption as compared with Zr montmorillonite adsorbent.

Bottero et al. (1994) compared the adsorption capacity of various hydrophilic solids (zeolites Y) and hydrophobic solids (zeolites ESM-5) together with organoclays in the presence of background organics. An interesting observation was that most hydrophobic solids and organoclays adsorbed atrazine better when background organics were present on the solid. However, hydrophilic solids zeolite Y showed lower adsorption for atrazine and this behaviour was attributed to the high affinity of atrazine for background organics.

3.7 Adsorption of Copper by Activated 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. Since copper is potentially harmful to humans, its monitoring in, and removal from drinking water is essential.
Quite a large variety of materials have been studied for the adsorption of copper. Yu et al. (2000) studied sawdust as a potential adsorbent for the removal of copper (II) from waste water. The equilibrium sorption level was found to be a function of solution pH, contact time, and sorbate concentration. Kim et al. (2001) reported the production of granular activated carbon from waste walnut shell and its adsorption characteristics for copper (II) ions. Adsorption of copper ions was shown to follow the Freundlich model. They also reported that the adsorption capacity of the resultant activated carbon was superior to the activated carbon from coconut shell. The walnut shell activated carbon also met the standard for commercialisation.

El-Shafey et al. (2002) investigated the adsorption behaviour of a wide range of heavy metals on acid treated flax shive. Kinetic studies showed a fast sorption kinetics following a first order rate equation. Further experiments using cadmium as representative of other metal ions showed that in the presence of other metal ions such as K+, Na+, Mg2+ and Ca2+ decreased the Cd2+ uptake and this was attributed to competition for the ion exchange sites. Increase in temperature did not significantly affect sorption capacity.

Toles et al. (1997) used activated carbon derived from almond and pecan shells. The materials were either activated chemically with H3PO4 or physically with CO2 under a variety of conditions. In the acid activated carbons, air oxidation significantly increased the ability of the carbon to remove Cu2+ but the increase was not as great in the CO2 activated carbons. Results indicated that with oxidation those carbons that were acid activated greatly increased their ability to bind metals from solution while oxidation did little to change the metal uptake capability of carbon dioxide treated carbons. The researchers postulated that the burn off due to oxidation of CO2 is greater than that of the acid activated carbons, and oxidation of the CO2 activated carbons would actually cause a loss of oxygen containing functions from some of the carbons, probably as CO2. Generally oxidation treatment improved Cu2+ adsorption on both types of carbon to levels significantly higher than commercial carbons.

Corapcioglu and Huang (1987) studied the adsorption of Cu2+, Pb2+, Ni2+ and Zn2+ onto hydrous activated carbon. They found that carbon type, pH and surface loading were the most important factors affecting the extent of metal removal. They realised
that carbons with the highest phosphoryl compounds (94.5% of total ash) had the highest adsorption capacity for the metals in the acidic region. However, results in the alkaline region could not be firmly confirmed because of metal precipitation. Also, it was noted that the increase in surface loading impacted negatively on metal adsorption. For example, the removal of Cu\(^{2+}\) as a function of pH decreased with increasing surface loading. When the initial concentration on the solution increased from 0.63 to 18 ppm by keeping the activated carbon dose constant at 10 g/L, the percentage copper removal decreased. But the copper removal efficiency of carbon F400 was insensitive to surface loading at pH < 2-3 or > 7. In general, the results showed that regardless of the type of heavy metal studied, the percentage of metal removal increased with decreasing surface loading. This was attributed to inter-adsorbent interaction that in turn impedes adsorption.

Corapcioglu and Huang (1987) also observed that as the temperature was increased from 298 K to 373 K, the uptake of Cu\(^{2+}\) on carbon F400 increased appreciably. For example at pH 3 the percentage removal increased from 15 to 60% as the temperature was raised from 298 K to 373 K. It was postulated that oxidation of carbon enhances the Cu\(^{2+}\) removal capacity. Seco et al. (1997) had also made similar observations; however, results by El-Shafey (2002) indicate that there is no appreciable change in adsorption capacity with increase in temperature.

Corapcioglu and Huang (1987) proposed a mechanism for Cu\(^{2+}\) adsorption on F400 as a surface complex formation. Since F400 has -COOH and -COH as major hydroxo groups, the adsorption reaction for Cu\(^{2+}\) was described by the following mechanism:

\[
\begin{align*}
2\text{COOH} + \text{Cu}^{2+} & \rightleftharpoons (\text{CO})_2^{2-}\text{Cu} + 2\text{H}^+ \quad (a) \\
2\text{COH} + \text{CuOH}^+ & \rightleftharpoons (\text{CO})_2^{2-}\text{CuOH}^+ + 2\text{H}^+ \quad (b) \\
2\text{COH} + \text{Cu(OH)}_2 & \rightleftharpoons (\text{CO})_2^{2-}\text{Cu(OH)}_2 + 2\text{H}^+ \quad (c) \\
2\text{COH} + \text{Cu(OH)}_3 & \rightleftharpoons (\text{CO})_2^{2-}\text{Cu(OH)}^+ + 2\text{H}^+ \quad (d)
\end{align*}
\]

The adsorption edge for Cu\(^{2+}\) was found to be in the pH range from 3 to 5.

Strelko (1999) studied the adsorption of copper, nickel and lead on modified activated carbons from a variety of sources, namely agricultural products (KAU), polymeric resins (CKC), and phosphorous containing carbonaceous sorbent (PGP-P). These
sorbents were compared with the commercially available adsorbents F400 and polymeric weakly acidic carboxylic resin, C104. This work confirmed that all the studied adsorbent materials showed a preference towards lead and copper over nickel and cadmium. Also the amount of metal removed by all carbons increased sharply between pH 1.5 and 3. Furthermore, results revealed that adsorption capacity of carbons strongly depends on the degree of surface oxidation. The carbon samples oxidised by nitric acid possessed greater sorptive capacity than those oxidised by air.

Other results showed that adsorption for copper as higher than that for lead for carbons with low concentration of the acid surface groups. However, as the degree of surface oxidation increased, the sorptive capacity approached that of copper. Phosphorus containing carbon displayed a relatively greater sorption capacity for lead than for copper when compared with oxidised carbons. Saha et al. (2001b) reported the superiority of acid oxidised carbon over air oxidised carbon for the removal of Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$. Air oxidised samples showed lower metal uptake capacity compared to acid oxidised samples. They were able to show that copper uptake capacity of a 24 h nitric acid oxidised sample was increased by a factor of 60 compared to the unoxidised as-received material. During the process of acid oxidation, alkali washing was performed to remove by-products that are produced in the oxidation process and it was realised that the sorption capacity of the materials reduced with subsequent treatments with hydroxide washing. This led to the conclusion that the organic by-products formed had some metal binding capacity.

Biniak et al. (1999) also looked at the adsorption of copper on modified activated carbons, using three methods of modification. The first sample was annealed in a vacuum at 1000 K, the second sample was oxidised with concentrated nitric acid, and the third sample was heat treated in an ammonia atmosphere at 1173 K. The nitric acid oxidised sample was acidic and the remaining two samples were basic.

Adsorption of copper on the three carbons revealed that the amount adsorbed was a function of the pH of the solution and the modification procedure. For the pH range 1-6, the cationic uptake increased linearly (0.07 mmol/pH) for the heat treated sample and in the case of the oxidised sample a sharp increase was observed between pH 1 and 3. The ammonia treated sample showed a smooth increase of 0.03 mmol/pH.
Results further showed that at pH 1, the ammonia treated sample had a higher copper uptake than the nitric oxidised sample, but at pH 3 the nitric oxidised sample showed a greater uptake. The authors postulated that the big leap in the adsorption found in the pH range 1 and 3 would indicate that the zero point of charge of the oxidised sample lay between the two values.

In accordance with the spectroscopic data obtained some mechanisms of adsorption were proposed by the same authors for each type of carbon; they are:

For the annealed carbon (Scheme 1)

\[ >C-H + Cu^{2+} \rightarrow C-H---Cu^{2+} \text{ (dipole-dipole, } \pi\text{-d interactions)} \] (a)

\[ >C^+ + Cu^{2+} \rightarrow >C---Cu^+ \rightarrow \Theta>C---Cu^0 \] (b)

\[ >C-O^+ + Cu^{2+} + H_2O \rightarrow >C-O-CuOH + H^+ \] (c)

\[ >C=O + Cu^{2+} + H_2O \rightarrow >C---Cu(OH)_2 \] (d)

For the nitric acid oxidised carbon (Scheme 2)

\[ >C-COOH + Cu^{2+} \rightarrow >C-COOCu^+ + H^+ \] (e)

\[ (>C-COOH)_2 + Cu^{2+} \rightarrow (>C-COO)_{2}Cu + 2H^+ \] (f)

\[ >C-OH + Cu^{2+} \rightarrow >C=O---Cu^+ + H^+ \] (g)

For the heat treated carbon in ammonia (Scheme 3)

\[ >C-NH_2 + Cu^{2+} + H_2O \rightarrow >C-NH_2---Cu(OH)^+ + H^+ \] (h)

\[ >N: + Cu^{2+} + H_2O \rightarrow >N-Cu(OH)^+ + H^+ \] (i)

\[ >N: + Cu^{2+} + H_2O \rightarrow \Theta>N-OH---Cu^0 + H^+ \] (j)

The symbols \( \bullet \) and \( \Theta \) marked the ion radical and positive holes in the carbon structure.

The mechanism proposed in scheme 2 above differs markedly from the mechanism proposed by Corapcioğlu et al. (1987) for an activated carbon containing -COOH and -COH groups.

Jia et al. (2002) recently studied the adsorption of metal ions on nitrogen surface functional groups in activated carbon. A wide variety of activated carbons were obtained after some modification processes that mainly involved oxidation with nitric
acid and heat treatment in ammonia. Part of the characterisation data are shown in Table 3.4.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Wt% nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.3</td>
</tr>
<tr>
<td>CA</td>
<td>2.3</td>
</tr>
<tr>
<td>CN2A</td>
<td>5.3</td>
</tr>
<tr>
<td>PANC</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 3.4 Selected characterisation data (Jia et al., 2002).

Their results indicated that the adsorption of \( \text{Cd}^{2+} \) and \( \text{Cu}^{2+} \) was enhanced by the surface nitrogen functionality incorporated through ammonia treatment or inherited from the precursor. A phenomenon that had previously been observed by Biniak et al. (1999). The capacities of adsorption capacity of \( \text{Cd}^{2+} \) (aq) and \( \text{Cu}^{2+} \) (aq) followed the order \( \text{PANC} > \text{CN2A} > \text{CA} > \text{C} \) and this followed the order of the nitrogen content of the carbons. The effect of functionalised nitrogen on the adsorption of \( \text{Ca}^{2+} \) was also investigated, and it was apparent that the adsorption of \( \text{Ca}^{2+} \) on the modified activated carbons showed no relationship with the nitrogen content of the activated carbons. In fact the adsorption of \( \text{Ca}^{2+} \) was not affected by the nitrogen functionality of the carbons. The authors then concluded that the nitrogen functionality had selectivity for transition metals due to coordination interactions. It was proposed that the interactions could take place through coordination bonding as illustrated in Figure 3.8.
Chen and Lin (2001) have looked at the equilibrium and kinetics of metal ion adsorption. They used an H-type activated carbon that is a carbon that has been activated at high temperatures and can adsorb H⁺ ions. The target metals were copper, zinc and cobalt. Results showed that metal removal was in the descending order: Cu²⁺ > Zn²⁺ = Co²⁺. They managed to correlate the effect of pH on diffusivity ($D_p$) and external mass transfer coefficient ($k_f$). For pH values of 6.0, 4.5, and 3.0, $D_p$ values were $5.0 \times 10^{-8}$, $5.0 \times 10^{-7}$ and $3.0 \times 10^{-6}$ cm²/s, and $k_f$ were $4.0 \times 10^{-3}$, $7.0 \times 10^{-3}$ and $1.0 \times 10^{-2}$ cm/s, respectively. Clearly it showed that as the pH increased, the parameters $D_p$ and $k_f$ decreased. The observed phenomenon was explained in terms of the formation of CuOH⁺ which was said to increase as the pH of the solution increased. Since CuOH⁺ has a higher molecular size that Cu²⁺, $D_p$ and $k_f$ were bound to decrease at higher pH due to the increased CuOH⁺ formation. Furthermore, the authors indicated that aqueous species were more at higher pH, which tends to increase the mass transfer resistance. Chen et al. (1996) also performed some adsorption of copper on activated carbon and they obtained the values of $D_p$ and $k_f$ as $1.5 \times 10^{-11}$ m²/s and $9.6 \times 10^{-7}$ m/s, respectively. They also used a dimensionless parameter $B_M$ to show the relative importance of macropores and micropores. $B_M$ is defined as:

$$B_M = \frac{a_p k_f}{D_p n_l}$$

(3.11)
Where \( a_p \) is the radius of adsorbent particle \( k_f \) is the external mass transfer coefficient, in m/s and \( D_f \) is the diffusivity, in m\(^2\)/s. It was found to be 13, which implied that adsorption occurred in the micropore region.

3.8 References


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4. MODIFICATION AND CHARACTERISATION OF ADSORBENTS

4.1 Introduction

Activated carbons have been proven to be effective adsorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media. Since the limits for pollutants are constantly being revised, the industry is left with the challenge of employing the most effective adsorbents with specific chemical properties. Hence, of late, research on activated carbons has focused on their modification and characterisation in order to meet the growing demand for cleaner air and water (Radovic et al., 1997; Biniak et al., 1999; Saha et al., 2001, 2003; Shim et al., 2001; Jia et al., 2002; Streat et al., 2004).

Since activated carbon consists of functional groups bonded to 'fused' aromatic rings, carbon would be expected to possess chemical properties similar to those in the aromatic hydrocarbons. Therefore, chemical reactions that apply to aromatic hydrocarbons would be expected to be similar with activated carbons. The existence of surface functional groups on the carbon matrix implies that they can be manipulated by thermal or chemical treatments to produce adsorbents that are tailored for particular functions. For example, a number of authors have successfully employed oxidation reactions to produce activated carbons that possess weakly acidic functional groups (Biniak et al., 1999; Shim et al., 2001; Saha et al., 2003). Such carbons are known to have a high affinity for metals when compared to the parent carbon. Introduction of nitrogen containing functional groups has also been performed and such carbons have been reported to increase catalytic activity of carbon in oxidation reactions (Biniak et al., 1997; Abe et al., 2000). Thermal treatments have produced activated carbons with basic character (Radovic et al., 1997).

Even though activated carbon has the largest market as an adsorbent in wastewater control, the specific sorption mechanisms for organic and inorganic solutes are still not clear. It has been postulated that organic compounds adsorb through a \( \pi-\pi \) dispersion interaction mechanism which assumes the interaction of the \( \pi \) electrons of the aromatic species with the \( \pi \) electrons of the basal planes of the carbon (Hayder et al., 2003).
Some experimental data suggest the sorption of organic species may be due to an electron donor-acceptor mechanism (Streat and Horner, 2000). This involves the formation of a complex between the adsorbed molecule and the carbonyl group of the activated carbon. Franz et al. (2000) have proposed a mechanism that involves a combination of hydrogen bonding with carboxylic groups and the π-π dispersion interaction. There is uncertainty surrounding the adsorption mechanism of inorganic species. Some researchers have suggested ion exchange and complex formation as the mechanism of adsorption (Strelko and Malik, 2000; Saha et al., 2001; Streat et al, 2004). However, evidence of the interaction of transition metal ions with the π electrons of the carbons has also been revealed.

In order to understand the adsorption mechanism of the organic/inorganic species with activated carbon, information about the physical properties and the chemical nature of the surface functional groups is required. The chemical nature of the adsorbate must also be known. However, understanding the sorption mechanisms from data derived from literature is difficult because the carbon materials reported are derived from a wide variety of precursors, hence the adsorbents vary considerably in their physical and chemical properties. If the above properties are not harmonised, it becomes difficult to make judgements on the exact nature of the adsorbent-adsorbate interaction. Therefore, the objective of this chapter is to describe the preparation and characterisation of a F400 sample for adsorption of the targeted pollutants. The preparation of the samples involved oxidation, annealing and amination to produce samples of different characteristics. Post-treatment of the oxidised samples was also accounted as a preparatory process for the oxidised samples.

4.2 Experimental

4.2.1. Oxidation of the Activated Carbon

Commercial granulated coal based activated carbon, F400, was used for surface modification with nitric acid. The carbon sample was obtained from Chemviron, USA. Before the oxidation process, the carbon was washed in deionised water and dried at 383 K for 24 hours. The dried sample was then subjected to different modes of
modification using part of a method described by Saha et al. (2001). A sketch of the equipment used for the oxidation process is shown in Figure 4.1.

A known amount of the washed and dried sample was introduced into the reaction vessel that contained 70% nitric acid and deionised water at a ratio of 1:1(v/v). The reaction mixture was heated to 363 K in a water bath and the reaction was allowed to continue for 6 hours with continued stirring from an impeller driven by a stirring motor. The reaction solution was removed and a fresh reaction mixture of nitric acid and water was introduced. The reaction was allowed to continue for a further 3 hours under the same reaction conditions. The oxidised carbon was then washed with deionised water until no further change in pH could be detected.

The resultant water washed sample was divided into 3 portions. The first portion was denoted AC1; this is a sample that was washed with water after the oxidation reaction. AC2 was a sample that was washed with 0.1 M sodium hydroxide to remove humic acids that were formed during the oxidation process. The washing was continued until no further colouration from the humic acids could be observed. Reconditioning of the sample to the hydrogen form was performed using 0.1 M hydrochloric acid and further washing with deionised water was done until the pH of the supernatant solution stabilised to a pH of around 4.0. The conversion was deemed complete when the inlet
and the outlet pH of the liquid flowing in the column were the same. The conditioning and washing apparatus is shown in Figure 4.2. The set-up involved connecting a large reservoir of the conditioning liquid or water to the column in which the adsorbent material was contained. The column was also connected to a flow control valve which was used to regulate the flow of the conditioning liquid or water. The third sample denoted AC3 was prepared by heating the third portion of the oxidised sample at a temperature of 580 K under a vacuum of 2 mm Hg for 12 hours to remove humic acids.

Figure 4.1 Experimental set up for the oxidation of F400.
4.2.2 Modification by Hydrogen Spillover

A second set of modified carbons with basic properties were prepared by annealing F400 sample in the presence of a flow of hydrogen gas. The objective of such a modification is to drive out weakly acidic functional groups bonded to the graphitic plane of the activated carbon. This enhances the \( \pi \) electron cloud of the activated carbon system, which further promotes basic properties.

A known quantity of washed and dried F400 sample was introduced into a quartz reactor and the sample was firmly positioned in the reactor by fitting quartz wool to both ends of the tube as illustrated in Figures 4.3 and 4.4. The reactor was fitted into the furnace and the sample was conditioned in a flow of hydrogen (3.3 x 10^{-6} \text{ m}^3 \text{s}^{-1}) for 45 minutes at ambient temperature. The flow of hydrogen into the reactor was monitored by a rotameter. After the conditioning period, the furnace temperature was raised at a rate of 10°/min until it reached 1173 K where it was maintained for two and half hours. After the annealing cycle, the furnace was allowed to cool down and the flow of hydrogen was maintained even during the cooling process. Hydrogen was allowed to flow out of the reactor through a gas bubbler, for visual inspection of the gas flow. The sample thus obtained was named AC4.
4.2.3 Modification by Amination.

The main objective of such a modification is to attach amino functional groups onto the activated carbon. From classical organic chemistry, it is well known that when an amine group is attached to an aromatic species, it tends to enhance the $\pi$ electron cloud of the aromatic nucleus. This is due to the presence of lone pair of electrons on the nitrogen atom which are believed to contribute to the $\pi$ electron cloud of the aromatic.
The enhanced π electron cloud renders the aromatic molecule more basic, and the basicity properties are of the Lewis type. Amination reactions are usually performed via a two stage process that involves electrophilic substitution of the hydrogen on the aromatic species by a nitro group that is generated in situ by sulphuric acid and nitric acid as shown in scheme (a). In the example of nitration of benzene, nitrobenzene is ultimately formed as illustrated by schemes (b) and (c).

\[
\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O} \quad (a)
\]

![Diagram of reaction](image)

The final step involves the reduction of the nitro compound to amine species. The reaction pathway for the synthesis of amine species is shown in Figure 4.5.

Part of the sample that was produced from the furnace treated (AC4) carbon was used for the amination experiment. A known amount of the carbon was charged together with acetic anhydride into a 1L five-neck flask immersed in an ice cold water bath. Sulphuric acid was slowly fed into the reaction flask, and this was followed by addition of nitric acid. Since the production of the nitronium ions by nitric acid and sulphuric acid is a highly exothermic reaction, nitric acid had to be added slowly into the reactor while keeping the reactor immersed in the cold water bath, and the temperature was monitored so that it would not exceed 283 K. After the addition of nitric acid, the reaction was allowed to continue for 24 hours at a temperature of 293 K with constant stirring. The modified carbon thus obtained was washed thoroughly with deionised water in a column. Washing was performed until the outlet solution reached
a pH of approximately 4. The washed sample was then dried for 24 hours at a temperature of 383 K.

The reduction process of the nitrated sample was performed using sodium dithionite as the reducing agent. The experimental set up of the reduction process is similar to the one for nitration. The reduction of the carbon was performed for 24 hours with continuous stirring in the presence of sodium dithionite, 35% aqueous ammonia and deionised water. The sample was thoroughly washed using deionised water until the pH at the outlet of the column was reduced to approximately 9. The sample was then dried for 24 hours at 383 K in an oven. This sample was designated AC5.

Figure 4.5 Reaction scheme for amination of activated carbon (N.B. The broken aromatic ring represents activated carbon).

The modification processes produced 5 different samples and all the processes are summarised in Table 4.1. The table also shows that post-treatments were performed on oxidised samples.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical treatment</th>
<th>Temperature (K)</th>
<th>Exposure time (h)</th>
<th>Post-treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>AC1</td>
<td>HNO₃</td>
<td>363</td>
<td>9</td>
<td>H₂O wash</td>
</tr>
<tr>
<td>AC2</td>
<td>HNO₃</td>
<td>363</td>
<td>9</td>
<td>NaOH wash</td>
</tr>
<tr>
<td>AC3</td>
<td>HNO₃</td>
<td>363</td>
<td>9</td>
<td>Heat-treat</td>
</tr>
<tr>
<td>AC4</td>
<td>N/A</td>
<td>1173</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>AC5</td>
<td>HNO₃/H₂SO₄/NH₃</td>
<td>298</td>
<td>48</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Na₂S₂O₄/(CH₃CO)₂O

Table 4.1 Summary of treatment of the samples.

4.3 Characterisation of the Carbon Samples

4.3.1 General Introduction and Background

Depending on the pH of the aqueous medium and the nature of the functional groups, the surface of the adsorbent may acquire surface charge. Radovic et al. (2001) has given a simplified diagram (see Figure 4.6) of the behaviour of the carbon adsorbent surface in aqueous solution. The surface of the activated carbon can acquire a negative charge through the dissociation of acidic functional groups. Positive charge can come from pyrones and chromenes, graphene layers that can form electron donor-acceptor complexes with water molecules and in the case where amino groups are present, protonation of the group is possible. Radovic et al. (2001) reported that electrostatic repulsion between the adsorbates and the adsorbent can be detrimental if it takes place between the adsorbate and the graphene layers because most of the surface area is in the graphene layers.
The adsorptive surface charge greatly influences the adsorption capacity for both organic molecules and metal ions. For example, Moreno-Castilla et al. (1995) noted that adsorption of substituted phenols on activated carbons was a function of pH, attributing the observation to the difference between the external and internal surface charge density of the activated carbon.

In an attempt to identify and characterise the functional groups on the surfaces of the carbon, a number of characterisation techniques have been employed. These include, among others, Fourier Transform infra-Red (FT-IR) spectroscopy, Elemental analysis, Nuclear Magnetic Resonance (NMR) spectroscopy, X-ray Photoelectron spectroscopy (XPS), direct titration, and surface charge analysis. The discussion in this chapter will be confined to the techniques that have been applied to this work.

Infrared spectroscopy has been successful in the analysis of a majority of organic compounds. However, earlier applications of the technique to activated carbons...
suffered a major drawback. Historically, analysis of activated carbons has always produced peaks that were poorly resolved due to light scattering and strong absorption, which is typical of carbonaceous materials. The technique, however, has improved and the light scattering phenomenon has been minimised. Mattson and Mark (1969) used internal reflection spectrometry method to improve on the effect of light scattering of the carbon during infrared analysis. The Diffuse Reflectance FT-IR (DRIFT) method has been used with success by a number of authors. Recently, Fourier Transform Spectrophotometers have been used with relative success because of their ability to resolve effectively peaks corresponding to different functional groups. A number of functional groups have been positively identified using FT-IR. Gomez-Serrano et al. (1999), Yang and Lua (2003) positively identified carbon–hydrogen atomic groupings and of oxygen groups and structures i.e. O-H, C=O and C-O-C. Vinke et al. (1994) and Biniak et al. (1997), further identified peaks emanating from C-N, C=N-, and C≡N in activated carbons with nitrogen containing surface groups.

XPS is a classical characterisation technique for carbonaceous materials, due to its simplicity and effectiveness in identifying the chemical composition and nature of chemical bonds. A number of authors have used this technique with success, for example, Gardner et al. (1995) and Pittman et al. (1999) succeeded in using the technique on electrochemically oxidised carbon fibres. Rangel-Mendez and Streat (2002) used the technique on activated carbon cloth. Although XPS has been successful when used with carbonaceous materials like carbon fibres that possess well defined chemical structures with minimal structural defects, the technique suffers drawbacks when applied to activated carbons derived from wood or coal. This is due to the fact that these materials are amorphous and they possess a lot of structural defects. The defects come from carbon atoms that are no longer in the sp² configuration and in activated carbons derived from coal and wood; the materials already exist in the amorphous state, hence upon activation the defects are further enhanced by the introduction of ‘foreign’ atoms. Despite this problem some authors have attempted using the technique to identify surface functional groups on coal or wood derived carbons. Estrade-Szwarckopf (2004) recently criticised the methods used for deconvolution of the peaks (for the identification of functional groups) and the
treatment of the C-C peak. He noted that peaks for C-C bonding are '...either fitted as
broadened or shifted, but it is not really defined and when it appears modified, the
reasons for this modification are not always given.' Estrade-Szwarckopf proposed the
introduction of a peak which is shifted by about +1 eV beside the aromatic graphitic
sp$^2$ peak. He demonstrated the existence of such a peak on anthracene samples of
different degrees of crystalinity and his results were in agreement with the total atomic
ratio after the identification of C-O and C=O bond peaks.

In the present work, use of the XPS technique on F400 and the modified series using
the conventional method met with no success. However, application of the defective
peak as proposed by Estrade-Szwarckopf gave promising data but it was felt more
research into the application of the XPS technique in amorphous carbon materials is
needed since many grey areas still exist. For example, what effect does the individual
type of defect have on the size and shape of the defect peak, since defects are a
contribution from defective crystalline order of the carbon and sp$^3$ state of some
carbon atoms? Also, relating defective peak area to the defect populations is a
challenge that fell out of the scope of this research work. Despite the drawbacks of the
technique on amorphous materials, identification of some elements bonded to carbon
can be achieved from a survey of spectra. The XPS technique was employed in this
study to identify nitrogen atoms bonded to an aromatic ring.

In view of the physical and chemical nature of activated carbon, characterisation of the
carbon samples was performed and the experimental techniques adopted for all the
characterisations are described below.

4.3.2 Scanning Electron Microscopy
The surface morphology of the carbons was analysed using a Cambridge Instrument
360 scanning electron microscope at accelerating voltages of 10-20 kV. The samples
were mounted on an aluminium platform and they were secured to the platform by
PVA glue. Prior to analysis, the samples were dried at 373 K overnight and
subsequently stored in a dessicator containing silica gel.
4.3.3 Surface Area and Pore Size Distribution

Surface area and pore size distributions of all the samples were measured using a Micromeritics (Accelerated Surface Area and Porosimetry) ASAP 2010 surface area analyser that uses a nitrogen adsorption-desorption method. The samples were initially out-gassed at 393 K under a vacuum of < 10 mm Hg for 24 hours on the degas port of the analyser, before adsorption isotherms were generated by dosing 99.99% pure nitrogen (at 77 K) on the carbons. The pore size distributions of the samples were then calculated using the density functional theory (DFT) model.

4.3.4 Elemental Analysis

Elemental analysis of the carbon samples was performed in the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, U.K. The analysis involved weighing the sample accurately on aluminium foil and then inserting into the Perkin-Elmer 2400 Elemental Analyser (Series 2) instrument. Prior to the flash combustion process, the system was purged with helium carrier gas. Flash combustion was then performed at 2073 K, and the gaseous combustion products were quantified using a thermal conductivity detector. Results were obtained as percentages of carbon and nitrogen, and the oxygen content was determined by difference.

4.3.5 FT-IR Measurements

Transmission infrared analysis of the activated carbons was performed on a Nicolet DXC20 FT-IR spectrometer. Samples of particle size < 45 µm were first dried for 24 hours at a temperature of 383 K. The dried samples were mixed with finely divided KBr at a ratio of 1:100 in order to achieve absorbance of less than one. FT-IR spectra were recorded at a resolution of 4 cm⁻¹ and with 200 scans per sample and an aperture setting of 15. Previously recorded background spectra of water vapour was subtracted from the spectrum of each sample.

4.3.6 X-ray Photoelectron Spectroscopy (XPS)

Sample AC5 was analysed by XPS. The analysis was performed on a VG ESCALAB MK I under 10⁻⁷ Torr vacuum. A pass energy of 100 eV was used in recording the scan spectra. The sample was dried at 283 K for 24 hours before the analysis.
4.3.7 Sodium Capacity Determination

Sodium sorption capacity experiments were performed in order to compare the total sorption capacity of the adsorbents for cations. This was achieved by contacting 200 mg of the sorbent with 25 ml of a 0.1M sodium hydroxide in 50 ml Erlenmeyer flasks and the resultant mixture was sealed with parafilm and allowed to equilibrate on an arm shaker for 72 hours. The mixture was filtered to remove the adsorbent and 20 ml of the mixture was pipetted out and back titrated using 0.1 M hydrochloric acid. Phenolphthalein was used as an indicator.

4.3.8 pH Titrations

pH titration curves of the carbons were generated by accurately weighing 75 mg portions of the adsorbents of particle size < 45 µm into 50 ml conical flasks. Standard solutions of a volume of 10 ml of 0.1 M NaCl were added into each flask. Different initial pH was obtained by adding 0.1 M HCl or 0.1 M NaOH and the resultant solution was made up to 25 ml using deionised water. The samples were allowed to equilibrate for 48 hours and the resultant pH was recorded using a Mettler-Toledo 340 pH meter. pH versus the acid or alkali added was plotted to obtain the titration curves. The presence of a salt (NaCl) in the titration procedure produces a titration curve with a gradual rise in the early stages but a steep rise at the point of neutralisation of the adsorbent.

4.3.9 Zeta Potential Measurements

Samples prepared for pH titration were used for the zeta potential measurements. The measurements were performed on a Malvern Zetasizer 3000 HSA. Measurements were performed immediately after the titrated pH measurements. The adsorbent suspension aliquots of 5 mls were injected into the electrophoretic quartz cell using a graduated Luer syringe. In order to provide average readings, three readings of the zeta potential were taken for each sample. The average count rate for the machine was set at 4000 s⁻¹. In between the sample analyses the cell was flushed with 30 ml of deionised water.
4.4 Results and Discussions

The following section gives the physical and chemical characterisation results for all the carbon samples used in this study. The proper interpretation of characterisation data is vital because sorption results are heavily dependent on the nature of the adsorbents.

4.4.1 Scanning electron micrograph (SEM)

The SEM pictures for selected samples are shown in Figure 4.7. Pictures of low and high magnification were taken, but not all the magnifications are presented for all the samples since there are similarities between a number of samples. Figure 4.7 (a) shows the typical low magnification picture of a coal based activated carbon which is typified by irregular particle shape. Figure 4.7 (a) and (b) shows the SEM of as-received and AC1 samples respectively. There is little difference in the surface morphology of the samples except for some apparent pore widening on AC1 that could have occurred from the oxidation process. It was noticed that the oxidised samples disintegrated to small particles when compared to F400 sample particles. Strelko (1999) reported that prolonged exposure of carbons to oxidising agents usually results in loss of particle strength. This observation could also be linked to the cleavage of C-O bridging bonds on the carbon surface during the oxidation process. The SEM images of AC2 and AC3 were similar in appearance to AC1 image. This implies that post oxidation treatments of the carbon samples did not make any apparent change in the surface morphology of the adsorbents. The surface morphology for AC4 was compared to that of AC5. Modification of AC4 to produce AC5 had a visual impact on surface morphology. The surface appearance is “spongy” and to some extent eroded.
(a) F400

(b) AC1
Figure 4.7 SEM images of as-received and selected modified carbon samples.

4.4.2 Surface Area Results

Brunauer-Emmett-Teller (BET) is the most widely used method for the determination of the surface area of porous materials. The method employs the equation:

$$\frac{p}{n(p^o - p)} = \frac{1}{n_m c} + \frac{(e - 1)}{n_m c} \frac{p}{p^o}$$  \hspace{1cm} (5.1)
where $n$ is the adsorption capacity, $n_m$ is the monolayer adsorption capacity, $c$ is a dimensionless constant related to the enthalpy of adsorption in the first adsorbed layer, $p$ is the pressure and $p^o$ is the saturation pressure of the system. When 
\[
\frac{P}{n(p^o - p)}
\]
is plotted against the relative pressure, $\frac{P}{p^o}$, a straight line would enable the evaluation of $c$ and $n_m$. The function $n_m$ is very useful in the evaluation of the specific surface area of the adsorbate. If the Avogadro Number is multiplied by $n_m$, then the number of molecules involved in the monolayer surface coverage can be evaluated. Evaluation of the specific surface area requires knowledge of the average molecular cross-sectional area occupied by the adsorbate molecule in the monolayer. The most common adsorbate for this purpose is nitrogen which has a cross-sectional area 162 nm$^2$. Even though the BET method is popular in the evaluation of surface areas of porous materials, Sing et al. (1985) reported that the range of linearity is restricted to a limited part of the isotherm and for most materials the range lies within relative pressures of 0.05-0.30. The BET surface area values for all the adsorbents used in this study are shown in Figures 4.8 and 4.9.

Figures 4.8 and 4.9 are results from the pore size distribution measurements for the stated carbons. The results show that oxidation of the carbon resulted in the decrease in the BET surface areas for AC1 sample compared to F400. This is a result of pore blockage in the micropores caused by the formation of humic substances during the oxidation process. Some researchers have attributed this observation to pore entrance blockage by the formation of oxygen containing functional groups that are direct products of oxidation. However, AC3 recorded higher values of surface area than AC1, implying that heat treatment partly removed some of the humic acids lodged in the micropores. Washing the oxidised carbons with sodium hydroxide seems to be a more effective way of removing the humic acids. AC2, which was a sample washed with sodium hydroxide, showed the highest surface area values amongst the oxidised samples. Similar results have been reported by Saha et al. (2001), who attributed such increases in surface area to the enhancement of the mesopore region. AC4 shows a higher value of the BET
than F400 and the oxidised carbons. The increase in the surface area seems to follow the sequence AC1 < AC3 < F400 < AC2 < AC5 < AC4.

Figure 4.8 BET surface area of F400 and its oxidised series.
4.4.3 Nitrogen Adsorption-Desorption Results

Nitrogen adsorption-desorption isotherms for the F400 and its modified series are shown in Figures (4.10-4.15). According to the IUPAC classification, the isotherms are Type 1. Type 1 isotherms are produced by microporous solids having relatively small external surfaces and the limited uptake of gas is governed by accessible micropore volume rather than by the internal surface area. Hence the sharp rise of the isotherms at low relative pressure represents the filling of the micropores and the adsorption process is completed at a relative pressure of 0.5. Strelko (1999) and Karounou (2004) made similar observations when they were characterising wood based activated carbons. Hysteresis in the isotherms is associated with capillary condensation; the hysteresis shape can be classified as H4 which is associated with materials possessing narrow slit shaped pores.

Figure (4.16) shows the comparison of the adsorption isotherms of all the adsorbents. AC4 has the highest nitrogen adsorption capacity, while AC1 has the lowest uptake capacity. This is expected since the annealing process is expected to remove some oxygen functional groups lodged within the porous adsorbent while
Nitric acid oxidation produces humic substances that blocks the micropores of the adsorbents. The reduction in the nitrogen uptake by the adsorbents follows the sequence AC4 > AC5 > AC2 > F400 > AC3 > AC1. It is interesting to note that the sequence is exactly the same as that of the BET surface areas of the adsorbents. This is evidence that nitrogen adsorption is a function of the available surface area.

Figure 4.10 Nitrogen adsorption-desorption isotherm for F400.
Figure 4.11 Nitrogen adsorption-desorption isotherm for AC1.

Figure 4.12 Nitrogen adsorption-desorption isotherm for AC2.
Figure 4.13 Nitrogen adsorption-desorption isotherm for AC3.

Figure 4.14 Nitrogen adsorption-desorption isotherm for AC4.
Figure 4.15 Nitrogen adsorption-desorption isotherm for AC5.

Figure 4.16 Comparison of the adsorption of nitrogen on all the samples.
4.4.4 Pore Size Distribution results

The increasing use of activated carbon materials in liquid and gas purification, catalysis and adsorption separation processes has spurned interest in the study of the measurement of pore size distribution to as small as a few molecular diameters. Methods based on Dubinin (Dubinin, 1967), t-plots and Horvath and Kawazoe (Horvath and Kawazoe, 1983) have been widely used, but in reality adsorption in micropores is very complex and hence a pore size distribution in the micropore region is less certain. This has led to the emergence of a method termed Density Functional Theory (DFT). This method takes into account the interactions of the adsorbate with the adsorbent and also adsorbate-adsorbate associations are factored into the method.

Basically, the DFT method is derived upon the assumption of a slit pore geometry and it has been found to be applicable to a broad spectrum of pore sizes up to 4000 Å which has made the method very attractive (Olivier and Conkin, 1991; Olivier, 1995).

The DFT pore size distributions are shown in Figures 4.17 and 4.18. Figure 4.17 shows the results of F400 and its oxidised series while Figure 4.18 gives F400, AC4 and AC5. Results for sample F400 have been included in both Figures to serve as comparison. The microporous nature of the samples is clearly demonstrated for all the samples. It is clear that the pore size distribution was not affected by the different modes of modification of the samples but for oxidised carbons a reduction in the surface area and the pore volume was observed. This phenomenon has been reported by other authors (Strelko and Malik, 2000; Saha et al., 2001) and it has been attributed to the formation of humic acids, which is a byproduct of nitric acid oxidation in the case of oxidised samples. Also it has been thought that pore entrance blockage by oxygen containing functional groups can be a factor. On the other hand, the pore volumes of samples AC4 and AC5 were significantly enhanced as illustrated in Figure 4.18. The enhanced micropores in the AC4 sample could be due to the removal of oxygen containing functional groups that are not stable at high temperatures. The aminated sample AC5 has the
largest proportion of micropores among all the samples. The reason for the enhanced pore volume and area is not clear, considering that the sample is derived from the annealed sample AC4. It is likely the enhancement of the pores could have occurred during the reduction of the nitrated product sample. A highly magnified SEM picture of the AC5 sample revealed a material that is highly porous as shown in Figure 4.19.

Figure 4.17 Pore size distribution for F400 and the oxidised series.
4.4.5 Elemental Analysis

Table 4.2 gives the results of the elemental analysis of all the samples under investigation. It is apparent that on oxidation of the conventional sample the oxygen content increased considerably. The descending order of the oxygen content is as follows: AC1 > AC2 > AC3 > F400 = AC5 > AC4. Generally, oxidation of activated carbon results in an increase of the oxygen content of the carbon; however the amount gained depends on the method and precursor used. In
contrast, the annealed sample possesses the lowest oxygen content. This is expected, since at elevated temperature most of the acidic oxygen-containing functional groups are unstable and are subsequently removed. For example, Swiatkowski et al. (2002) used voltammetric studies to monitor the gradual thermal decomposition of activated carbon surface oxygen complexes. They reported that at 1173 K the functional groups -COOH and >COO will have diminished to zero while >C=O and -C-OH is reduced to about 50 and 14%, respectively. Menéndez and Radovic (1996) annealed a wood based carbon at 1223 K for 3 hours in the presence of hydrogen, which reduced the oxygen content from 15.1% for the conventional carbon to 0.3% for the annealed sample. In this work, annealing the conventional carbon achieved a 27% reduction to 7.27%. The difference in results could be due to the difference in the precursor of the conventional carbons used, and Menéndez and Radovic (1996) subjected their sample to more severe conditions. Also, exposure of the annealed sample to the atmosphere would have resulted in a significant uptake of oxygen from the atmosphere. The oxygen content of the intermediate nitration product *C-NO₂ is higher than the parent sample (AC4), implying that the nitration process fixed some oxygen containing functional groups on the intermediate sample. A closer look at the elemental values for the intermediate product shows that the amount of oxygen added during the nitration process is not in direct stoichiometric relationship to the nitrogen added in the expected *C-NO₂ product. Hence this implies that some of the oxygen is involved in the formation of carbon-oxygen functional groups. It is interesting to note that the percentage nitrogen in the intermediate product is the same as in the AC5 sample. Also, it is apparent that the reduction process was effective since the oxygen content of the intermediate product is higher than the supposedly reduced product, AC5.

Nitric acid oxidation introduced small amounts of nitrogen as shown in Table 4.2. Also it can be observed that annealing totally removes the nitrogen but the amination process fixes a marginally higher content of nitrogen than in the oxidised samples. Bautista-Toledo et al. (1994) attributed this observation to the formation of nitro and nitrate aromatic compounds.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Elements (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
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<td>89.48</td>
</tr>
<tr>
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<td>82.70</td>
</tr>
<tr>
<td>AC2</td>
<td>83.80</td>
</tr>
<tr>
<td>AC3</td>
<td>84.30</td>
</tr>
<tr>
<td>AC4</td>
<td>92.73</td>
</tr>
<tr>
<td>*C-NO₂</td>
<td>84.91</td>
</tr>
<tr>
<td>AC5</td>
<td>88.12</td>
</tr>
</tbody>
</table>

*Supposed intermediate nitration product in the nitration process

Table 4.2 Elemental analysis of the adsorbents.

4.4.6 Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

FT-IR spectra for the F400 oxidised carbon range are depicted in Figure 4.20. The results show some pronounced peaks at wave numbers 1240, 1610 and 1750 cm⁻¹. The spectra for AC1, AC2 and AC3 show some marked similarities, suggesting that they could possess similar groups on their surfaces. The received sample (F400) does not show a peak at 1750 cm⁻¹, and also its peak at 1240 cm⁻¹ is less pronounced than that for the other oxidised carbon species.

The peak at 1240 cm⁻¹ is usually difficult to assign because of a number of overlapping bonds that are superimposed. The superimposed peaks can be as a result of ether, epi-oxide and phenolic structures in various chemical environments. Biniak et al. (1997) reported that tertiary C-N stretching vibration may also result in the contribution of the peak in the region of 1240 cm⁻¹. The C-N contribution can probably explain the lack of a pronounced peak on as-received F400 sample.
which did not undergo nitric acid oxidation. The peak at 1610 cm⁻¹ can be attributed to quinone like structures, and this peak appears in all the samples. Sutherland *et al.* (1996) and Shim *et al.* (2001) have also observed such a peak. As mentioned earlier, the peak at 1750 cm⁻¹ appears on the oxidised samples only, but its position on the spectra of the other samples makes it difficult for positive identification. However, Lopez *et al.* (2003) obtained peaks in this region when they modified carbon samples by air oxidation and they assigned it to free carboxyl groups, lactone groups, esters and carbonyl groups near the hydroxyl groups. The most logical explanation for the peak at 1750 cm⁻¹ would be the existence of carboxyl groups that are formed as a result of nitric acid oxidation. This is also supported by the high sodium capacity results on the oxidised samples as opposed to the F400 sample.

**Figure 4.20** FT-IR spectra for F400 and some selected samples.

Figure 4.21 shows the FT-IR spectra for the humic substances obtained from samples F400, AC1 and AC5. The humic material from samples F400 and AC5 exhibit similar FT-IR spectra and this suggests they have similar structures and functional groups. However, the spectra for AC1 differ markedly from F400 and
AC5 samples, thus confirming that significant chemical structural changes occurred during nitric acid oxidation. A strong absorption band was observed at around 3400 cm\(^{-1}\) wave number and this is assigned to carboxylic group O-H stretching (Pradhan and Sandle, 1999; Chen et al., 2004). The peak is more pronounced in the AC1 humic sample and this would imply the presence of more O-H groups from increased carboxylic groups than in AC5 and F400 humic samples. An absorption peak was observed on 1660 cm\(^{-1}\) wave number and this peak is distinct in the AC1 humic sample, while in F400 and AC5 it appears as a shoulder along the 1450 cm\(^{-1}\) peak. Pradhan and Sandle (1999), when studying oxidised carbons, assigned the peaks to carboxyl-carbonate structures in cases of HNO\(_3\) oxidised carbons. Schepetkin et al. (2003) characterised humic substances from mumie and they observed strong absorbance at 1650-1720 cm\(^{-1}\) which they attributed to -COOH group vibrations. The fact that the peak appears as a distinct peak in sample AC1 would suggest a higher amount of -COOH groups than in the AC5 sample where the peak appears as a shoulder peak. The shoulder peak at 1660 cm\(^{-1}\) wave number is more pronounced on the AC5 humic sample than in F400. The relative intensity of the peak follows the trend, AC1 humic > AC5 humic > F400 humic. As shown in Figure 4.21, the change in the relative intensity of this band parallels the oxygen content of the samples. Hence, it would be reasonable to suggest that there is more -COOH group in the AC5 sample than in the F400 sample. The peak at 1440 cm\(^{-1}\) can be attributed to CH bending of -CH\(_2\)- or -CH\(_3\)- groups while the peaks at 1160 cm\(^{-1}\) have been assigned to alcohols or ethers.
Figure 4.21 FTIR spectra for the humic substances from F400, AC1 and AC5.

Figure 4.22 shows the XPS N(1s) measurements for the AC5 sample. A peak assigned to nitrogen bonded to an aromatic group was detected at 399 eV. The peak at 399 eV is usually associated with amino (-NH₂) groups attached to aromatic groups. The elemental results for the nitrated product *C-NO₂ and the final aminated product AC5 showed the presence of nitrogen introduced by the nitration process. As mentioned previously, the oxygen content of AC5 sample was lower than the intermediate *C-NO₂ thus giving evidence of the effectiveness of the reduction process. The reduction process involves the conversion of -NO₂ species in the intermediate product to -NH₂ of the final product, AC5. It is to be noted that the nitrogen content of the two samples (intermediate and AC5) was the same. It is appropriate to mention also that there was no N(1s) peak that could be detected on the other samples. It implies that the nitrogen observed in the oxidized samples through the elemental analysis could be a result of nitrate ions (-NO₃) trapped in the pores of the oxidized carbons (AC1, AC2 and AC3), in a form difficult to remove even by extensive washing.
Sodium uptake capacity results (see Figure 4.23) show the high affinity of oxidised carbons for sodium compared to as-received F400. This is due to the existence of carboxylic acid functionality in oxidised carbons. FT-IR results seem to confirm the existence of such a group. Various treatments on AC2 and AC3 seem to reduce their sodium capacity when compared with the AC1 sample that did not undergo oxidation post treatment. A possible explanation for the observation could be that oxidation post treatment removed some humic acids. Humic acids have also been shown to participate in metal sorption (Saha et al., 2001). The annealed sample AC4 showed no noticeable sodium capacity. This is expected since at high temperatures the acidic functional groups responsible for the sodium uptake are destroyed. However, in sample AC5 there is a significant sodium uptake and this implies that the amination process resulted in simultaneous fixation of some acidic functional groups.

Figure 4.22 XPS spectra for AC5 sample.
Figure 4.23 Sodium capacity values for as-received and modified sample.

4.4.7 pH Titrations
The results for the pH titrations for as-received F400 and its modified series can be seen in Figures 4.24 and 4.25. The most important aspect of the pH titration curves is the crossover point or point of zero charge (PZC). By definition, PZC is the pH at which the net surface charge of an adsorbent is zero. Depending on the modification process, it can be noted that oxidised carbons (AC1, AC2, AC3) possess lower PZC values than the rest of the carbon samples. This implies that acidic properties are more dominant in these carbons and are as a result of a higher number of weakly acidic functional groups than in other carbon samples. Also, Figure 4.24 shows a more retarded decrease in pH for the oxidised samples, and this is further evidence of the presence of weakly acidic functional groups. These weakly acidic functional groups are known to dissociate over a wide range of pH. The PZC for AC5 is relatively low compared to F400 and AC4 as illustrated in Figure 4.25. This can be due to the presence of similar functional groups as in oxidised samples since modification of this sample involved the use of concentrated nitric acid.
**Figure 4.24** pH titrations for F400 and its oxidised series.

**Figure 4.25** pH titrations for F400, AC4 and AC5.
4.4.8 Zeta Potential Results

The results for zeta potential measurements are shown in Figures 4.26 and 4.27. The electrokinetic behaviour of activated carbon in solution is one of the most important properties in characterisation. Since activated carbons are amphoteric due to the various functional groups on their surfaces and the presence of a π electron system that confers them with Lewis basic properties, it is always important to evaluate their isoelectric point (IEP). IEP is the pH at which the zeta potential is zero. The results show that there is a marked difference in the IEP between the oxidised samples (~1.5) and as-received material (6.0). The low IEP values for oxidised samples are due to the presence of weakly acidic carboxylic functional groups. It is known that dissociation of the carboxylic groups in activated carbon lies between pH 2 and 6. Thus, the dissociation of the groups renders the carbon surface negative. The dissociation of the carboxylic groups could be the reason for the steepness of the zeta potential curves of the oxidised carbons between pH ranges 1.5 and 5. Similar observations on zeta potential curves for oxidised carbons have been reported in literature (Menéndez and Radovic, 1996; Strelko and Malik, 2000). It is also interesting to note that the zeta potential remains negative for the range of conditions studied. The as-received F400 sample may consist of weakly acidic functionality with a higher dissociation pH and that might have caused higher isoelectric point when compared to oxidised carbons. AC5 sample also shows higher zeta potential than the oxidised carbons but its value is lower than in the conventional carbon. It can be seen that the zeta potential for this sample crosses the zero potential line which would imply the amphoteric nature of the sample. This is due to the presence of some amino groups as evidenced by the XPS spectra on AC5 sample. These groups impart basic properties to the sample. However, the IEP of AC5 remains low probably due to the high ratio of the acidic functional groups. Sample AC4 showed the highest IEP value (7.8) among all the samples. Heat-treatment seems to have removed some oxygen containing surface groups as evidenced by the low oxygen ratio in the elemental analysis results. Reduction of oxygen groups after heat treatment has also been reported (Menendez et al., 1996; Pradhan and Sandle, 1999).
Figure 4.26 Zeta potential values for F400 and the oxidised series.

Figure 4.27 Zeta potential values for F400, AC4 and AC5.
4.5 General Discussions

Since activated carbon consists of condensed aromatic structures, organic chemical reactions can be used to modify their surfaces. In the case of modification by oxidation, the reaction site is most likely to occur on the aliphatic side chains of the carbon because such sites are highly susceptible to oxidation (Vinke et al. 1994). Modification of the conventional carbon, F400, produced by various techniques described in Section 4.2 produced carbons with a variety of properties as shown by the different characterisation techniques. Generally, the oxidised carbons showed that there was fixation of weakly acidic functional groups on their surfaces, as shown by the FTIR peak at 1750 cm\(^{-1}\) and the low values of the PZC and IEP. The fixation of the weakly acidic functional groups is thought to be similar to the reaction involving the oxidation of 9,10-dihydrophenanthrene and diphenylmethane with nitric acid (Vinke et al., 1994). The formation of the dicarboxylic group is thought to occur on the aliphatic side of the molecule especially if the side chains consist of more than one carbon atom (reaction scheme (d)). The reaction is initiated by the splitting of the C-C at the \(\alpha\)-position of the benzylic carbon atom (Vinke et al., 1994). Oxidation involving a methylene (-CH\(_2\)) group would result in the formation of a ketone as shown in scheme (e).

Nitrogen can be added to the carbon by a similar reaction as in the nitration of benzene. The mechanism would involve the formation of the highly reactive nitronium ion (NO\(_2^+\)), which will ultimately form the nitrated product as shown in scheme (f). In the case of oxidised carbons, however, the nitrated ‘product’ would appear in small quantities due to the limited amount of the nitronium ion since its formation is favoured in the presence of concentrated sulphuric acid. In the case of sample AC5, the amination reaction was achieved via a two stage process. The first stage was the nitration stage where the nitric acid was mixed with concentrated sulphuric acid to form the nitronium ions which then reacts via electrophilic
substitution of the hydrogen ion of the carbon matrix as shown in scheme (g). The nitro-species formed is reduced using a suitable reducing agent and in this case sodium dithionite was employed. If the elemental analysis results are considered, the intermediate species of the amination process, \( \text{C}-\text{NO}_2 \) has higher oxygen content than the final product ACS. This result then shows the effectiveness of the reduction reaction shown in scheme (h). This modification process is another example of the application of a classic organic reaction on activated carbon modification. The reaction scheme is shown in the illustration of the amination of phenanthrene.
The presence of humic substances in samples F400, AC1 and AC5 is clearly shown in Figure 4.21. The mechanism for the formation of humic substances is not clearly understood. Vinke et al. (1994) attributed it to the presence of aliphatic carbon that is contained between aromatic structures of the parent carbon. They postulated that the oxidation process results in the splitting of the aliphatic segments into smaller molecules that are readily soluble and can subsequently be washed. Verheyen et al. (1995) also reported the formation of humic substances during nitric acid oxidation of coal. They used different concentrations of nitric acid and investigated the effect of the acid strength on the chemical structural changes of the coal. It was realised that some humic acids could be extracted from the oxidised coal using 0.5 M sodium hydroxide. In this study, samples AC1 and AC5 showed that they contained humic substances, while AC3 and AC4 did not show signs of humic substances when washed with 0.1 M sodium hydroxide solution. It is interesting to note, however, that for samples AC1 and AC5, nitric acid was involved during their modification while in AC3 and AC4 heat-treatment was employed. This implies that humic substances are a by-product of the oxidation process. The reason for failure to extract humic substances in sample AC3 even though it had been oxidised would be due to heat treatment of the sample. However, heat treatment of the sample did not remove the humic substances as shown in the pore size distribution results. From this observation it is likely that heat treatment causes some structural changes to the humic substances, but the nature of the changes are not clear and the resultant material is not soluble in 0.1 M sodium hydroxide. Humic substances were also extracted from the F400 sample even though it did not undergo oxidation. Possibly the humic material in this sample was developed during its activation process.
It is now widely accepted that the IEP represents the net external charge on the surface of the activated carbon in solution, while the PZC is a representation of the change 'in response to the net total surface charge of the particles' (Menéndez et al., 1995). Effectively, the difference between PZC and IEP would give an indication of the surface charge distribution of the porous adsorbent. The electrochemical properties of the various samples are summarised in Table 4.3.

Positive values would indicate more negatively charged external surface than the interior and vice-versa for negative values (Menéndez et al., 1995; Świątkowski et al., 2002). The F400 sample shows a positive value indicating more acidic functional groups on its external surface than its interior surface. However, in spite of their low PZC and IEP, oxidised carbons possess higher difference of PZC and IEP (PZC-IEP) values than F400, implying preferential external oxidation of the samples. Since activated carbon is a highly porous material it is inevitable that the oxidation process will be a diffusion controlled process with oxidation occurring faster on the external surface than the interior surface. Also, among the oxidised carbons it is noticeable that the value of PZC-IEP for sample AC2 is higher than for AC1 and AC3. Since AC2 was a sample washed with sodium hydroxide after oxidation, it is apparent that the removal of the humic substances had a bearing on the observed result. It is well known that humic substances contain functional groups (carboxylic, phenolic, carbonyl, hydroxyl and others) in varying amounts. The removal of such groups implies that a significant amount of the negative charge in the interior of the microporous carbon is removed since the humic substances are contained in this region as shown by the pore size distribution diagram (see Figure 4.17). The high values of the IEP and PZC on AC4 indicate its basic properties and these are expected to come as a result of (i) the elimination of weakly acidic functional groups through heat treatment since such groups are unstable at 1173 K, and (ii) from the oxygen free Lewis base sites within the activated carbon graphene layers. The low value of their difference, (PZC-IEP ≈ 0.2) therefore indicates that heat-treatment was effective in removing the acidic groups from both the external and the interior surface of the carbon matrix. AC5 on the other hand possesses relatively low PZC and IEP compared to AC4. Figure
4.27 shows that the sample possesses some acidic character. The use of nitric acid in the nitration process would have resulted in the formation of such groups and its PZC-IEP value lies in the same region as that for the oxidised carbons implying the diffusion dependent nature of the process.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$pH_{PZC}$</th>
<th>$pH_{IEP}$</th>
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<td>4.0</td>
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</tr>
<tr>
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<td>4.7</td>
<td>1.3</td>
<td>3.4</td>
</tr>
<tr>
<td>AC3</td>
<td>3.9</td>
<td>1.3</td>
<td>2.6</td>
</tr>
<tr>
<td>AC4</td>
<td>8.0</td>
<td>7.8</td>
<td>0.2</td>
</tr>
<tr>
<td>AC5</td>
<td>6.5</td>
<td>3.7</td>
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</tr>
</tbody>
</table>

Table 4.3 Electrochemical properties of the F400 series.

4.6 Conclusions

It has been shown that applying different modes of modification of the carbon leads to samples with different chemical characteristics. Modification by oxidation led to the fixation of weakly acidic functional groups as indicated by FTIR, pH titration results, sodium capacity and zeta potential results. The oxidation process, however, produced by-products in the form of humic substances which could be extracted by sodium hydroxide solution. The humic substances tend to get lodged in the micropores resulting in loss of microporosity as evidenced by the pore size distribution results. Besides the weakly acidic surface oxygen complexes, nitrogen was also detected by elemental analysis in the oxidised samples but it was attributed to nitrate ions lodged in the pores of the oxidised carbons. Hydrogen treatment at elevated temperature produced a sample with some basic characteristics. The basic nature of the sample is due to the removal of acidic functional groups that are not stable at high temperatures. A sample with some amino groups was also successfully prepared by a two stage process that involved nitration followed by reduction. The XPS results clearly showed the presence of such groups. However, the process also produced some weakly acidic functionality.
because nitric acid (known for its high oxidising power) was used as one of the reagents. The results of the investigation demonstrate that it is possible to apply classic organic chemical reactions to achieve desired modified carbon samples. Therefore, from a practical point of view, by carefully applying relevant modification techniques, it is possible to prepare carbons targeted for specific environmental applications.

4.7 References


special reference to the determination of surface area and porosity, Pure and Applied Chemistry, 57 (4), 603-619.


5. ANALYTICAL METHOD DEVELOPMENT AND ADSORPTION STUDIES

5.1 Introduction
This chapter describes the quantification methods adopted in the study of the adsorption of atrazine, benazolin and 2,4-dichlorophenoxyacetic acid (2,4-D) using an HPLC. A concentration procedure in the form of a solid phase extraction (SPE) method is described. Experiments on the adsorption of the herbicides on F400 and its modified series were undertaken and the adsorption mechanisms of the herbicides were elucidated. Adsorption of copper on all the adsorbents is described in this chapter as well as the effect of the copper on the adsorption of the target herbicides.

5.2 HPLC Method Development
The objective of the analysis is to quantify the herbicides atrazine, 2,4-D and benazolin in ultrapure water at low levels (0.1 ppb or below). The quantification method makes use of an HPLC system (Hewlett Packard 1100 series) fitted with a diode array detector, column thermostat, auto-sampler and a binary pump.

There is a large amount of literature pertaining to the quantification of atrazine, benazolin and 2,4-D using different types of equipments. However, the discussion on the method employed for this work focused on the work done by Sweetland (1997) and Horner (1999) because they used the same equipment as described above, and also they worked on two of the 3 herbicides of interest to this work (atrazine and benazolin). Streat and Sweetland (1998) successfully analysed atrazine in our laboratory in conjunction with simazine, isoproturon, chlorotoluron and diuron. They made use of the above mentioned HPLC fitted with a genesis C18 column (4 µm, 150 x 3 mm) with a 1 cm guard column attached. After a series of experimental trials, they established that quantitative analysis of the compounds could be achieved using an isocratic elution method at a flow rate of 0.8 ml/min at a temperature of 313 K. They used 29% acetonitrile/THF (60:40 v/v) and 71% buffer that consisted of 10 mM KH₂PO₄ at pH 4.5 as the eluent.

Streat and Horner (1999) attempted to employ the method that had been used by Streat and Sweetland (1998a), for the quantification of atrazine, benazolin...
bentazone, imazapyr and trichlopyr. This method did not give good results for the compounds of interest because of co-elution of herbicides and short retention times. This necessitated the development of a new HPLC method for the determination of their pesticides.

During the development process they attempted using a gradient elution method employing methanol-buffer starting at 5% methanol to 100% methanol. The results showed an unstable base-line which reduced the limit of detection of the compounds. After isocratic elution trials with tetrahydrofuran/water and acetonitrile/water mobile phase compositions, Streat and Homer (1999) realised that the acetonitrile/water mobile phase was ideal for the separation of their compounds. The method for separating their compounds used an isocratic elution at a flowrate of 0.88 ml/min at a temperature of 311 K. An eluent of 30:70 acetonitrile-buffer solution was found to be appropriate. The authors, however, were faced with a major difficulty in the extraction and recovery of the five herbicides using a single solid phase extraction (SPE) method. This was caused by the more hydrophobic nature of atrazine compared to other pesticides. This then implied that atrazine could not be included in multi-component work since the volume of samples and analysis time required would have been too high.

Based on the background information extracted from Sweetland (1997) and Homer (1999), an attempt to quantify atrazine, benazolin and 2,4-D using HPLC was undertaken using a genesis C18 (4 μm, 150 x 3 mm) column. Prior to the method development for the three herbicides, a survey scan on each herbicide was performed on a UV-Vis spectrophotometer in order to establish the maximum wavelength at which they absorb. The survey spectra are shown in Figures 5.1-5.3. Since a single SPE method is not able to extract and recover atrazine, benazolin and 2,4-D the HPLC methods for the two compounds had to be developed separately. Initially, the method used by Streat and Homer (1999) was used for the quantification of benazolin. The method gave a retention time of five minutes which was appropriate, however the method produced a broad benazolin peak. The eluent composition was then altered from 30% to 50% acetonitrile. The change in eluent composition resulted in a sharp peak but of short retention time which was affected by the background noise (<1 min). Further adjustment of the eluent
composition to 40% acetonitrile gave a good chromatogram with a retention time of 2 minutes. The final method for the quantification of benazolin is shown in Table 5.1. The same eluent composition was applied for 2,4-D. Good chromatograms were obtained with benazolin eluting after 2.01 minutes while 2,4-D eluted after 3.8 minutes. Adopting the method employed by Sweetland (1998) for the quantification of atrazine gave a chromatogram with atrazine eluting after 11 minutes. It was felt that 11 minutes was a long elution time since simultaneous analysis of atrazine with the other herbicides was not possible. Trial runs were performed with acetonitrile buffer as the mobile phase. The first trial runs were performed with 50% acetonitrile and the elution time was considered very short (≈ 1 minute). Reducing the eluent composition to 40% eventually gave an elution time of 4.2 minutes. The results of the chromatograms are shown in Figures 5.4 and 5.5.

![Figure 5.1 UV absorption spectra for Atrazine.](image-url)

Figure 5.1 UV absorption spectra for Atrazine.
Figure 5.2 UV absorption spectra for benazolin.

Figure 5.3 UV absorption spectra for 2,4-D.
Figure 5.4 HPLC chromatograms for benazolin and 2,4-D.

Figure 5.5 HPLC chromatogram for atrazine at 225 nm.
Table 5.1 HPLC analysis method for the herbicides.

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>Benazolin</th>
<th>2,4-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluent composition</td>
<td>40:60</td>
<td>40:60</td>
<td>40:60</td>
</tr>
<tr>
<td>(Acetonitrile:Buffer)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate (ml/min)</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>Injection volume (µL)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Detection wavelength (nm)</td>
<td>225</td>
<td>222</td>
<td>205</td>
</tr>
</tbody>
</table>

The limit of detection of the targeted herbicides was obtained by performing solid phase extraction for each herbicide using subsequent low concentrations. The limit of detection is the minimum concentration of solute that can reliably be determined. The limit of detection obtained for atrazine, benazolin and 2,4-D were 0.006 µg/L for atrazine and 0.01 µg/L for benazolin and 2,4-D.

![Figure 5.6 HPLC calibration curve for the targeted herbicides.](image)

The maximum detection wavelengths of the herbicides were taken from their UV absorption spectra (Figures 5.1-5.3). Calibration results of the herbicides are shown in Figure 5.6. The results showed that benazolin and atrazine were linear in the
concentration range 0-8 ng/μL while for 2,4-D, the linear range was in the range 0-10 ng/μL.

5.3 SPE Background Information

The tolerated concentrations of herbicides in drinking water are very low (< 0.1 ppb for a single herbicide) such that quantification of the target herbicides would require a pre-concentration process. The pre-concentration methods for herbicides are well documented in the field of analytical chemistry. Most of the work involves complex multi-residual analysis of the herbicides contained in water, soil and some biological materials. The selection of the pre-concentration method is governed by the nature of the sample and the analyte concentration. Liquid-liquid extraction (LLE), and solid phase extraction (SPE), are the most common techniques applied in the pre-concentration and separation procedures.

LLE has been applied as a pre-concentration and separation procedure for a long time and it has the advantages that it is a well documented procedure that offers a wide variety of experimental routes that can give improved extraction efficiencies and selectivities, and also it is a simple method (it does not require instrumentation). However, because LLE suffers from a number of disadvantages it is gradually being replaced with SPE. The disadvantages include:

(i) low extraction yields, hence a pre-concentration procedure is often required before analysis;
(ii) formation of emulsions that often interfere with phase separation;
(iii) large amount of solvents that are known to be toxic and hazardous;
(iv) the procedure is slow and also difficult to automate.

Because of these drawbacks, SPE has emerged as a viable alternative to LLE for the separation, purification and concentration of solutes from water. Wells and Yu (2000) claimed that SPE began to appear when disposable cartridges and columns containing bonded silica sorbents were introduced by Waters associates in 1977. Even though SPE techniques have existed for over 3 decades, there is still on-going research focusing on improved recovery efficiency of a variety of solutes. The technique however suffers from the fact that it is a high cost procedure since the adsorbent cartridges/columns are disposed of after each analysis. However, SPE is very attractive in that it:
(i) can pre-concentrate traces of herbicides from low concentrations in solution;
(ii) has high selectivity;
(iii) is rapid and can easily be automated;
(iv) offers great reduction in the use of toxic and hazardous solvents

The SPE method generally follows the procedure shown in Figure 5.7. Matrix
modification is a process where the sample is conditioned to effect a good
separation. This is usually performed by altering the pH of the sample. For
example, when applying SPE to acidic herbicides, their pKa values have to be taken
into consideration as they are ionisable compounds. Hence if the separation process
is to be performed when the herbicide is in the unionised state, the pH would need
to be below its pKa value. The clean-up process involves masking and suppressing
those compounds that can interfere with the analysis of the target solutes. The
choice of instrumentation and method of chromatographic separation is a vital
component of the SPE method and usually the choice of chromatographic method
is made before SPE procedure is tested.

![Diagram](image-url)

**Figure 5.7 General procedures for solid phase extraction (SPE).**

The use of the SPE technique is based on the solute adsorbing onto active carbon,
grahitised carbon black, an organic polymer, and analyte partitioning between
sample solution and chemically modified HPLC phases such as C₈ and C₁₈. These
phases are usually packed in tubes or immobilised in membrane disks. Understanding the interaction between the adsorbent phase and the solute is vital in choosing the appropriate SPE extraction sorbent. Wells and Yu (2000) claimed that to select a SPE sorbent a good understanding of the hydrophobic, polar and ionogenic properties of the solute and sorbent are required. They also noted that interaction forces between the sorbent and the solute are usually van der Waals or electrostatic in nature.

The target herbicides for this study belong to two different classes. Atrazine belongs to a class called triazines while benazolin and 2,4-D belong to the acidic herbicides. Atrazine is derived from s-triazine which is a six-membered heterocyclic compound with nitrogen atoms located in positions 2, 4 and 6. The substituted nitrogen atoms ultimately affect the $\pi$-bond system of the supposedly aromatic ring resulting in higher electron density in positions 1, 3, and 5 than in positions 2, 4 and 6 (Pacáková et al., 1996). This behaviour is different from the benzene ring in the acidic herbicides 2,4-D and benazolin. Also, acidic herbicides most frequently exist in the ionised form at near neutral pH which are the pHs usually encountered in the environment. Hence when the different types of SPE sorbents are applied to the herbicides under investigation, it would be expected that the target adsorbents should respond differently since they belong to different classes.

Sabik et al. (1995) investigated SPE of atrazine and its degradation products in run-off water and sediments using mainly C18 and sulphonic acid bonded columns. Prior to their main investigations, they made preliminary SPE runs with the objective of comparing the recovery rate of different materials. They compared the recovery rate of C18, C8, C2, CH, CN, 2OH, and SCX columns for atrazine and its degradation products. Their results showed that for atrazine, C18 had the highest recovery rate of 99% for run-off water and 92% on sediment samples, while the C8 cartridge achieved a recovery rate of 98% on run-off water. The reasons for the high recovery rate on C18 were not revealed by the authors. Contrary to the results obtained by Sabik et al. (1995), Viana et al. (1996) observed that C8 achieved a higher recovery of atrazine than C18 columns. The authors reported that 72% could be recovered by C8 column compared to 67% by C18 columns. High recovery rates
of atrazine on C18 were reported by Giraud et al. (1997) who were quantifying traces of pesticides in water by solid phase extraction. They used spiked water extracts at 0.04 and 0.08 µg/L in 250 mL of the herbicides and they reported recovery rates of 97.3% for atrazine.

However, regardless of the success by Sabik et al. (1995) in recovering atrazine using C18 phases, relatively low recovery rates on atrazine have been reported in literature using the same phase. For example, Pinto and Jardim (2000) obtained a recovery rate of 76% from drinking water that had been spiked with 0.1 and 1.0 µg/L of atrazine contained in a volume of 250 mL. Albanis and Hela (1995) performed a multi-residue analysis of pesticides on environmental samples that involved atrazine. They employed C18 extraction disks to extract a variety of pesticides. Spiking levels of (0.1-50) µg/L in a volume of 1 L were used in the extraction experiments. They reported recovery rates of 88% from distilled water samples and 58.45% from Ionian Sea. It was observed that that ionic strength had an effect on the recovery rate of the investigated pesticides.

Balinova (1996) investigated SPE of dicamba, bentazone, benazolin, 2,4-D and MCPA C18 at neutral pH. The author also applied triethylamine as an ion-pairing reagent for increasing the retention of the herbicides. The work focussed on 1 L samples that were spiked with herbicides in the concentration range 0.05-1 µg/L at a pH of 6.9. The analysis of spiked drinking water samples showed average recovery rates of 78% and 72% for benazolin and 2,4-D respectively, while for ground water samples, benazolin samples had 85.5% recovery and 2,4-D had 83.7% recovery. Wells and Yu (2000) reported that the recovery rates of acidic herbicides could be enhanced by increasing sorbent mass and by 'performing appropriate matrix modification.' Sutherland et al. (2003) investigated the development of an analytical scheme for simazine, and 2,4-D in soil and water run-off from ornamental plant nursery plots using C18 columns. They acidified the water samples (300 mL) to a pH of 2. For a sample of 50 ng/mL of 2,4-D of spiked water, the authors obtained a recovery rate of 104% and for a sample concentration of 25 ng/mL, a recovery rate of 107% was achieved. These results (Sutherland et al. 2003) clearly show that by adjusting the pH of the samples to acidic conditions, good recovery rates of some acidic herbicides can be realised. Low recovery rates
obtained by Balinova (1996) may have been caused by the high pH values of their samples.

5.4 SPE Experimental Method for the Herbicides
Based on the information derived from literature, SPE experiments were performed on the herbicides of interest using C18 and C8 columns. These columns were chosen mainly because they are the most commonly employed solid phases and they are effective for a wide variety of organic molecules.

S-triazine SPE columns were obtained from International Sorbent Technology and are based on C18 packing. Various concentrations of the herbicide were prepared in 500 mL of ultrapure water contained in 500 mL amber bottles. Since benazolin and 2,4-D are retained primarily by hydrophobic interactions, pH adjustment was required to ensure high recovery since acidic herbicides are effectively retained in their unionised state when using C18 packing (Sutherland et al. 2003). This was achieved by acidifying the samples to a pH of 2.0 (since benazolin and 2,4-D pKa values are 3.04 and 2.64 respectively) using a few drops of concentrated sulphuric acid. In order to maintain an active sorbent surface in each column, 10 mL of methanol was passed under gravity followed by 10 mL of 2% methanol in water. The samples were drawn through the columns using a Masterflex peristaltic pump connected to a 16 port manifold and the rate of flow was maintained at a rate between 2-4 mL/min (see Figure 5.8). In the experimental set-up, the flow was effected through a vacuum that was generated by drawing out water from a 3 L glass tank which was part of the manifold system. When the 500 mL herbicide solutions were drawn through the columns, the columns were then dried using an oxygen free nitrogen stream which ran for 10 minutes. Before the analyte could be recovered, the eluent was allowed to soak into the sorbent bed for 10 minutes. Elution of the analyte into 7 mL vials was performed using 6 mL of acetonitrile. The eluent was then evaporated to dryness using a stream of nitrogen. Reconstitution of the dried sample was required before the samples could be analysed on the HPLC. The reconstitution process was done using 0.5 mL of 40% acetonitrile, 60% 10 mmol KH₂PO₄ buffer at pH 3.0 to re-dissolve the analytes. The analytes were then shaken violently by use of a WhirliMixer™ vibrator (manufactured by Fisons, UK). The contents were then transferred into HPLC auto-
sampler vials for analysis. The summary of the SPE procedures are shown in Table 5.2.

<table>
<thead>
<tr>
<th>Conditioning</th>
<th>Benazolin and 2,4-D</th>
<th>Atrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 mg, 6 mL C18 triazine columns were conditioned by passing 10 mL of HPLC grade methanol followed by 10 mL of 2% MeOH in water under gravity.</td>
<td>200 mg, C8 non end capped 3 mL columns were conditioned by passing 10 mL of HPLC grade methanol followed by 10 mL of 2% MeOH in water under gravity.</td>
</tr>
<tr>
<td>Extraction</td>
<td>500 mL sample solution were passed through the column at a flow rate of 2-4 mL/min</td>
<td>6 mL of acetonitrile was allowed to soak in the columns for 20 min before being passed through at approximately 0.5 mL/min and the eluent collected in 7 mL vials. The columns were then blown dry with nitrogen and then solvent was evaporated to dryness using a stream of nitrogen.</td>
</tr>
<tr>
<td>Elution</td>
<td>6 mL of acetonitrile was allowed to soak in the columns for 20 min before being passed through at approximately 0.5 mL/min and the eluent collected in 7 mL vials. The columns were then blown dry with nitrogen and then solvent was evaporated to dryness using a stream of nitrogen.</td>
<td>3 mL of acetonitrile was allowed to soak in the columns for 20 min before being passed through at approximately 0.5 mL/min and the eluent collected in 7 mL vials. The columns were then blown dry with nitrogen and then solvent was evaporated to dryness using a stream of nitrogen.</td>
</tr>
<tr>
<td>Reconstitution</td>
<td>500 µL of 40% acetonitrile, 60% 10mmol KH₂PO₄ buffer at pH 3 was added to the vials to re-dissolve the analytes. The vials were shaken vigorously and their contents transferred to HPLC auto-sample vials.</td>
<td>500 µL of 40% acetonitrile, 60% 10mmol KH₂PO₄ buffer was added to the vials to re-dissolve the analytes. The vials were shaken vigorously and their contents transferred to HPLC auto-sample vials.</td>
</tr>
</tbody>
</table>

**Table 5.2** Summary procedures for solid phase extraction

**Figure 5.8** Experimental set-up for the SPE of the herbicides.
C18 columns were also tried with atrazine but the recovery was low (<55%). This then necessitated the use of C8 columns which subsequently gave recovery of 100%. The percentage recoveries of the herbicides are shown in Tables 5.3 and 5.4. The results show that the recovery of 2,4-D is lower than that of benazolin even though the same packing is employed on the two herbicides. Chiron et al. (1994) obtained recoveries of 58% and 74% for benazolin and 2,4-D respectively when they used C18 columns to recover acidic herbicides from spiked estuarine water. The observed low recoveries achieved by Chiron et al. (1994) can be attributed to competition for the adsorption sites on the C18 sites from the mixture of herbicides they were investigating. Their results also revealed that recovery of the acidic herbicides was improved at low pH values. However, the percentage recovery for benazolin obtained in this investigation is in good agreement with the value obtained by Horner (2000) for benazolin spiked in ultra-pure water.

<table>
<thead>
<tr>
<th>Concentration (ppb)</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benazolin</td>
<td>2,4-D</td>
<td>Atrazine</td>
</tr>
<tr>
<td>2</td>
<td>101.00</td>
<td>95.23</td>
<td>102.01</td>
</tr>
<tr>
<td>4</td>
<td>99.98</td>
<td>96.80</td>
<td>101.83</td>
</tr>
<tr>
<td>6</td>
<td>99.78</td>
<td>94.64</td>
<td>101.22</td>
</tr>
<tr>
<td>8</td>
<td>99.60</td>
<td>92.92</td>
<td>99.66</td>
</tr>
<tr>
<td>10</td>
<td>98.00</td>
<td>91.02</td>
<td>100.40</td>
</tr>
<tr>
<td>15</td>
<td>98.55</td>
<td>90.00</td>
<td>99.04</td>
</tr>
<tr>
<td>20</td>
<td>97.50</td>
<td>91.47</td>
<td>98.65</td>
</tr>
<tr>
<td>30</td>
<td>96.90</td>
<td>87.46</td>
<td>98.80</td>
</tr>
<tr>
<td>40</td>
<td>95.20</td>
<td>85.21</td>
<td>98.08</td>
</tr>
</tbody>
</table>

Table 5.3 Recovery efficiency of benazolin at concentration range 2-30 ppb.
Table 5.4 Relative standard deviation and recovery of the herbicides.

<table>
<thead>
<tr>
<th></th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin</td>
<td>1.8</td>
<td>98.5</td>
</tr>
<tr>
<td>2,4-D</td>
<td>3.7</td>
<td>91.6</td>
</tr>
<tr>
<td>Atrazine</td>
<td>4.1</td>
<td>100</td>
</tr>
</tbody>
</table>

5.5 Copper Batch Adsorption Experiments

A series of batch experiments were performed on all the F400 carbon range for the adsorption of copper. The equilibrium adsorption isotherms were obtained by the following method. A series of 500 mL solutions of varying copper concentrations in the region 1-10 mg/L were placed in 500 mL amber Winchester bottles. 5 mg of the adsorbents were accurately weighed onto aluminium foils and then transferred to the solution bottles. The resultant mixture was adjusted to pH 5 using either 0.1 M sodium hydroxide or 0.1 M hydrochloric acid. The bottles were agitated for 7 days in a New Brunswick C Series incubator shaker set at 100 rpm and thermostatically controlled to 298± 0.1 K. During the course of the experiments, the pH of the samples was maintained at 5 using small amounts of 0.01 M sodium hydroxide. After equilibration, an amount of solution was filtered from each sample bottle and the copper ion content was analysed using a Varian SpectraAA-200 atomic absorption spectrophotometer (AAS). The AAS was set on the flame mode using an air-acetylene mixture.

5.6 Herbicides Batch Adsorption Experiments

Analytical standard grade benazolin and 2,4-D was supplied by Sigma Aldrich. A stock solution of 20 mg/L of each herbicide was prepared by dissolving an appropriate amount of the herbicide in ultra-pure water (18 MΩcm) from a Milli-Q plus 185 water purifier. Batch adsorption isotherms were performed by shaking 500 mL amber Winchester bottles containing the required concentration of the herbicide in a Gallenkamp incubator shaker. The shaker was set at a temperature of 298 K and a speed of 100 rpm. The volume of solution in each bottle was maintained at 500 mL and the solutions were adjusted to pH 5. About 5 mg of each adsorbent were weighed accurately on aluminium foils using a Sartorious (model BP 201D) analytical balance. The adsorbents were transferred carefully into the solution.
bottles. The bottles were shaken vigorously before shaking for 7 days in the incubator shaker. Before the solid phase extraction technique, the adsorbents were filtered from solution and the solutions were adjusted to pH 2.

The low solubility of atrazine in water limited the concentration of atrazine stock solution to 10 mg/L. The stock solution was prepared by saturating an amount of water with atrazine powder. In order to enhance dissolution, the saturated mixture was subjected to ultrasonic sound energy (using a Fisherbrand model FB11012 sonicator). The solution was then filtered and the concentration of the solution was established by comparing it with standard atrazine solutions run on the HPLC. Necessary dilutions were then undertaken to achieve the desired concentration of 10 mg/L. The methods for the preparation of atrazine adsorption experiments were similar to those described for benazolin and 2,4-D.

The effect of temperature on the uptake of the herbicides was also investigated for the three herbicides. The sample preparation procedure is similar to the one described for the samples run at 298 K. However in this method, the temperature of the incubator shaker was adjusted accordingly while maintaining the incubator speed at 100 rpm. Adsorption experiments were performed at 308 K and 318 K.

5.7 Simultaneous Adsorption Experiments

The effect of copper on the adsorption of the herbicide was investigated by sorbing the herbicides in the presence of a known amount of copper. The method for the preparation of the adsorption experiments is the same as described in Section 5.6 except the herbicide solutions were prepared in a 5 mg/L solution of copper in 500 mL bottles.

5.8 Kinetic Experiments

Kinetic experiments were performed in an experimental set up shown in Figure 5.9. The procedure involved preparation of known concentration of the herbicides in a 2 L volumetric flask and the contents were subsequently transferred to a round bottomed flask. Adsorbents of different particle size (500 mg) were weighed and transferred to a rotating basket made of Perspex and plastic mesh (40 µm opening). The basket was then connected to a stirring rod attached to a stirrer motor. The
contents were contacted with the solution and the stirrer motor was immediately started. For all the experiments the motor was set at 250 rpm. During the experiments, samples of quantities 0.5 mL were taken after every 10 minutes and put into HPLC vials for quantification.

1. Variable speed motor
2. Plastic syringe
3. Thermometer
4. Temperature control unit
5. Filter
6. Herbicide solution
7. Adsorbent in basket

![Experimental apparatus for kinetic studies.](image)

**Figure 5.9** Experimental apparatus for kinetic studies.

### 5.9 Results and Discussions

#### 5.9.1 Adsorption of Copper

The sorption of copper on F400 and its oxidised series is given in Figure 5.10. The results clearly show that oxidised samples have a higher uptake capacity than all the remaining samples. The isotherm for AC4 sample could not be established because the uptake capacity of copper on the sample was virtually negligible. The enhanced capacity observed on AC1, AC2, and AC3 could be as a result of the oxidation process which generated carboxylic functional groups as evidenced in the FTIR spectra and the high sodium capacity of the above sorbents. These groups would be dissociated in aqueous solution at pH 5 (Strelko, 1999), and they are
responsible for copper sorption. The oxidised and heat treated sample AC3 showed reduced capacity compared to AC1 and AC2. This is due to the decomposition of the carboxylic acid groups during the heat treatment, and this observation is confirmed by the slightly lower sodium capacity of this sample as compared to AC1 and AC2. Also, from the characterisation results in Chapter 4, heat-treatment could have 'denatured' the humic substances in this sample since extraction of the humic substance from this sample yielded no results. There is strong evidence in the literature which indicates that humic substances also participate in the sorption of metal ions (Abate and Masini, 2005; Chen and Wu, 2004; Baker and Khalili, 2004). Hence AC3 would give lower copper sorption capacity than AC1 and AC2.

The sorption of copper seems to be similar in samples AC1 and AC2 even though the humic substances had been washed out with sodium hydroxide in sample AC2. The possible explanation could be the difference in pore size distribution of the two samples.

![Figure 5.10 Equilibrium sorption results of copper on F400 and the oxidised carbons.](image)

It is interesting to note that there was significant copper sorption in sample AC5 although it was not targeted for oxidation. Characterisation results of this sample proved that it had a relatively high sodium capacity and also partial oxidation of
the sample had taken place during its modification as evidenced from the spectra of the extracted humic substances. The existence of acidic functionality in this sample was also shown on the FT-IR spectra of its humic substances. Therefore, binding of the copper ions in AC5 was due to the existence of the acidic functionality and the humic substances.

Streat et al. (2004) reported that the formation of metal surface complexes on the oxidised carbon would involve cooperative action. They arrived at such a conclusion after having evaluated an approximate number density of the oxygenated functional groups for an oxidised carbon. They estimated that the density per unit area for F400(ox) was 0.02 functional groups per square Angstrom (Å). They assumed that it would be possible for complex formation between copper and the oxygen functional groups to occur in the micropores of the carbon adsorbent. Given that the oxidised carbons evaluated in the present study possess a large proportion of pores with sizes in the range of 5-20 Å and the diameter of the hydrated metal ions is approximately 8 Å (Nightingale, 1959), it is reasonable to assume a complex formation binding mechanism (see Figure 5.11). Copper is known to engage in the formation of stable complexes through Jahn-Teller distortion which gives rise to tetrahedral shaped complexes. This then implies that effective complexes of copper and the oxygen containing functional groups occurs in the micropores where maximum contact can be realised.

![Image of postulated complexation reaction](image)

*Figure 5.11 Postulated complexation reaction between copper (II) and oxidised carbon surface (Streat et al., 2004).*
5.9.2 Adsorption of Herbicides

Figures 5.12-5.14 illustrate the adsorption of atrazine, benazolin and 2,4-D on the F400 and it modified series. In all cases, the non-oxidised samples performed better than the oxidised carbons. The adsorption performance of the samples for atrazine seems to follow the sequence AC4 > F400 > AC3 ≈ AC2 ≈ AC5 > AC1. This sequence shows that AC4 was the best performer among all the samples. This sample was generated through annealing at high temperature resulting in the elimination of acidic functional groups and the enhancement of micropores which subsequently resulted in a higher surface area than the parent sample, F400. Hence, the enhancement of micropores in this sample (AC4) is a positive contributor to the enhanced adsorption capacity of atrazine because it promotes accessibility of adsorption sites. However, it is worth pointing out the fact that the aminated sample (AC5) possesses more enhanced micropores than AC4 but its sorption capacity was less than that of AC4. This gives an indication that pore size distribution is not the only factor in the sorption of atrazine. When the characterisation results of these samples are taken into consideration, it is apparent that the main difference between the two samples is the higher iso-electric charge in AC4 than in AC5. The difference is due to the existence of acidic functional groups in the AC5 sample and this indicates the strong effects of the surface oxygen groups on the adsorption mechanism.

[Equilibrium solution concentration vs. Equilibrium concentration on solid graph]

- AC2
- AC3
- AC5
- F400
- AC4
- AC1

Equilibrium solution concentration (mmol/L) vs. Equilibrium concentration on solid (μmol/g)
Figure 5.12 Adsorption of atrazine on F400 and its modified series.

Figure 5.13 Adsorption of benazolin on F400 and its modified series.

Figure 5.14 Adsorption of 2,4-D and its modified series.

Ideally, atrazine is expected to adsorb more on oxidised samples including sample AC5 which contains oxygen containing functional groups. This is
because atrazine has the potential to form hydrogen bonds with various oxygen functional groups like the carboxyl and phenolic functional groups. Welhouse et al. (1993) employed nuclear magnetic resonance (NMR) on atrazine to prove that the nitrogen para to the chloride ion carries the highest electron density and hence has the potential to 'accommodate' a proton while the ethyl amino nitrogen had a slight positive charge which would make it another potential site for hydrogen bonding. The possible structures are shown in Figure 5.15. The adsorption results show that the hydrogen bonding mechanism is not the predominant uptake mechanism for atrazine in oxidised carbons. The mechanism behind the decrease in adsorption of atrazine in oxidised carbons is due to water adsorbing on oxygen functional groups, especially carboxylic acids. When the water molecules get into contact with the oxygen functional groups, it adsorbs through hydrogen bonding on the hydrophilic polar oxygen groups, thereby forming clusters on the entrance of adsorbent pores. This makes the pores highly inaccessible to the atrazine molecules thus resulting in the reduced uptake of the herbicide.

Müller and Gubbins (1998) confirmed the formation of water clusters in activated carbon when they were investigating molecular simulation of hydrophilic and hydrophobic behaviour of activated carbon surfaces. Through their simulation results the authors were able to conclude that adsorption of water does not occur through the formation of a monolayer followed by additional layers, but rather through the 'formation of three-dimensional clusters centred on active sites' of the adsorbent surfaces. They also reported that these adsorbed water clusters are further enhanced if there is a possibility of cluster interconnection causing bridging effects which result in the formation of dense regions of water in the pores. The dense water regions result in pore blockage, blocking the surface to other molecules. Franz et al. (2000) concluded that adsorption of phenol (which has a potential of forming hydrogen bonds) from aqueous solutions by 'oxidised' carbons was hampered by the presence of water clusters which would block the entrance of micro- or mesopores where adsorption takes place. The latter proved the hypothesis by employing hexane as a solvent and comparing the results for the two solvents (water and hexane). Their results were able to prove that the more hydrophilic
carbon adsorbed more phenol with hexane solvent than when water was used as solvent. Also, the ‘oxidised’ sample outperformed the hydrophobic sample when hexane was employed as the solvent.

![Possible hydrogen bonding configurations of atrazine on oxidised activated carbon.](image)

**Figure 5.15** Possible hydrogen bonding configurations of atrazine on oxidised activated carbon.

Figures 5.13 and 5.14 represent the adsorption isotherms of benazolin and 2,4-D respectively. In all the graphs, it is clear that samples F400 and AC4 perform better than the oxidised carbons. A clear trend of the adsorption isotherms for the oxidised carbons could not be established, and Figure 5.13 shows that the adsorption isotherm of benazolin on AC5 was less favourable when compared to sorption of benazolin on F400 and AC4. The low uptake of benazolin and 2,4-D by oxidised carbons may be due a combination of factors. Pore blockage by water molecules cannot be ruled out, and also oxidation of the carbon resulted in micropore blockage from the formation of humic acids (which are themselves a by-product of oxidation). This is illustrated in Chapter 4 from the pore size distribution and the FT-IR spectra of the extracted humic materials. Also, the adsorption experiments were conducted at a pH value that was higher
than the pKa values of benazolin and 2,4-D. In such conditions, the two herbicides are expected to be in the dissociated form. Since it was established from the IEP-PZC values that the surface of the oxidised samples was negative, then mutual repulsion of the adsorbents and the herbicides is expected, and this subsequently results in low sorption capacity.

It has been argued that adsorption of substituted aromatic molecules (especially with electron withdrawing groups) on activated carbon can be through the formation of electron donor-acceptor complexes. This case would favour sample F400 to have the highest uptake capacity of the herbicides, since in this sample the existence of carbonyl groups (which can participate in donor-acceptor complexes) is expected. This is not the case, since sample AC4 performs better than F400.

The π-π dispersion interaction mechanism seems to be the dominant form of association between the two herbicides and the adsorbents. This mechanism is promoted by a high electron density in the basal plane of the carbon and functionalisation of the carbon by electron-withdrawing groups such as oxygen would result in decreased electron density, subsequently leading to suppressed or weaker adsorption as observed in oxidised carbons. The results for sample AC5, even though it has electron-donor constituents in the form of amino groups, show that it cannot compete with F400 and AC4. The reason for this is that the sample still contains oxygen containing functional groups. Annealing of the activated carbon to produce sample AC4 contributed to the enhancement of the adsorption capacity of this sample on both benazolin and 2,4-D. As mentioned in Chapter 5, annealing of the carbon results in a sample with low oxygen content and high iso-electric point values. This is consistent with the removal of acidic functional groups which contribute in the reduction of π electron density in the basal plan of the carbon. The removal of these functional groups therefore gives rise to a sample with a higher intensity of the π electron system than its parent sample. This condition promotes higher association of the π electron system of the herbicide aromatic ring and the π electron system of the basal plane of the carbon. This is indeed evidenced by the high uptake of the herbicides on AC4 sample.
Figures 5.16 and 5.17 present the comparison of single component adsorption of the three herbicides on the best performing samples i.e. F400 and AC4. In all cases the adsorption capacity follows the trend 2,4-D > benazolin > atrazine. The structural and chemical differences between atrazine (classified as triazine) and the acidic herbicides, benazolin and 2,4-D, makes it difficult to explain the reasons for the difference in the observed uptake capacity. However, the three dimensional representation of the structures shown in Figures 5.22-5.24 reveal that, the atrazine molecule is less linear and appears more bulky as compared to the other two molecules. Hence, atrazine is most likely to suffer from size exclusion since it is the largest molecule in this study.

![Figure 5.16 Comparison of the single component adsorption of the herbicides on F400.](image)

**Figure 5.16** Comparison of the single component adsorption of the herbicides on F400.
Figure 5.17 Comparison of the single component adsorption of the herbicides on AC4.

Figure 5.18 Adsorption isotherms of benazolin and 2,4-D on F400 and AC4

Figure 5.18 shows the comparison of the adsorption of benazolin and 2,4-D on F400 and AC4. The basis for comparison of the two herbicides is valid since
they belong to the same class of acidic (aromatic) herbicides. Generally, the results reveal that AC4 performs better than F400 on the two herbicides. This is expected since the characterisation results showed that the BET surface area of AC4 was higher than that of F400 sample. Also, the pore size distribution results in Chapter 4 show that sample AC4 had a higher proportion of micropores than F400. The high proportion in micropores is desirable for the sorption of a larger quantity of organic molecules because in this region the contact points between the adsorbent and the adsorbate molecules is higher than in mesopores and macropores. Also, it is widely accepted that there is significant overlap of potential forces in the micropores which results in increased adsorption forces. From Figure 5.18 the sorption capacity follows the sequence AC4 (2,4-D) > AC4 (benazolin) > F400 (2,4-D) > F400 (benazolin). It would normally be expected that benazolin should be adsorbed more than 2,4-D because of its low solubility (600 mg L\(^{-1}\)) in water compared to 2,4-D (890 mg L\(^{-1}\)). Also, benazolin possesses a greater functional variability which normally favours increased adsorption.

The lower adsorption capacity of benazolin in sample AC4 may be as a result of steric hindrances in its structure. One source of the steric hindrances in the two molecules is the existence of the carboxylic functional groups which are out of plane with the aromatic ring. However, the benazolin molecule consists of the heterocyclic ring adjacent to an aromatic ring and the heterocyclic ring consists of hetero-atoms nitrogen and sulphur. It is known that during chemical bonding involving a nitrogen atom, the resultant molecules with a nitrogen atom usually form out of plane configurations. The nitrogen atom during bonding is known to form four pairs of \(\sigma\) electrons which adopt a tetrahedral distribution in order to minimise electron pair repulsions. One of the four tetrahedral positions is occupied by a lone pair while the other three are involved in bonding pairs (Companion, 1964; Barrett, 2001). Hence the nitrogen atom ultimately forms molecules structured in the form of a trigonal pyramid. Therefore, if the same notion is applied to the benazolin molecule, it would imply that the two ring systems that are linked to the nitrogen molecule are not in the same plane and this makes the molecule less linear and more bulky than the 2,4-D molecule. This is further evidenced by the side view of the spatial arrangement of the
atoms of 2,4-D and benazolin shown in Figures 5.20 and 5.21. Figures 5.20 (b) and 5.21 (b) show a leaner 2,4-D molecule (width of 2.074 Å) than the benazolin molecule (width of 3.113 Å).

Table 5.5 shows the Langmuir and Freundlich parameters of benazolin and 2,4-D adsorption onto F400 and AC4. The correlation coefficients of the two isotherms show that the Langmuir isotherm has higher correlation coefficient compared to the Freundlich isotherm. This suggests that adsorption of the two herbicides occur on localised sites that are able to accommodate a single molecule. The value of $K_R$ in the Langmuir isotherm gives an indication of the strength of the association between the adsorbent and the adsorbate. In this case, the values are almost the same which indicates that the nature of the adsorption forces in the two adsorbent samples are the same. The values of $q_m$ are higher for AC4 sample than F400 sample, which shows the higher performance of AC4 to that of F400.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$</td>
<td>$K_R$</td>
</tr>
<tr>
<td>Benazolin on F400</td>
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<td>26.09</td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>45.25</td>
<td>27.63</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>36.76</td>
<td>27.20</td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>53.19</td>
<td>20.89</td>
</tr>
</tbody>
</table>

Table 5.5 Parameter and correlation coefficients for benazolin and 2,4-D sorbing on F400 and AC4. Constants based on units of $q_m$ (µmol g$^{-1}$) and (µmol L$^{-1}$). pH constant at 5.0 for all determinations.
Figure 5.19 Spatial arrangements of the atoms of atrazine molecule.
**Figure 5.20** Spatial arrangements of the atoms of benazolin molecule.
Figure 5.21 Spatial arrangements of the atoms of 2,4-D molecule.
5.9.3 Effect of Metal Ions on Herbicides Uptake

Wastewater streams consist of a mixture of pollutants that can generally be classified as organic and inorganic. Amongst the inorganic pollutants, heavy metals form a major part in the classification. Heavy metals constitute a class of environmental pollutants that are of particular concern in the treatment of industrial wastewater because of their potential danger to humans and the environment. In this study, the effect of metal ions on the uptake of the herbicides was investigated. Copper was chosen as a representative of the metal ions.

The effect of copper on the sorption of atrazine for F400, AC2 and AC4 samples is illustrated in Figures 5.22, 5.23 and 5.24. Sample AC2 was chosen as a representative of the oxidised samples. Generally, the presence of copper ions has a negative effect on the uptake of the herbicide. Samples F400 and AC2 appear to be more affected than AC4. The low uptake of atrazine suggests competitive adsorption between the herbicide and the copper. However, in section 5.9.2 it is discussed that adsorption of atrazine is through π-π interactions between the herbicide and the adsorbent while copper ions adsorb through complex formation and ion exchange. It is interesting to note that the two adsorption mechanisms do not involve the same active sites. The interference of copper on the adsorption of atrazine most likely would come from pore blockage once copper ions have adsorbed onto the active sites. Since copper is a transition metal, it forms hydrated complexes with water molecules. Therefore, the adsorbed copper ions in the pores of the adsorbent should be associated with water molecules. This association then leads to pore blockage and reduced uptake of atrazine. This hypothesis is supported by the isotherms on Figures 5.22 and 5.23. The reason for the marginal effect of copper ions for the adsorption of atrazine in sample AC4 is due to the absence of acidic functional groups that favour adsorption of copper. This implies that sample AC4 is capable of binding with atrazine alone, which eliminates the possibility of pore blockages through the adsorption of copper. Samples F400 and AC2 have a higher affinity for metal ions than sample AC4 as shown by the sodium
capacity results. Therefore, it is expected that pore blockage effects can be prevalent in F400 and AC4.

**Figure 5.22** Metal ion effect on the adsorption of atrazine on F400.

**Figure 5.23** Metal ion effect on the adsorption of atrazine on AC2.
Figure 5.24 Metal ion effect on the adsorption of atrazine on AC4.

Figures 5.25-5.30 show the effect of the presence of copper ions on the adsorption of benazolin and 2,4-D onto F400, AC2 and AC4 samples. A similar adsorption trend as that of atrazine can be observed in the case of benazolin and 2,4-D. Pore blockage caused by the adsorption of copper ions is the probable cause. Nightingale (1959) states that the diameter of a hydrated copper ion is in the region of 8 Å; if this diameter is compared to the width of the molecules, it can be seen that the dimensions are comparable. Hence the hydrated copper ions can occupy the micropores of the adsorbents, which are also favoured by the target adsorbates.
Figure 5.25 Metal ion effect on the adsorption of benazolin on F400.

Figure 5.26 Metal ion effect on the adsorption of benazolin on AC2.
Figure 5.27 Metal ion effect on the adsorption of benazolin on AC4.

Figure 5.28 Metal ion effect on the adsorption of 2,4-D on F400.
Figure 5.29 Metal ion effect on the adsorption of 2,4-D on AC2.

Figure 5.30 Metal ion effect on the adsorption of 2,4-D on AC4.

5.10 Conclusions
An HPLC method of analysing atrazine, benazolin and 2,4-D was successfully developed using acetonitrile and a buffer. Quantification of the low concentrations of the herbicides was achieved through a concentrating process
that involves solid phase extraction. High recoveries were achieved for atrazine molecules when C8 phases were applied, while benazolin and 2,4-D responded well to a C18 phase. However, concentration of benazolin and 2,4-D required conditioning through pH adjustments to below the pKa values of the herbicides.

Adsorption of the targeted herbicides were performed on a conventional carbon and its modified series. The adsorption results revealed that all the targeted herbicides had a high affinity for the sample AC4 carbon. This gave an indication that the adsorption mechanism was dominantly through π-π interaction between the aromatic ring system of the herbicides and the π system of the basal plane of the adsorbent sample. The uptake of the herbicides was also high on the conventional carbon sample F400, but it was marginally outperformed by sample AC4. The oxidised samples performed poorly compared to samples AC4 and F400 for herbicides sorption. This was attributed to the existence of carboxylic functional groups on the adsorbent surfaces. These functional groups are known to reduce the π electron intensity in the carbon system, and this leads to reduced interaction between the herbicides and the adsorbents. The aminated sample AC5 could not achieve a high uptake of the herbicides even though it had the highest surface area and a much more enhanced microporosity than all the other adsorbent samples. This was attributed to the oxygen functionality on its surface. Structural configurations of the herbicides also played a major role in their sorption capacity.

The effect of the presence of a metal ion on the uptake of the herbicides was also investigated. The presence of copper ions showed an adverse effect on the adsorption of all the herbicides. This was attributed to the competition between the copper ions and the herbicides to occupy sites in the micropore region where adsorption forces are strongest.

5.11 References


Giraud D., Ventura A., Camel V., Bermond A., Arpino P., 1997, Determination of traces of pesticides in water by solid-phase extraction and liquid


Streat, M., Malik D., Saha, B., 2004, Adsorption and ion-exchange properties of engineered activated carbons and carbonaceous materials, Ion Exchange and


6. THERMODYNAMIC PARAMETERS AND KINETIC STUDY

6.1 Thermodynamic Parameter Studies

Thermodynamic parameters of adsorption can be obtained when adsorption isotherms are produced at different temperatures. These parameters include the change in the Gibbs free energy ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$). The parameter $\Delta G$ gives an indication of the spontaneity of the adsorption process while $\Delta H$ shows whether the adsorption process is endothermic or exothermic. The absolute values of $\Delta H$ can also reveal the mechanism of adsorption i.e. physisorption or chemisorption. In the physisorption mechanism, the adsorbate retains its identity while in a chemisorption process, breaking and formation of bonds occurs and this leads to loss of identity of the adsorbate. The parameter $\Delta S$ gives the degree of randomness at the solid/liquid interface and also shows the affinity of the adsorbents for the adsorbates.

A series of experiments were performed at temperatures of 298 K, 308 K and 318 K in order to evaluate the effect of temperature on the adsorption of the herbicides. These experiments subsequently led to the evaluation of the thermodynamic parameters. A full description of the experimental procedures has been given in Chapter 5. In order to evaluate the thermodynamic parameters, the following equations were employed;

$$\Delta G^0 = -RT \ln K_0$$  \hspace{1cm} (6.1)

where $R$ is the universal gas constant (8.314 J/K/mol) and $T$ is the temperature in Kelvin. $K_0$ can be evaluated using a method described by Niwas et al. (2000) and Li et al. (2005). In this method, $K_0$ can be defined as:

$$K_0 = \frac{a_s}{a_e} = \frac{v_s}{v_e} \frac{C_s}{C_e}$$  \hspace{1cm} (6.2)

where $a_s$ and $a_e$ are the activities of the adsorbed solute and the solute in solution at equilibrium, respectively, while $v_s$ and $v_e$ represent the activity coefficients of the adsorbed solute and the solute present in solution, respectively. When the concentration of the solute in solution approaches zero, the activity coefficient will approach unity and subsequently $K_0$ can be evaluated by plotting $\ln(C/C_e)$ against $C_s$ and extrapolating to zero. Subsequently, the intercept with the Y-axis gives the
value of $K_0$. The enthalpy change $\Delta H^0$ and entropy change $\Delta S^0$ were calculated using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$  \hspace{1cm} (6.3)

A plot of $\Delta G^0$ against temperature $T$ was found to be linear, hence the values of $\Delta S^0$ and $\Delta H^0$ were obtained from the gradient and intercept of the plot (Ho, 2003).

Figures 6.1-6.2 show the effect of temperature on the adsorption of atrazine on F400 and AC4. The results show that an increase in temperature results in a decrease in sorption capacity and this is typical of an exothermic process. Table 6.1 shows that $\Delta G^0$ is negative for the two adsorbents, and this is a clear indication of the feasibility and the spontaneity of the adsorption process. Evaluation of $\Delta H^0$ and $\Delta S^0$ was not possible in this instance, because a linear relationship between $\Delta G^0$ and $T$ could not be established. The most probable cause of the non-linear relation of $\Delta G^0$ and $T$ would be that the heat capacity of atrazine is not constant over the temperature range adopted in the experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
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<tr>
<td></td>
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<td>Atrazine on F400</td>
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<td>Atrazine on AC4</td>
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<td>-14.852</td>
<td>-15.599</td>
</tr>
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</table>

Table 6.1 Thermodynamic parameters for the adsorption of atrazine on F400 and AC4.
Figures 6.3-6.6 show the effect of temperature on the uptake of both benazolin and 2,4-D on F400 and AC4 samples. In all cases, the adsorption of the herbicides was enhanced by the corresponding increase in temperature. This observation is a clear indication of an endothermic process. Endothermic processes involving sorption of
organic molecules have also been recorded in literature (Al-Ghouti et al., 2005; Alam et al., 2005; Akçay et al., 2005). Table 6.2 shows the thermodynamic parameters derived from the adsorption isotherms shown in Figures 6.3-6.6. However, the thermodynamic values of benazolin on F400 need to be treated with caution because as shown in the Appendix section, a plot of ΔG against T did not give a good linear relationship. The standard free energy change (ΔG°) was found to be in the region of -16.650 to -19.414 kJ mol⁻¹. A negative standard free energy change indicates that benazolin and 2,4-D adsorption onto F400 and AC4 is a spontaneous process. Silva et al. (2004) mentioned that such low values of free energy change were an indication of a spontaneous physisorption process. Akçay et al. (2005) obtained molar free energy change of -2.831 kJ mol⁻¹ at 298 K and -1.863 kJ mol⁻¹ at 313 K while adsorbing 2,4-D on organophilic sepiolite. Aksu and Kabasakal (2004) obtained a free energy value of -6.8 kJ mol⁻¹ when they were investigating batch adsorption of 2,4-D on granular activated carbon. This difference is mainly attributed to the difference in experimental conditions, however, in all cases it was noted that the adsorption of 2,4-D was a spontaneous process. The positive values of the enthalpy change suggest that the adsorption process is endothermic, a phenomenon that was observed by Akçay et al. (2005) and Aksu and Kabasakal (2004). Bhattacharyya and Sharma (2005) reported that such small values in enthalpy change are not consistent with the formation of strong chemical bonds between the adsorbent and the adsorbate. The positive values of the entropy are an indication of increased randomness at the solid/liquid interface and an affinity of the adsorbents for the herbicides.
Figure 6.3 Effect of temperature on sorption of benazolin on F400.

Figure 6.4 Effect of temperature on sorption of benazolin on AC4.
Figure 6.5 Effect of temperature on sorption of 2,4-D on F400.

Figure 6.6 Effect of temperature on sorption of 2,4-D on AC4.
Table 6.2 Thermodynamic parameters for the adsorption of benazolin and 2,4-D on F400 and AC4.

Table 6.3 and 6.4 show the Langmuir and Freundlich isotherm constants for the temperature ranges in which the isotherms were obtained. The values of $q_m$ (see Table 6.3) for atrazine shows that they decrease as the temperature is increased. This is consisted with the exothermic nature of the sorption process of atrazine on activated carbons. The correlation coefficients in Tables 6.3 and 6.4 show that adsorption of atrazine follows the Freundlich isotherm more closely than the Langmuir isotherm. This observation is different from benazolin and 2,4-D which clearly follows Langmuir isotherm more than the Freundlich isotherm. The difference in the sorption behaviour of atrazine from benazolin and 2,4-D can possibly be explained in the differences in the structures of the molecules. As was noted in Chapter 4, atrazine belongs to a group of herbicides called triazines, which have more localised $\pi$ electrons in their aromatic structures than in acidic aromatic herbicides benazolin and 2,4-D. The Freundlich constant $1/n$ value is less than 1 for all the samples, and this shows that adsorption of the target herbicides is favourably adsorbed on F400 and AC4 samples at all temperatures.

<table>
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<tr>
<th>Sample</th>
<th>$\Delta G^0$(kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J mol$^{-1}$K$^{-1}$)</th>
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<td>Benazolin on F400</td>
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<td>Benazolin on AC4</td>
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<td>-18.319</td>
<td>11.930</td>
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<td>-17.231</td>
<td>7.764</td>
</tr>
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<td>2,4-D on AC4</td>
<td>-17.223</td>
<td>-17.832</td>
<td>6.410</td>
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† The thermodynamic values of benazolin on F400 need to be treated with caution.
### Table 6.3 Langmuir equilibrium isotherm constants. (Constants based on units of $q_m$ (µmol g$^{-1}$) and (µmol L$^{-1}$). pH was kept constant at 5.0 for all determinations)

<table>
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<th>308 K</th>
<th>318 K</th>
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<td>2,4-D on AC4</td>
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<td>20.89</td>
<td>0.9826</td>
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### Table 6.4 Freundlich equilibrium isotherm constants. (Constants based on units of $q_m$ (µmol g$^{-1}$) and (µmol L$^{-1}$). pH was kept constant at 5.0 for all determinations.)

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<tbody>
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<td>$R^2$</td>
</tr>
<tr>
<td>Atrazine on F400</td>
<td>331</td>
<td>0.82</td>
<td>0.9737</td>
</tr>
<tr>
<td>Atrazine on AC4</td>
<td>458</td>
<td>0.79</td>
<td>0.9661</td>
</tr>
<tr>
<td>Benazolin on F400</td>
<td>734</td>
<td>0.69</td>
<td>0.9852</td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>1009</td>
<td>0.71</td>
<td>0.9736</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>790</td>
<td>0.79</td>
<td>0.9651</td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>921</td>
<td>0.75</td>
<td>0.9641</td>
</tr>
</tbody>
</table>

#### 6.2 Kinetic Studies

Adsorption kinetics form one of the fundamental requirements for the design of adsorption systems. Hence it is necessary that accurate and reliable data on adsorption isotherms and sorption kinetics be made available. Generally, the rate of
adsorption can be governed by film resistance at the external surface of the activated carbon particles, or by intra-particle diffusion within the activated carbon particles, or by both film and intra-particle diffusion resistances.

A series of batch kinetic experiments were performed using the experimental set-up described in chapter 5 which involved placing the adsorbent into a porous basket that is rotated in the solution of the adsorbent. The conventional batch kinetic experimental set-up usually involves free adsorbent particles in a reactor where the solution is stirred by the impeller. The major disadvantage of the conventional method is the breaking up of particles through contact with the fast rotating blades. Lloyd-Jones (2003), while investigating the sorption performance of *azolla filiculoides* for metal ion uptake, also revealed that sorption rates were slower in the conventional set-up than in the 'basket' method. This was attributed to a possibly thinner liquid film in the basket method in which the adsorbent is essentially static while the liquid is forced between the particles, resulting in higher mass transfer rates. However, the relative velocity between the adsorbent particles and the liquid solution is low in the conventional set-up, and this results in lower mass transfer rates.

Kinetic experiments were conducted at different initial concentrations and different particle sizes. The initial concentrations chosen were 10, 4 and 2 mg/L while the size ranges chosen were 355-420 µm and 710-850 µm diameters. Kinetic experiments on atrazine were limited to 4 mg/L and 2 mg/L at size range 355-420 µm due to solubility limitations.

Kinetic properties of the different size range particles and different initial solution concentrations were compared by applying the pseudo-second order kinetic model. The pseudo-second order equation is based on the sorption capacity of the solid phase and can be expressed using the equation developed by Ho and McKay (1999) as:

\[
\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2
\]

(6.4)
where \( q_{eq} \) is the amount of solute adsorbed at equilibrium and \( q \) is the amount of solute adsorbed at time \( t \), while \( k_{2,ad} \) is the rate constant for pseudo-second order adsorption. For initial conditions \( t=0, q=0 \) and at time \( t=t \), \( q=q_{eq} \), the integrated form of the equation becomes:

\[
\frac{t}{q} = \frac{1}{k_{2,ad}q_{eq}^2} + \frac{1}{q_{eq}} t
\]  

(6.5)

If second order kinetics are applicable, the plot of \( \frac{t}{q} \) against \( t \) should give a linear relationship, from which \( q_{eq} \) and \( k_{2,ad} \) can be determined.

Ho and McKay (1999) were able to demonstrate that the majority of adsorption systems follow the pseudo-second order kinetic equation. Prior to their publication in 1999 concerning sorption kinetic studies of a variety of sorption systems, many investigators had attempted to fit their sorption data using the pseudo-first order Lagergren equation of the form:

\[
\frac{dq}{dt} = k_{1,ad}(q_{eq} - q)
\]

(6.6)

where the integrated form of the equation for the conditions \( t=0 \) to \( t=t \) and \( q=0 \) at \( t=0 \) gives:

\[
\log(q_{eq} - q) = \log q_{eq} - k_{1,ad} t \div 2.303
\]

(6.7)

A linear plot of \( \log(q_{eq} - q) \) vs \( t \) verifies the first order kinetics with the slope yielding the pseudo first order rate constant. Most investigators found that their data followed the first order equation only after a short period, after which the experimental data deviated considerably from the theoretical data. This led to the idea of complex sorption kinetic systems where the sorption system was described by multiple first order kinetics. In this system, the linear plot of the first order equation is divided into two or three linear sections with each section representing a pseudo first order reaction mechanism. Varshney et al. (1996) proposed multiple order kinetics for the pesticide phosphamidon sorbing on antimony (V) phosphate. Sarkar and Chattoraj (1993), showed that sorption of selected proteins followed
first order kinetics with two kinetic constants. Ho and McKay (1999) also compiled a comprehensive list of comparison of mechanisms of sorption from the literature mostly pertaining to first order and complex kinetics.

Ho and McKay (1999) showed that data that had previously been thought to obey Lagergren first order kinetics and multiple first order kinetics was well represented by the pseudo-second order equation over the entire time range of the experiments. They verified the equation over a wide range of solutes which involved metal ions and organic molecules. Ho and McKay (1999) postulated that the sorption mechanisms for systems that follow pseudo-second order kinetics involves chemisorption which comes as a result of 'valency forces through sharing and exchange of electrons between sorbent and sorbate.' However, the postulate does not adequately explain systems involving aromatic molecules that follow a pseudo-second order model. For example, Ho and MacKay (1999) were able to show that p-nitrophenol and o-cresol sorbed onto fly ash through a pseudo second order kinetics even though chemisorption process is highly unlikely in this system.

However, in view of the findings by Ho and Mckay (1999), kinetic data for the sorption of benazolin, 2,4-D and atrazine were fitted using the pseudo second order equation. The first order equation could not be employed in this instance because of solubility limitations.

The effect of temperature on the kinetics of the sorption of benazolin and 2,4-D was also investigated. In all the temperature ranges applied to the system, pseudo second order kinetics was obeyed and the pseudo second order rate constant of the herbicides adsorption was expressed as a function of temperature by the Arrhenius-type relationship given as:

$$k_{2,\text{ad}} = A \exp\left(\frac{-E_a}{RT}\right)$$

where $k_{2,\text{ad}}$ is the rate constant for pseudo-second order adsorption, $A$ is the Arrhenius factor, $E_a$ is the activation energy of adsorption, $R$ is the gas constant (8.314 J/mol K) and $T$ is the solution temperature. When $\ln k_{2,\text{ad}}$ is plotted against
the reciprocal of $T$, a straight line is obtained with a gradient of $E_a/R$ and this subsequently leads to the evaluation of $E_a$.

The parameters $k_{2,ad}$ and $q_{eq}$ were directly obtained from the intercept and slope of the plot of $1/q$ against $t$ of which the results are shown in Table 6.5. The tabulated results show the list of the amount of the adsorbed herbicide $q_{eq}$, pseudo-second order constant $k_{2,ad}$, and the regression coefficients $r^2$. It is clear from the tabulated results that the correlation coefficients are generally greater than 0.99. The very high value of the correlation coefficients is presented as evidence that the sorption process follows the pseudo-second order rate equation. Also, it is clear that the herbicide uptake increases with an increase in initial concentration. A similar trend was observed by Aksu and Kabasakal (2004) when they performed sorption kinetic experiments on 2,4-D using conventional activated carbon. They also recorded a high correlation coefficient of 0.99 for the second order kinetic model. However, the kinetic parameters could not be compared with this system because Aksu and Kabasakal (2004) employed high initial concentration of 2,4-D for their kinetic experiments (100-600 mg/L) compared to 4-10 mg/L employed in the work in this thesis. They also used KOH solution which assisted in the dissolution of 2,4-D. Hence, their solutions were of higher ionic strength than the solutions applied in this investigation.
### Table 6.5 Kinetic constants for benazolin, 2,4-D and atrazine on F400 and AC4, particle size 355-420 µm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration (mg L(^{-1}))</th>
<th>(q_e) (mg g(^{-1}))</th>
<th>(k_2) (g mg(^{-1}) min(^{-1}))</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin on F400</td>
<td>10</td>
<td>43.86</td>
<td>5.44x10(^{-4})</td>
<td>0.9966</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>17.57</td>
<td>1.79x10(^{-3})</td>
<td>0.9962</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.97</td>
<td>1.42x10(^{-3})</td>
<td>0.9955</td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>10</td>
<td>47.17</td>
<td>3.01x10(^{4})</td>
<td>0.9967</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>19.46</td>
<td>1.35x10(^{-3})</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.84</td>
<td>1.96x10(^{-3})</td>
<td>0.9969</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>10</td>
<td>50.00</td>
<td>3.29x10(^{-4})</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.87</td>
<td>1.71x10(^{-3})</td>
<td>0.9981</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18.02</td>
<td>2.74x10(^{-4})</td>
<td>0.9809</td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>10</td>
<td>48.54</td>
<td>5.35x10(^{-4})</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.79</td>
<td>9.11x10(^{-4})</td>
<td>0.9977</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15.53</td>
<td>4.03x10(^{-4})</td>
<td>0.9938</td>
</tr>
<tr>
<td>Atrazine on F400</td>
<td>4</td>
<td>18.59</td>
<td>1.93x10(^{-3})</td>
<td>0.9985</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.51</td>
<td>3.42x10(^{-3})</td>
<td>0.9985</td>
</tr>
<tr>
<td>Atrazine on AC4</td>
<td>4</td>
<td>18.87</td>
<td>1.35x10(^{-3})</td>
<td>0.9965</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.23</td>
<td>3.44x10(^{-3})</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

Figures 6.7 - 6.9 show the comparison of the experimental sorption kinetic data of benazolin, 2,4-D and atrazine with the theoretical data obtained from the pseudo second order equation. The graphs in the linear form are also shown in the Appendix. It is apparent from the results that the higher the initial concentration, the faster the adsorption rate. A closer look at the results shows that the sorption rate is high at the initial period of the adsorption process. This may be due to the high concentration gradient existing between the solute in solution and that in the adsorbent phase in the initial stages of the process. The higher concentration gradient is promoted by an increased number of vacant active sites available at the initial stage of the experiment. As the adsorption process proceeds, the gradual filling of the vacant sites takes place resulting in the decrease of the concentration gradient. This leads to the gradual decrease in the sorption rate in the final stages from 50 to ≈ 150 minutes.
Figure 6.7 Sorption kinetics for benazolin on F400 and AC4.

Figure 6.8 Sorption kinetics for 2,4-D on F400 and AC4.
The effect of particle size on the rate of removal of benazolin and 2,4-D are shown in Figures 6.10 and 6.11. The experiments were performed using initial solute concentration of 10 mg/L in all instances. It can be observed that for both molecules, the sorption rate is faster for particle size 355-420 µm than for 710-850 µm. This is expected because finer particle sizes offer a larger surface area that can easily be accessed by the solute molecules. Table 6.6 shows the pseudo second order kinetic parameters for benazolin and 2,4-D for size ranges 355-420 µm and 710-850 µm. The parameter $q$ does not show significant change with decreasing particle size. Hamadi et al. (2004) made similar observations when they were investigating the adsorption of paraquat dichloride from solution by activated carbon derived from used tyres. They concluded that such observation was consistent with sorption process where intra-particle diffusion was negligible. The results also show that the rate constant $k_2$ varies inversely with the particle size, and Tsai et al. (2005) also made similar observations when they investigated the adsorption of bisphenol-A onto minerals and carbon adsorbents.

**Figure 6.9** Sorption kinetics for atrazine on F400 and AC4.
Figure 6.10 Effect of adsorbent particle size on sorption kinetics of benazolin on F400 and AC4. (N.B. Size range is in µm)

Figure 6.11 Effect of adsorbent particle size on sorption kinetics for 2,4-D on F400 and AC4. (N.B. Size range is in µm)
Table 6.6 Kinetic constants for benazolin, 2,4-D and atrazine on F400 and AC4, particle size 355-420 μm and 710-850 μm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size range</th>
<th>$q$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$min$^{-1}$)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin on F400</td>
<td>355-420</td>
<td>43.86</td>
<td>$5.44 \times 10^{-4}$</td>
<td>0.9966</td>
</tr>
<tr>
<td></td>
<td>710-850</td>
<td>43.10</td>
<td>$2.16 \times 10^{-4}$</td>
<td>0.9962</td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>355-420</td>
<td>47.17</td>
<td>$3.01 \times 10^{-4}$</td>
<td>0.9967</td>
</tr>
<tr>
<td></td>
<td>710-850</td>
<td>45.87</td>
<td>$2.69 \times 10^{-4}$</td>
<td>0.9980</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>355-420</td>
<td>50.00</td>
<td>$3.29 \times 10^{-4}$</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>710-850</td>
<td>49.50</td>
<td>$1.77 \times 10^{-4}$</td>
<td>0.9981</td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>355-420</td>
<td>48.54</td>
<td>$5.35 \times 10^{-4}$</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>710-850</td>
<td>52.63</td>
<td>$1.44 \times 10^{-4}$</td>
<td>0.9977</td>
</tr>
</tbody>
</table>

The effect of temperature on the sorption kinetics of benazolin and 2,4-D was carried out at temperatures 298, 308 and 318 K and the results are as illustrated in Figures 6.12 and 6.13. As shown by the graphs, an increase in temperature led to an increase in sorption rate of the herbicides. Al-Ghouti et al. (2005) reported that an increase in temperature results in the corresponding increase of the rate of diffusion of the solute molecules across the external boundary layer and in the internal pores of the adsorbent. This is caused by the reduction of the viscosity of the solution as the temperature is increased. From equation 6.6, the activation energy parameters were evaluated and the correlations are given in Table 6.7. The linear plots for the evaluation of activation energy are given in the Appendix. The activation energies were in the region between 26-39 kJ mol$^{-1}$; such values are too low to cause breaking and formation of bonds. It is widely accepted that activation energies lower than 42 kJ mol$^{-1}$ indicate diffusion controlled processes while higher activation energies (greater than 42 kJ mol$^{-1}$) indicate chemically controlled processes. Al-Ghouti et al. (2005) maintains that the diffusion process is related to the movement of the adsorbate to the external surface of the adsorbent and not the diffusivity of solute molecules along micropore wall surfaces in the adsorbent particle, since the temperature dependence of the pore diffusivity is relatively weak.

The positive values of the activation energies indicate that an increase in solution temperature favours the adsorption of benazolin and 2,4-D on F400 and AC4. The
positive values of activation energies also indicate that the sorption process of benazolin and 2,4-D on F400 and AC4 is endothermic. This result is consistent with the observation in Section 6.1 concerning positive $\Delta H$, which are also an indication of an endothermic system. The low value of the activation energy shows that adsorption of benazolin and 2,4-D on F400 and AC4 is by a physisorption process. Therefore, the rate limiting step of the sorption process would predominantly involve a physical process.

**Figure 6.12** Effect of temperature on the sorption kinetics of benazolin on F400 and AC4.
Figure 6.13 Effect of temperature on the sorption kinetics of 2,4-D on F400 and AC4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature K</th>
<th>( k_2 ) (gm g(^{-1}) min(^{-1}))</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin on F400</td>
<td>298</td>
<td>5.44x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>7.94x10(^{-4})</td>
<td>26.610</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.072x10(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>298</td>
<td>3.01x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6.59x10(^{-4})</td>
<td>38.925</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>8.12x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>298</td>
<td>3.29x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6.48x10(^{-4})</td>
<td>38.012</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>8.66x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>298</td>
<td>5.35x10(^{-4})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>1.08x10(^{-3})</td>
<td>32.873</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.24x10(^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.7 Activation energy parameters of benazolin and 2,4-D on F400 and AC4.
Solid-liquid sorption processes are usually characterized by three consecutive steps: external diffusion, internal diffusion and the adsorption stage. The adsorption stage is usually fast and can be considered negligible. External diffusion involves the movement of adsorbate molecules from the bulk of the solution towards the surface of the adsorbent. This is followed by movement of molecules through the boundary layer while internal diffusion involves the movement of molecules in the interior of the particles. In the solid-liquid adsorption processes, there is always the involvement of the two mechanisms. For example, the first stage of the process is usually dominated by external diffusion which facilitates loading of the solute to the adsorbent before internal diffusion takes place. Therefore, it is essential to distinguish between external and internal diffusion and the information is also required for design purposes. If the external transport resistance is greater than the internal transport resistance, then the rate is controlled by film diffusion; if the external transport is less than the internal transport, particle diffusion becomes the dominant mechanism. Mohan and Singh (2002), postulated that external transport is the rate-limiting step in systems in which there is poor mixing, low concentration of adsorbate, small particle size and high affinity of adsorbate for the adsorbent. On the contrary, internal diffusion dominates in systems with high concentration of adsorbate, good mixing, large particle size of adsorbent and low affinity of adsorbate for the adsorbent.

In order to identify the slowest steps in the adsorption process, the Boyd kinetic equation was employed. The equation was derived by Boyd et al. (1947) when they were investigating equations governing the rate of ion-exchange based on diffusion mechanisms. Two types of diffusion processes were considered and these are “particle diffusion” and “film diffusion.” The authors concluded provisionally that at low solute concentrations, film diffusion is rate controlling while at high concentrations, particle diffusion becomes rate controlling. Reichenberg (1953) followed up the work by Boyd et al. (1947) when he investigated the kinetics of sodium-hydrogen exchange on sulphonated crosslinked polystyrenes in bead form. Reichenberg arrived at the same conclusion as Boyd et al. (1947) when he realised that at low concentration of the solute, the rate is controlled by film diffusion, while at high concentrations, the rate is controlled by particle diffusion.
Boyd et al. (1947) derived an equation for the kinetics of particle diffusion with the assumption that the adsorbent particles were uniform spheres of radius $r_o$ and they maintained that under conditions where particle diffusion was the sole rate-controlling process, the following expression should hold:

$$F = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_i t}{r_o^2}\right)$$

(6.9)

where $F$ is the fractional approach to equilibrium at time $t$, and $B$ is given as:

$$B = \frac{\pi^2 D_i}{r_o^2}$$

(6.10)

$D_i$ is the effective diffusion coefficient of solute in the adsorbent phase. Equation (6.9) can be re-arranged while taking natural logarithm to obtain the equation

$$Bt = -0.4977 - \ln(1 - F)$$

(6.11)

The values of $Bt$ can be evaluated for different time intervals using equation (6.11). A plot of $-0.4977 - \ln(1 - F)$ against time $t$ can be employed to test the linearity of the experimental values. If the plots are linear and passing through the origin, then the slowest step in the adsorption process is the internal diffusion and vice versa.

The plot $-0.4977 - \ln(1 - F)$ against $t$ for benazolin and 2,4-D for different initial concentrations are shown in Figures 6.14 and 6.15. It is apparent from the graphs that the plot $-0.4977 - \ln(1 - F)$ against $t$ do not pass through the origin, hence the adsorption process is mainly controlled by film diffusion. As mentioned previously, film diffusion controlled processes are favoured when mixing is poor, when the concentration of adsorbate is low, when the particle size is small and when there is high affinity of adsorbate for the adsorbent. Vadivelan and Kumar (2005) investigated the sorption kinetics of methylene blue and they obtained linear $Bt$ against $t$ plots but not passing through the origin for all the initial concentration range they employed, and they concluded that the sorption process was film diffusion controlled.

Mittal et al. (2005) investigated the removal of malachite green from wastewater and they found out that at low initial concentrations ($< 5 \times 10^{-5}$ M), the $Bt$ against $t$ plots were linear but did not pass through the origin, and they attributed the
observation to film diffusion controlled process. At concentrations higher than $5 \times 10^{-5}$ M, the $Bt$ against $t$ plots were found to be linear and passing through the origin.

In this investigation, the maximum initial concentrations employed are $4.1 \times 10^{-5}$ M and $4.5 \times 10^{-5}$ M for benazolin and 2,4-D respectively. The calculated effective diffusion coefficient ($D_i$) values at different initial herbicide concentrations are given in Table 6.8. The average $D_i$ values were found to be $1.63 \times 10^{-12}$ and $1.66 \times 10^{-12}$ m$^2$s$^{-1}$ for benazolin on F400 and AC4, respectively while for 2,4-D, the average values were $1.55 \times 10^{-12}$ and $1.40 \times 10^{-12}$ m$^2$s$^{-1}$ in samples F400 and AC4, respectively. Atrazine had average $D_i$ values of $2.19 \times 10^{-12}$ for the samples F400 and AC4. Similar $D_i$ values were obtained by Gupta et al. (2002) when they were investigating the removal of herbicides (i.e. lindane and malathion) from wastewater using bagasse fly ash derived from waste from the sugar industry.

Figure 6.14 Plot of $Bt$ versus time for benazolin on F400 and AC4.
Figure 6.15 Plot of $B_t$ versus time for 2,4-D on F400 and AC4.

Figure 6.16 Plot of $B_t$ versus time for atrazine on F400 and AC4.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration (mg L⁻¹)</th>
<th>Effective diffusion coefficient, $D_i$ (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin on F400</td>
<td>10</td>
<td>1.43x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.79x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.66x10⁻¹²</td>
</tr>
<tr>
<td>Benazolin on AC4</td>
<td>10</td>
<td>1.47x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.83x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.67x10⁻¹²</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>10</td>
<td>1.40x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.86x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.39x10⁻¹²</td>
</tr>
<tr>
<td>2,4-D on AC4</td>
<td>10</td>
<td>1.56x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.49x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.15x10⁻¹²</td>
</tr>
<tr>
<td>Atrazine on F400</td>
<td>4</td>
<td>1.86x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.52x10⁻¹²</td>
</tr>
<tr>
<td>Atrazine on AC4</td>
<td>4</td>
<td>2.10x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.28x10⁻¹²</td>
</tr>
</tbody>
</table>

Table 6.8 Effective diffusion coefficient for benazolin and 2,4-D on F400 and AC4.

6.3 Conclusions

Experiments on the effect of temperature on the adsorption of the target herbicides resulted in the extraction of some thermodynamic parameters, i.e $\Delta G$, $\Delta H$ and $\Delta S$. The thermodynamic parameters revealed that adsorption of the target herbicides on activated carbon was spontaneous and endothermic for benazolin and 2,4-D, while atrazine showed that its sorption mechanism was exothermic. The values of $\Delta H$ for benazolin and 2,4-D indicated that adsorption involved a physisorption mechanism, implying that the molecules retain their identity in the sorbed state. The sorption kinetic data fitted the pseudo-second order kinetic model very well for all the herbicides. Kinetic studies on benazolin and 2,4-D confirmed that adsorption of the two herbicides involved an endothermic process and also, the activation energy evaluation revealed that a physisorption mechanism was involved in the uptake of the herbicides. The Boyd plot indicated that external mass transfer was the slowest step in the sorption process.
6.4 References


7 CONCLUSIONS AND FUTURE WORK

7.1 General Conclusions

The main objective of this research was to evaluate the sorption performance of a coal based activated carbon F400 and its modified series for the removal of atrazine, benazolin, 2,4-D and copper ions from water. In order to understand the mechanism of the adsorbent-adsorbate association, physical and chemical characterisation of the carbon samples was performed. The characterisation results also gave an indication of the physical and chemical changes that occurred during surface modification of the conventional sample F400.

Characterisation results revealed that nitric acid oxidised samples possessed weakly acidic functional groups and the by-product of oxidation was the formation of humic substances which caused blockage in the micropore regions of the oxidised samples. Post oxidation treatments of the oxidised samples revealed that the humic substances in the oxidised samples could be washed out by 0.1 M sodium hydroxide. Annealing of the conventional sample resulted in the elimination of weakly acidic oxygen containing functional groups and the resultant sample showed some basic properties. A sample possessing some amino functional groups was successfully produced from the annealed sample through a two stage process that involved nitration and reduction. Characterisation results however showed that weakly acidic functional groups were simultaneously formed during the amination process.

Modification of the conventional adsorbent sample affected the adsorption performance of the target adsorbate samples. Sorption of herbicides was highly favoured in the conventional and annealed sample while lower performances were observed on oxidised and aminated samples. The results gave an indication that sorption of the herbicides was through a $\pi-\pi$ association of the adsorbate and the adsorbate. The low performance in the oxidised and aminated samples was caused by the high amounts of oxygen which in turn reduces the $\pi$ electron intensity in the basal plan of the carbon samples. In the conventional and annealed sample, the sorption capacity followed the trend 2,4-D > benazolin > atrazine. The trend is related to the structural configuration (size) of the molecules. 2,4-D is favoured
most because it is the smallest molecule while atrazine is least favoured due to its large size. Investigations revealed that adsorption of benazolin and 2,4-D was through an endothermic process while that for atrazine was through an exothermic process. Oxidised carbon samples showed higher affinity of copper ions than the remaining samples. The observed high affinity of oxidised carbons for copper was thought to be due to a combination of ion exchange mechanism and co-ordination bonding with oxygen containing functional groups.

Sorption kinetic experiments were performed for all the herbicides on the best performing samples. The model that was employed to analyse the data showed that at the experimental conditions employed, film diffusion is thought to be the rate controlling mechanism. The results showed that the kinetics of the herbicides was affected by changes in the initial concentration and the particle size of the adsorbents. The investigation also showed that kinetics of the herbicides were affected by changes in temperature. It was established from the kinetic experiments that the activation energy of adsorption was in the region where adsorption through physisorption is favoured.

The investigations showed that removal efficiency of the herbicides can be increased through carbons with minimal oxygen containing acidic functional groups. On the other hand, increased oxygen containing acidic functional groups improves the uptake of copper ions.

7.2 Future Work
The present study has given a basic understanding of the interaction between the target adsorbates and a conventional activated carbon and its modified series. However, this study only investigated spiked ultrapure water samples and hence further trials are required using water from treatment works prior to granular activated carbon adsorption.

The effect of pH on the sorption of the herbicides and metal ions needs also to be investigated since adsorption organic molecules is dependant on their pKa values. Also, it is well known that metal ions in water exist in different forms, depending
on the pH of the solution, hence it would be interesting to monitor the sorption of capacity of the various forms with respect to pH.

The chemistry of activated carbon is not well defined because of structural defects; hence its chemical and physical properties can be difficult to control. Therefore, investigations using carbonised polymers can bring more conclusive data since their chemistry is well defined and desired modifications can easily be achieved.

Studies aimed at regenerating the herbicide and metal laden activated carbon need also to be investigated. Sorbent regeneration is vital as this results in prolonged use of the adsorbents which ultimately leads to increased economic viability of a treatment plant.
APPENDIX

A.1 Effect of temperature on the adsorption of benazolin on F400.

A.2 Effect of temperature on the adsorption of benazolin on AC4.
A.3 Effect of temperature on the adsorption of 2,4-D on F400.

A.4 Effect of temperature on the adsorption of 2,4-D on AC4.
A.5 Plot of $\Delta G$ versus Temperature for atrazine

A.6 Plot of $\Delta G$ versus Temperature for benazolin and 2,4-D
A.7 Pseudo-second order plot for benazolin sorption on F400 and AC4.

A.8 Pseudo-second order plot for 2,4-D sorption on F400 and AC4.
A.9 Pseudo-second order plot for atrazine sorption on F400 and AC4.

A.10 Pseudo-second order plot for benazolin sorption on F400 and AC4. Effect of particle size.
A.11 Pseudo-second order plot for 2,4-D sorption on F400 and AC4. Effect of particle size.

A.12 Arrhenius plot of the pseudo second-order kinetics for benazolin.
A.13 Arrhenius plot of the pseudo second-order kinetics for 2,4-D.
PUBLICATIONS

Conference Proceedings


Chingombe, P., Saha B. and Wakeman R.J., "Sorption of herbicide and metal ions onto conventional and surface modified active carbons", *7th World Congress of Chemical Engineering (WCCE 7)*, Glasgow, Scotland, 2005, Ref 82461 (1-10 p), [CD-ROM].

Journal Papers


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Surface modification and characterisation of a coal-based activated carbon

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Abstract

Surface modification of a coal-based activated carbon (F400) was performed using thermal and chemical methods. Nitric acid oxidation of the conventional sample produced samples with weakly acidic functional groups and the presence of such groups was confirmed by Fourier transform infra red (FTIR) spectroscopy, pH titration, zeta potential measurements and sodium uptake capacity results. There was a significant loss in microporosity of the oxidised samples which was caused by humic substances that were formed as a by-product during the oxidation process. Thermal treatment produced a carbon with some basic character while amination of the thermally treated carbon gave a sample containing some amino (–NH₂) groups and these groups were detected by X-ray photoelectron spectroscopy (XPS) analysis.

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Keywords: Activated carbon; Chemical treatment; Heat treatment; Surface oxygen complexes; Characterisation

1. Introduction

Activated carbons have been proven to be effective adsorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environments [1–4]. Their large sorption capacity is linked to their well developed internal pore structure, surface area and the presence of a wide spectrum of surface functional groups. Since the limits for pollutants are constantly being revised, the industry is left with the challenge of employing the most effective adsorbents with specific chemical properties. Hence, of late research on activated carbons has focused on their modification and characterisation in order to meet the growing demand for cleaner air and water [3–8].

Since activated carbon consists of functional groups bonded to ‘fused’ aromatic rings, they would be expected to possess chemical properties similar to those in the aromatic hydrocarbons. Therefore, chemical reactions that apply to aromatic hydrocarbons would be expected to apply to activated carbons. The existence of surface functional groups on the carbon matrix therefore implies they can be manipulated by thermal or chemical treatments to produce adsorbents that are tailored for particular functions. For example, a number of authors have successfully employed oxidation reactions to produce activated carbons that possess weakly acidic functional groups [3,4,7]. Such carbons are known to have a high affinity for metals when compared to the parent carbon. Introduction of nitrogen-containing functional groups has also been performed and such carbons have been reported to increase catalytic activity of carbon in oxidation reactions [9,10]. Thermal treatments have produced activated carbons with basic character.
and such carbons are effective in the treatment of some organic hydrocarbons [6].

Even though activated carbon has the largest market as an adsorbent in wastewater control, the specific sorption mechanisms for organic and inorganic solutes are still not clear. It has been postulated that organic compounds adsorb through a \( \pi-\pi \) dispersion interaction mechanism [11]. This mechanism assumes the interaction of the \( \pi \) electrons of the aromatic species with the \( \pi \) electrons of the basal planes of the carbon. However, some experimental data suggest the sorption of organic species may be due to an electron donor–acceptor mechanism [1]. This involves the formation of a complex between the adsorbed molecule and the carbonyl group of the activated carbon. The idea of the formation of hydrogen bonding on the surface oxides of the carbon by the organic solutes has also been put forward. Pinto and co-workers [12] have also proposed a mechanism that involves a combination of hydrogen bonding with carbonylic groups and the \( \pi-\pi \) dispersion interaction. There has also been uncertainty pertaining to the adsorption mechanism of inorganic species. Some researchers have suggested ion exchange and complex formation as the mechanism of adsorption [3,13]. However, evidence of the interaction of transition metal ions with the \( \pi \) electrons of the carbons has also been revealed.

In order to understand the adsorption mechanism of the organic/inorganic species with activated carbon, information about the physical properties and the chemical nature of the surface functional groups is required. The chemical nature of the adsorbate must also be known. However, understanding the sorption mechanisms from data derived from literature is difficult because the carbon materials reported are derived from a wide variety of precursors. Furthermore, the adsorbents vary considerably in their physical and chemical properties. If the above properties are not harmonised, it becomes difficult to make judgements on the exact nature of the adsorbent–adsorbate interaction. Therefore, the objective of this work is to investigate the effect of surface modification on the adsorption of trace metal ions and organic micropollutants from water. This paper highlights the first part of our research, i.e. the preparation and characterisation of surface modified active carbon samples for environmental remediation.

2. Experimental

2.1. Materials

A coal-based commercial granular activated carbon, F400, was used as a starting material in the present investigations. The activated carbon sample was obtained from Chemviron, USA. Before the modification processes, the carbon was washed with deionised water and dried at 383 K for 24 h. The dried sample was then subjected to different modes of modification which involved nitric acid oxidation, amination and annealing in the presence of hydrogen. Concentrated nitric acid solution (specific gravity 1.42, 70%) was obtained from Fisher Scientific, UK. All other chemicals were of analytical grade and obtained from the same source (Fisher Scientific, UK).

2.2. Sample preparation

A known amount of the washed and dried F400 sample was oxidised at 363 K using nitric acid and distilled water at a ratio of 1:1 (v/v). The reaction mixture was heated to 363 K and the reaction was allowed to continue for 6 h with continued stirring. The reaction solution was removed and a fresh reaction mixture of nitric acid and water was introduced. The reaction was allowed to continue for a further 3 h under the same reaction conditions. The oxidised carbon was then washed with distilled water until no further change in pH could be detected. The resultant water washed sample (after oxidation) was divided into three portions. The first portion was denoted AC1, and this is a sample that was washed with water after the oxidation reaction. AC2 was a sample that was washed with 0.1 M sodium hydroxide to remove humic substances that are a by-product of the oxidation process. The washing was continued until no further colouration from the humic substances could be detected. Reconditioning of the sample to the hydrogen form was performed using 0.1 M hydrochloric acid and further washing with distilled water was done until the pH of the supernatant solution stabilised to a pH of about 4.0. The third sample, denoted AC3, was as a result of heating the oxidised sample at a temperature of 580 K under vacuum of 2 mm Hg for 12 h to remove humic substances. Sample AC4 was obtained by annealing F400 in a quartz reactor. Prior to the annealing process the sample was conditioned in a flow of hydrogen (3.3 \( \times \) 10\(^{-6} \) m\(^3\)/s) for 45 min at ambient temperature. The furnace temperature was then raised at a rate of 10 °C/min until it reached 1173 K where it was maintained for 3 h. After the annealing cycle, the furnace was allowed to cool down and the flow of hydrogen was maintained even during the cooling process.

Part of the sample that was produced from the furnace treated carbon (AC4) was used to generate an aminated sample AC5. The carbon was charged together with acetic anhydride ([CH\(_3\)CO\(_2\)O]) into a 1 L five-neck flask immersed in an ice cold water bath. Sulphuric acid was slowly fed into the reaction flask, and this was followed by addition of nitric acid. During the addition of the acids, the temperature was maintained below 283 K. The reaction was then allowed to continue for 24 h at a temperature of 293 K with constant stirring. The modified carbon thus obtained was washed.
Table 1

Summary of treatment of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical treatment</th>
<th>Temperature (K)</th>
<th>Exposure time (h)</th>
<th>Post-treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>AC1</td>
<td>HNO3</td>
<td>363</td>
<td>9</td>
<td>H2O wash</td>
</tr>
<tr>
<td>AC2</td>
<td>HNO3</td>
<td>363</td>
<td>9</td>
<td>NaOH wash</td>
</tr>
<tr>
<td>AC3</td>
<td>HNO3</td>
<td>363</td>
<td>9</td>
<td>Heat-treat</td>
</tr>
<tr>
<td>AC4</td>
<td>N/A</td>
<td>1173</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>AC5</td>
<td>HNO3/H2SO4/NH3</td>
<td>298</td>
<td>48</td>
<td>Na2S2O4/(CH3CO)2O</td>
</tr>
</tbody>
</table>

thoroughly with deionised water contained in a glass column. Washing was performed until the outlet solution reached pH of approximately 4. The washed sample was then dried for 24 h at a temperature of 383 K. The reduction process of the nitrated sample was performed using sodium dithionite (Na2S2O4) as the reducing agent. The reduction of the carbon was performed for 24 h with continuous stirring in the presence of sodium dithionite, 35% aqueous ammonia and deionised water. The sample was thoroughly washed using deionised water until the pH at the outlet of the column was reduced to approximately 9. The sample was then dried for 24 h at 383 K in an oven. These various treatments are summarised in Table 1.

3. Characterisation methods

The details of various characterisation techniques that were employed for this work are detailed below.

3.1. Scanning electron micrograph (SEM)

The surface morphology of the carbons were analysed using a Cambridge Instrument 360 scanning electron microscope at accelerating voltages of 10–20 kV. Prior to analysis, samples were dried at 373 K and stored in a desiccator overnight. The samples were then mounted on an aluminium platform for analysis.

3.2. Surface area and pore size distribution

Surface area and pore size distributions for the samples were measured using a Micromeritics ASAP 2010 surface area analyser that uses a nitrogen adsorption–desorption method. The samples were initially outgassed at 393 K for 24 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the carbons. The density functional theory (DFT) model was used to analyse the results.

3.3. Elemental analysis

Elemental analysis of the carbon samples was performed in the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, UK. The analysis involved weighing the sample accurately on aluminium foil and then inserting into the instrument. Prior to the flash combustion process, the system was purged with Helium carrier gas. Flash combustion was then performed at 2073 K, and the gaseous combustion products were quantified using a thermal conductivity detector. Results were obtained as percentages of carbon and nitrogen, and the oxygen content was determined by difference.

3.4. Fourier transform infra red (FTIR) spectroscopy analysis

Transmission infrared analysis of the activated carbons was performed on a Nicolet DXC20 FTIR spectrometer which consisted of liquid nitrogen cooled mercury–cadmium–telluride detector and a Spectra Tech diffuse reflectance accessory. Samples of particle size <45 µm were first dried for 24 h at a temperature of 383 K. The dried samples were mixed with finely divided KBr at a ratio of 1:100. FTIR spectra were recorded at a resolution of 4 cm−1 and with 200 scans per sample and an aperture setting of 15. A previously recorded background spectra of water vapour was subtracted from the spectrum of each sample.

3.5. X-ray photoelectron spectroscopy (XPS)

Sample AC5 was analysed by XPS. The analysis was performed on a VG ESCALAB MK I under 10−7 Torr vacuum. A pass energy of 100 eV was used in recording the scan spectra. The sample was dried at 283 K for 24 h before the analysis.

3.6. Sodium capacity determination

Sodium sorption capacity was determined in order to compare the total sorption capacity of the adsorbents for cations. This was achieved by contacting 200 mg of the sorbent with 25 mL of 0.1 M sodium hydroxide and the resultant mixture was allowed to equilibrate on an arm shaker for 72 h. The mixture was filtered to remove the adsorbent and 20 mL of the mixture was
pipetted out and back titrated using 0.1 M hydrochloric acid. Phenolphthalein was used as the indicator.

3.7. pH titrations

pH titration curves of the carbons were generated by accurately weighing 75 mg portions of the adsorbents of particle size <45 \mu m into 50 mL conical flasks. A standard solution of a volume of 10 mL of 0.1 M NaCl was added into each flask. Different initial pH was obtained by adding 0.1 M HCl or 0.1 M NaOH and the resultant solution was made up to 25 mL using deionised water. The samples were allowed to equilibrate for 48 h and the resultant pH was recorded using a Mettler-Toledo 340 pH meter. A pH against acid or alkali added was plotted to obtain the titration curves.

3.8. Zeta potential measurements

Samples prepared for pH titrations were used for the zeta potential measurements. The measurements were performed on a Malvern Zetasizer 3000 HSA. Measurements were done immediately after the pH measurements of the pH titration samples. The samples were injected to the Malvern Zetasizer 3000 HSA and the zeta potential was measured three times for a single sample to provide an average reading. Between the samples the cell was flushed with 30 mL of deionised water.

4. Results

4.1. Scanning electron micrograph (SEM)

Fig. 1 shows the SEM of (a) as-received and (b) AC1 samples. There is little difference in the surface morphology of the samples except for some apparent pore widening on AC1 that could have occurred from the oxidation process. It was noticed that the oxidised samples disintegrated to small particles when compared to F400 sample particles. This observation could be linked to the cleavage of C-O bridging bonds on the carbon surface during the oxidation process. The SEM images of AC2 and AC3 were similar in appearance to AC1 image. This implies that post-oxidation treatments of the carbon samples did not make any apparent change in the surface morphology of the adsorbents. The surface morphology for AC4 was compared to that of

![SEM images](image-url)
AC5. Modification of AC4 to produce AC5 had a visual impact on surface morphology. The surface looks spongy and to some extent eroded.

4.2. Surface area and pore size distribution

Figs. 2 and 3 are results from the pore size distribution measurements for the stated carbons. The results show that oxidation of the carbon resulted in the decrease in the BET surface areas for AC1 sample compared to F400. This is as a result of pore blockage in the micropores caused by the formation of humic substances during the oxidation process. Some researchers have attributed this observation to pore entrance blockage by the formation of oxygen functional groups that are direct products of oxidation. However, AC3 recorded higher values of surface area than AC1, implying that heat-treatment partly removed some of the humic acids lodged in the micropores. Washing the oxidised carbons with sodium hydroxide seems to be a more effective way of removing the humic acids. AC2, which was a sample washed with sodium hydroxide, showed the highest surface area values amongst the oxidised samples as shown in Table 2. Similar results have been reported by Saha et al. [14]. They attributed that such increase in surface area is due to the enhancement of the mesopore region. AC4 shows a higher value of the BET than F400 and the oxidised carbons.

This is expected since heat-treatment eliminates some oxygen-containing functional groups that are not stable at high temperatures. The appearance on the graph of a 'well' in the region between 9 and 10 Å is caused by a DFT model induced artifact which cannot account for values in that region and it does not suggest a decrease in surface area.
Table 2
BET surface area results

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>790</td>
</tr>
<tr>
<td>AC1</td>
<td>658</td>
</tr>
<tr>
<td>AC2</td>
<td>822</td>
</tr>
<tr>
<td>AC3</td>
<td>736</td>
</tr>
<tr>
<td>AC4</td>
<td>960</td>
</tr>
<tr>
<td>AC5</td>
<td>836</td>
</tr>
</tbody>
</table>

Table 3
Elemental analysis of the adsorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Elements (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>F400</td>
<td>89.48</td>
</tr>
<tr>
<td>AC1</td>
<td>82.70</td>
</tr>
<tr>
<td>AC2</td>
<td>83.80</td>
</tr>
<tr>
<td>AC3</td>
<td>84.30</td>
</tr>
<tr>
<td>AC4</td>
<td>92.73</td>
</tr>
<tr>
<td>*C-NO₂</td>
<td>84.91</td>
</tr>
<tr>
<td>AC5</td>
<td>88.12</td>
</tr>
</tbody>
</table>

* Supposed intermediate nitration product in the nitration process.

in pore volume. Mesoporosity on both samples remained comparable the same.

4.3. Elemental analysis

Table 3 gives the results of the elemental analysis of all the samples under investigation. It is apparent that on oxidation of the conventional sample the oxygen content increased considerably. The descending order of the oxygen content is as follows: AC1 > AC2 > AC3 > F400 ≈ AC5 > AC4. Generally, oxidising activated carbon always results in the increase of the oxygen content of the carbon; however the amount gained depends on the method and precursor used. In contrast, the annealed sample possesses the lowest oxygen content. This is expected, since at elevated temperature most of the acidic oxygen-containing functional groups are unstable and are subsequently removed. For example, Swiatkowski et al. [15] used voltammetric studies to monitor the gradual thermal decomposition of activated carbon surface oxygen complexes. They reported that at 1173 K functional groups –COOH and =COO will have diminished to zero while =C=O and –C=OH is reduced to about 50% and 14%, respectively. Radovic and Menéndez [16] annealed a wood-based carbon at 1223 K for 3 h in the presence of hydrogen, and they reduced the oxygen content from 15.1% for the conventional carbon to 0.3% for the annealed sample. In this work, annealing the conventional carbon only achieved a 27% reduction to 7.27%. The difference in results could be due to the difference in the precursor of the conventional carbons used and also Radovic and Menéndez [16] subjected their sample to more severe conditions. Also, exposure of the annealed sample to the atmosphere would have resulted in a significant uptake of oxygen from the atmosphere. The oxygen content of the intermediate nitration product *C-NO₂ is higher than the parent sample (AC4), implying that the nitration process fixed some oxygen-containing functional groups on the intermediate sample. A closer look at the elemental values for the intermediate product however shows that the amount of oxygen added during the nitration process is not in direct stoichiometric relationship to the nitrogen added in the expected *C-NO₂ product. Hence this implies that some of the oxygen is involved in the formation of carbon–oxygen functional groups. It is interesting to note that the percentage nitrogen in the intermediate product is the same as in the AC5 sample. Also, it is apparent that the reduction process was effective since the oxygen content of the intermediate product is higher than the supposedly reduced product, AC5.

Nitric acid oxidation introduced small amounts of nitrogen as shown in Table 3. Also it can be observed that annealing totally removes the nitrogen but the amination process fixes a marginally higher content of nitrogen than in the oxidised samples. Bautista-Toledo et al. [17] attributed this observation to the formation of nitro and nitrate aromatic compounds.

4.4. Fourier transform infra red (FTIR) spectroscopy analysis

FTIR spectra for the F400 oxidised carbon range are depicted in Fig. 4. The results show some pronounced peaks at wave numbers 1240, 1610 and 1750 cm⁻¹. The spectra for AC1, AC2 and AC3 show some marked similarities, suggesting that they could possess similar groups on their surfaces. The received sample (F400) does not show a peak at 1750 cm⁻¹, and also its peak at 1240 cm⁻¹ is less pronounced than that for the other oxidised carbon species.

The peak at 1240 cm⁻¹ is usually difficult to assign because of a number of overlapping bonds that are superimposed. The superimposed peaks can be as a result of ether, epoxide and phenolic structures in various chemical environments. Beniak et al. [18] reported that tertiary C–N stretching vibration may also result in the contribution of the peak in the region of 1240 cm⁻¹. The C–N contribution can probably explain the lack of a pronounced peak on as-received F400 sample which did not undergo nitric acid oxidation. The peak at 1610 cm⁻¹ can be attributed to quinone like structures, and this peak appears in all the samples. Sutherland et al. [19] and Shim et al. [7] have also observed such a peak. As mentioned earlier, the peak at 1750 cm⁻¹ appears on the oxidised samples only, but its position on the spectra of the other samples
Fig. 4. FTIR spectra for F400 and some selected samples.

Fig. 5. FTIR spectra for the humic substances from F400, AC1 and AC5.

makes it difficult for positive identification. However, Lopez et al. [20] obtained peaks in this region when they modified carbon samples by air oxidation and they assigned it to free carboxyl groups, lactone groups esters and carbonyl groups near the hydroxyl groups. The most logical explanation for the peak at 1750 cm\(^{-1}\) would be the existence of carboxyl groups that are formed as a result of nitric acid oxidation. This is also supported by the high sodium capacity results on the oxidised samples as opposed to F400 sample.

Fig. 5 shows the FTIR spectra for the humic substances obtained from samples F400, AC1 and AC5. The humic material from samples F400 and AC5 exhibit similar FTIR spectra and this suggests they have similar structures and functional groups. However, the spectra for AC1 differ markedly from F400 and AC5 samples, thus confirming that significant chemical structural changes occurred during nitric acid oxidation. A strong absorption band was observed at around 3400 cm\(^{-1}\) and this is assigned to carboxylic group O-H stretching [21,22]. The peak is more pronounced in the AC1 humic sample and this would imply the presence of more -OH groups from increased carboxylic groups than in AC5 and F400 humic samples. An absorption peak was observed on 1660 cm\(^{-1}\) and this peak is distinct in the AC1 humic sample, while in F400 and AC5 it appears as a shoulder along the 1450 cm\(^{-1}\) peak. Pradhan and Sandle [21], when studying oxidised carbons, assigned the peaks to carboxyl–carbonate structures in cases of HNO\(_3\) oxidised carbons. Schepetkin et al. [23] characterised humic substances from mumie and they observed strong absorbance at 1650–1720 cm\(^{-1}\) which they attributed to –COOH group vibrations. The fact that the peak appears as a distinct peak in sample AC1 would suggest a higher amount of –COOH groups than in the AC5 sample where the peak appears as a shoulder peak. The shoulder peak at 1660 cm\(^{-1}\) is more pronounced on the AC5 humic sample than in F400. The relative intensity of the peak follows the trend AC1 humic > AC5 humic > F400 humic. As shown in Fig. 5, the change in the relative intensity of this band parallels the oxygen content of the samples. Hence, it would be reasonable to suggest that there is more –COOH group in the AC5 sample than in the F400 sample. The peak at 1440 cm\(^{-1}\) can be attributed to CH bending of –CH\(_2\)- or –CH\(_3\)- groups while the peaks at 1160 cm\(^{-1}\) have been assigned to alcohols or ethers.

Fig. 6 shows the XPS N(1s) measurements for the AC5 sample. A peak assigned to nitrogen bonded to an aromatic group was detected at 399 eV. The peak at 399 eV is usually associated with amino groups attached to aromatic groups. The elemental results for the nitrated product \(\text{C}-\text{NO}_2\) and the final aminated product AC5 showed the presence of nitrogen introduced by the nitration process. As mentioned previously, the oxygen content of sample AC5 was lower than the intermediate \(\text{C}-\text{NO}_2\) thus giving evidence of the effectiveness of the reduction process. The reduction process involves the conversion of –NO\(_2\) species in the intermediate product to –NH\(_2\) of the final product AC5. It is also interesting to mention that the nitrogen
content of the two samples (intermediate and ACS) was the same. It is appropriate to mention also that there was no N(1s) peak that could be detected on the other samples. It implies that the nitrogen observed in the oxidised samples through the elemental analysis could be as a result of nitrate ions trapped in the pores of the oxidised carbons (AC1, AC2 and AC3), in a form difficult to remove even by extensive washing.

4.5. Sodium capacity

Sodium uptake capacity results (see Fig. 7) show the high affinity of oxidised carbons for sodium compared to as-received F400. This is due to the existence of carboxylic acid functionality in oxidised carbons. FTIR results seem to confirm the existence of such a group. Various treatments on AC2 and AC3 seem to reduce their sodium capacity when compared with the AC1 sample that did not undergo oxidation post-treatment. A possible explanation for the observation could be that oxidation post-treatment removed some humic acids. Humic acids have also been shown to participate in metal sorption [3]. The annealed sample AC4 showed no noticeable sodium capacity. This is expected since at high temperatures the acidic functional groups responsible for the sodium uptake are destroyed. However, in sample AC5 there is a significant sodium uptake and this implies that the amination process resulted in simultaneous fixation of some acidic functional groups.

4.6. pH titrations

The results for the pH titrations for as-received F400 and its modified series can be seen in Fig. 8. The most important aspect of the pH titration curves is the crossover point or point of zero charge (PZC). By definition, PZC is the pH at which the net surface charge of an adsorbent is zero. Depending on the modification process, it can be noted that oxidised carbons (AC1, AC2, AC3) possess lower PZC values than the rest of the carbon sample. This implies that acidic properties are more dominant in these carbons and are as a result of a higher number of weakly acidic functional groups than in other carbon samples. Also, Fig. 8 shows a more retarded decrease in pH for the oxidised samples, and this is another evidence of the presence of weakly acidic functional groups.

These weakly acidic functional groups are known to dissociate over a wide range of pH. PZC for AC5 is relatively low compared to F400 and AC4. This can be due to the presence of similar functional groups as in oxidised samples since modification of this sample involved the use of concentrated nitric acid.

4.7. Zeta potential measurements

The results for zeta potential measurements are shown in Fig. 9. The electrokinetic behaviour of activated carbon in solution is one of the most important properties in characterisation. Since activated carbons are amphoteric in nature due to the various functional groups on their surfaces and the presence of a π electron system that confers them with Lewis basic properties, it is always important to evaluate their isoelectric point (IEP). This is the pH at which the zeta potential is zero. The results show that there is a marked difference in the IEP between the oxidised samples (~1.5) and as-received material (6.0). The low IEP values for oxidised samples are due to the presence of weakly acidic carboxylic functional groups. It is known that dissociation of the carboxylic groups in activated carbon lies between pH 2
and 6. Thus, the dissociation of the groups renders the carbon surface negative. The dissociation of the carboxylic groups could be the reason for the steepness of the zeta potential curves of the oxidised carbons between pH ranges 1.5 and 5. Similar observations on zeta potential curves for oxidised carbons have been reported in literature [13,14,16]. It is also interesting to note that the zeta potential remains negative for the range of conditions studied. The F400 sample may consist of weakly acidic functionality with a higher dissociation pH and that might have caused higher isoelectric point when compared to oxidised carbons. AC5 sample also shows higher zeta potential than the oxidised carbons but its value is lower than in the conventional carbon. It can be seen that the zeta potential for this sample crosses the zero potential line which would imply the amphoteric nature of the sample. This is due to the presence of some amino groups as evidenced by the XPS spectra on AC5 sample. These groups impart basic properties to the sample. However, the IEP of AC5 remains low probably due to the high ratio of the acidic functional groups. Sample AC4 showed the highest IEP (7.8) value among all the samples. Heat-treatment seems to have removed some oxygen-containing surface groups as evidenced by the low oxygen ratio in the elemental analysis results. Reduction of oxygen groups after heat-treatment has also been reported by Pradhan and Sandle [21] and Menéndez and Radovic [16].

5. Discussion

Since activated carbon consists of condensed aromatic structures, organic chemical reactions can be used to modify their surfaces. In the case of modification by oxidation, as described by Vinke et al. [24] the reaction site is most likely to occur on the aliphatic side chains of the carbon because such sites are highly susceptible to oxidation. Modification of the conventional carbon, F400 produced by various techniques described in section 2 produced carbons of a variety of properties as shown by different characterisation techniques. Generally, the oxidised carbons showed that there was fixation of weakly acidic functional groups on their surfaces as shown by the FTIR peak at 1750 cm⁻¹ and the low values of the PZC and IEP. The fixation of the weakly acidic functional groups are thought to be similar to the reaction involving the oxidation of 9,10-dihydrophenanthrene and diphenylmethane with nitric acid [24].

Nitrogen can be added to the carbon by a similar reaction as in the nitration of benzene. The mechanism would involve the formation of the highly reactive nitronium ion (NO₂⁺), which will ultimately form the nitrated product as shown in reaction (c). In the case of oxidised carbons however, the nitrated 'product' would appear in small quantities due to the limited amount of the nitronium ion since its formation is favoured in the presence of concentrated sulphuric acid. In the case of sample AC5, the amination reaction was achieved via a two stage process. The first stage was the nitration stage where the nitric acid was mixed with concentrated sulphuric acid to form the nitronium ions which then reacts via electrophilic substitution of the hydrogen ion of the carbon matrix as shown in reaction (d). The nitro-species formed is reduced using a suitable reducing agent and in this case sodium dithionite was employed. If the elemental analysis results are considered, the intermediate species of the amination process, C-NO₂ has higher oxygen content than the final product AC5. This result then shows the effectiveness of the reduction reaction shown in reaction (e). This modification process is
another example of the application of a classic organic reaction on activated carbon modification. The reaction is shown in the illustration of the amination of reaction on activated carbon modification. The reaction of the particles' [26]. Effectively, the difference between PZC and IEP would give an indication of the surface charge distribution of the porous adsorbent. The electrochemical properties of the various samples are summarised in Table 4. Positive values would indicate more negatively charged external surface than the interior and vice-versa for negative values [15,26]. The F400 sample shows a positive value indicating more acidic functional groups on its external surface than its interior surface. However, oxidised carbons in spite of their low PZC and IEP possess higher PZC-IEP values than F400, and this would imply preferential external oxidation of the samples. Since activated carbon is a highly porous material it is inevitable that the oxidation process will be a diffusion controlled process with oxidation occurring faster on the external surface than the interior surface. Also, among the oxidised carbons it is noticeable that the value of PZC-IEP for sample AC2 is higher than for AC1 and AC3. Since AC2 was a sample washed with sodium hydroxide after oxidation, it is apparent that the removal of the humic substances had a bearing on the observed result. It is well known that humic substances contain in varying amounts functional groups in the form of carboxylic, phenolic, carbonyl, hydroxyl and others. The removal of such groups would imply that a significant amount of the negative charge in the interior of the microporous carbon is removed since the humic substances are contained in this region as shown by the pore size distribution diagram. The high values of the IEP and PZC on AC4 indicate its basic properties and these are expected to come as a result of (i) the elimination of weakly acidic functional groups through heat-treatment since such groups are unstable at 1173 K and (ii) from the oxygen free Lewis base sites within the activated carbon graphene layers. The low value of their difference, PZC-IEP (0.2) therefore indicates that heat-treatment was effective in removing the acidic groups from both the external and the interior surface of the carbon matrix. AC5 on the other hand possesses relatively low PZC and IEP compared to AC4. Fig. 9 shows that the sample possesses some acidic character. As has been mentioned previously the use of nitric acid in the nitration process would have resulted in the formation of such groups and its PZC-IEP value lies in the same region as that for the oxidised carbons implying the diffusion dependent nature of the process.

The presence of humic substances in samples F400, AC1 and AC5 is clearly shown in Fig. 5. The mechanism for the formation of humic substances is not clearly understood. However, Vinke et al. [24] have attributed it to the presence of aliphatic carbon that is contained between aromatic structures of the parent carbon. They postulated that the oxidation process results in the splitting of the aliphatic segments into smaller molecules that are readily soluble and can subsequently be washed. Verheyen et al. [25] also reported the formation of humic substances during nitric acid oxidation of coal. They used different concentration of nitric acid and they investigated the effect of the acid strength on the chemical structural changes of the coal. It was realised that some humic acids could be extracted from the oxidised coal using 0.5 M sodium hydroxide. In this study, for all the modified carbons, samples AC1 and AC5 showed that they contained humic substances, while AC3 and AC4 did not show signs of humic substances when washed with 0.1 M sodium hydroxide solution. It is interesting to note, however, that for samples AC1 and AC5, nitric acid was involved during their modification while in AC3 and AC4 heat-treatment was employed. This implies that humic substances are a by-product of the oxidation process. The reason for failure to extract humic substances in sample AC3 even though it had been oxidised would be due to heat-treatment of the sample. However, heat-treatment of the sample did not remove the humic substances as shown in the pore size distribution results. From this observation it is likely that heat-treatment causes some structural changes to the humic substances, but the nature of the changes are not very clear and the resultant material in not soluble in 0.1 M sodium hydroxide. Humic substances were also extracted from F400 sample even though it did not undergo oxidation. Possibly the humic material in this sample was developed during its activation process.

It is now widely accepted that the IEP represents the net external charge on the surface of the activated carbon in solution, while the PZC is a representation of the change in response to the net total surface charge of the particles' [26]. Effectively, the difference between

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>pH_PZC</th>
<th>pH_IEP</th>
<th>pH_IEP - pH_PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>7.5</td>
<td>6.0</td>
<td>1.5</td>
</tr>
<tr>
<td>AC1</td>
<td>4.0</td>
<td>1.2</td>
<td>2.8</td>
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<tr>
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<td>4.7</td>
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<td>1.3</td>
<td>2.6</td>
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<tr>
<td>AC5</td>
<td>6.5</td>
<td>3.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

It is now widely accepted that the IEP represents the net external charge on the surface of the activated carbon in solution, while the PZC is a representation of the change in response to the net total surface charge of the particles' [26]. Effectively, the difference between
6. Conclusions

It has been shown that applying different modes of modification of the carbon leads to samples with different chemical characteristics. Modification by oxidation led to the fixation of weakly acidic functional groups as indicated by FTIR, pH titration results, sodium capacity and zeta potential results. The oxidation process, however, produced some by-products in the form of humic substances which could be extracted by sodium hydroxide solution. The humic substances tend to get lodged in the micropores resulting in loss of microporosity as evidenced by the pore size distribution results. Besides the weakly acidic surface oxygen complexes, nitrogen was also detected by elemental analysis in the oxidised samples but it was attributed to nitrate ions lodged in the pores of the oxidised carbons. Hydrogen treatment at elevated temperature produced a sample with some basic characteristics. The basic nature of the sample is due to the removal of acidic functional groups that are not stable at high temperatures. A sample with some amino groups was also successfully prepared by a two stage process that involved nitration as one of the reagents. The results of the investigation demonstrate that it is possible to apply classic organic chemical reactions to achieve desired modified carbon samples. Therefore, from a practical point of view, by carefully applying relevant modification techniques, it is possible to prepare carbons targeted for specific environmental applications. We are currently engaged in further studies to apply these ranges of new materials for the removal of trace metal ions and organic micropollutants from aqueous solutions.

Acknowledgements

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References


Effect of surface modification of an engineered activated carbon on the sorption of 2,4-dichlorophenoxy acetic acid and benazolin from water

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Abstract

The performance of a conventional (F400) and a surface modified activated carbon (F400AN) has been investigated for the sorption of benazolin and 2,4-dichlorophenoxy acetic acid (2,4-D) from water. It was observed that the modified carbon, F400AN, which was obtained by annealing the conventional sample had a higher BET surface area (960 m² g⁻¹ compared to 790 m² g⁻¹) and it had a higher proportion of micropores. This was attributed to the loss of oxygen containing functional groups during the thermal treatment. Zeta potential and pH titration measurements also showed that acidic functionality had been lost on the F400AN sample. The adsorption data were analysed and were fitted well using the Langmuir isotherm. The modified carbon marginally out-performed the conventional activated carbon for sorption of these two herbicides. Thermodynamic parameters (∆G°, ∆H°, and ∆S°) were determined and their values indicated that the sorption process was spontaneous and endothermic for both herbicides. A pseudo-second-order kinetic model was employed for analysing the kinetic data. It was concluded that the herbicide sorption process was controlled by a film diffusion mechanism.

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Keywords: Activated carbon; Chemical treatment; Thermal treatment; Surface oxygen complexes; Characterisation; Benazolin; 2,4-Dichlorophenoxy acetic acid (2,4-D); Adsorption isotherm; Kinetic studies; Pseudo-second-order kinetic model

1. Introduction

The harmful effects of herbicides on human health and the environment have resulted in stringent legislation being imposed on the purity of drinking water. The contamination of drinking water by herbicides results from the control of weeds, leaching from agricultural lands, accidental spills, discharge from manufacturing plants and various other sources. Since there is a wide variety of herbicides varying in physical and chemical properties, it is difficult to apply a single method for their removal from water. Conventional water treatment processes such as filtration, disinfection, coagulation, and sedimentation have been reported to be more effective in removing less water soluble and easily degradable pesticides [1]. Ozone technology is a potentially attractive technique in wastewater treatment, but in some cases the ozone degradation products can be equally harmful.

Adsorption on activated carbon is one of the well-established and effective techniques for the removal of herbicides from water. The adsorptive efficiency of activated carbon is due to its well-developed internal pore structure, surface area, and surface reactivity. Typically, activated carbon consists of interwoven micropores, mesopores, and macropores, which are responsible for the high surface area of the carbons and hence high capacity for the adsorption of organic pollutants. The existence of surface functional groups in the activated carbon matrix also plays a part in the adsorption of organic molecules. The functional groups confer amphoteric character to the surface of the carbon and hence, depending on the pH and the chemical nature of the adsorbate, the adsorption mechanism may be governed through dipole–dipole interaction, H-bonding, covalent bonding, and ion exchange. Consequently, a conventional and a modified activated carbon were employed in this study for the adsorption...
of benazolin and 2,4-dichlorophenoxy acetic acid (which is referred to as 2,4-D).

Benazolin and 2,4-D are highly soluble herbicides which can be applied to control broad-leaved weeds in gardens and farming. Benazolin is a herbicide that was identified as a potential replacement for atrazine after it was banned for nonagricultural use in UK, while 2,4-D is a widely used herbicide due to its low cost and good selectivity. Because of its poor biodegradability, 2,4-D has been frequently detected in water bodies in various regions of the world [2-4]. Although considerable research has been carried out on adsorption of herbicides on activated carbon, not much focus has been given to benazolin and 2,4-D sorption from water. Homer and Streat [5] investigated the removal of highly soluble herbicides including benazolin on polymeric adsorbents while Aksu and Kabasakal [3] studied the adsorption of 2,4-D from aqueous solution by granular activated carbon. However, no systematic investigation on the performance of a conventional and a modified activated carbon toward the sorption of these two herbicides has appeared to date. Therefore, the objective of this study is to investigate the sorption performance of a conventional and a surface modified carbon in detail. Since the levels of herbicides in drinking water are tolerated at very low concentrations (<0.1 µg L⁻¹ for each herbicide) this work has generated its adsorption isotherms from adsorbate concentrations in the range 2-140 µg L⁻¹. Hence, for the quantification of the equilibrium concentrations of the herbicides, a solid phase extraction technique has been developed. Kinetic studies and adsorption isotherms of benazolin and 2,4-D onto these adsorbents have been investigated and the results have been analysed by applying conventional theoretical models.

2. Experimental

2.1. Materials

Acetonitrile and methanol (HPLC grade) were obtained from Fisher Scientific, UK, while analytical reagent grade 2,4-D and benazolin were obtained from Sigma-Aldrich, UK. The chemical structures of the two herbicides are shown in Fig. 1.

2.2. Adsorbent preparation and characterisation

A coal based commercial granular activated carbon, F400 obtained from Chemviron, USA, was used as a starting material in the present investigation. Before the modification process, the carbon was washed in deionised water and dried at 383 K for 24 h. The dried sample was then annealed in the presence of hydrogen. The modified sample was obtained by annealing F400 in a quartz reactor. Prior to the annealing process the sample was conditioned in a flow of hydrogen (3.33 x 10⁻⁶ m³ s⁻¹) for 45 min at ambient temperature. The furnace temperature was then raised at a rate of 10 K min⁻¹ until it reached 1173 K where it was maintained for 3 h. After the annealing cycle, the furnace was allowed to cool and the flow of hydrogen was maintained during the cooling process. The resultant engineered sample (annealed) was kept in an airtight container and it was labelled as F400AN. The detailed characterisation procedures adopted for this work are given below.

2.2.1. Surface area and pore size distribution measurements

Surface area and pore size distributions for the samples were measured using a Micromeritics ASAP 2010 surface area analyser that uses a nitrogen adsorption-desorption method. The samples were initially outgassed on the degas port of the analyser at 393 K for 24 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the carbons. The density functional theory (DFT) model was used to analyse the results.

2.2.2. pH titration

pH titration curves of the carbons were generated by accurately weighing 75 mg of the adsorbents of particle size < 45 µm into 50 ml conical flasks. Standard solutions of a volume of 10 ml of 0.1 M NaCl were added into each flask. Different initial solutions pH were obtained by adding successively larger amounts of 0.1 M HCl or 0.1 M NaOH and the resultant solution was made up to 25 ml using deionised water. The samples were allowed to equilibrate for 48 h and the resultant pH was recorded using a Mettler-Toledo 340 pH meter. The pH was plotted against the acid or alkali added to obtain the titration curves.

2.2.3. Zeta potential measurements

Samples prepared for pH titrations were used for the zeta potential measurements. The measurements were performed on a Malvern Mastersizer 3000 HSA. Measurements were done immediately after the pH measurements of the pH titration samples. The samples were injected and the zeta potential was measured 3 times for a single sample to provide an average reading. Between the samples the cell was flushed with 30 ml of deionised water.

Fig. 1. Chemical structures of (a) 2,4-D and (b) benazolin.
2.2.4. Sodium capacity determination

Sodium sorption capacity was determined in order to compare the total sorption capacity of the adsorbents for cations. This was achieved by contacting 200 mg of the sorbent with 25 ml of 0.1 M sodium hydroxide and the resultant mixture was allowed to equilibrate on an arm shaker for 72 h. The mixture was filtered to remove the adsorbent and 20 ml of the mixture was pipetted out and back titrated using 0.1 M hydrochloric acid using phenolphthalein as an indicator.

2.2.5. Elemental analysis

Elemental analysis of the carbon samples involved weighing the sample accurately on an aluminum foil and then inserted into the Perkin-Elmer 2400 Elemental Analyser (Series 2) instrument. Prior to the flash combustion process, the system was purged with helium carrier gas. Flash combustion was then performed at 2073 K, and the gaseous combustion products were quantified using a thermal conductivity detector. Results were obtained as weight percentages of carbon, hydrogen and nitrogen.

2.3. Batch adsorption experiments

A stock solution of 20 mg L⁻¹ for each herbicide was prepared by dissolving an appropriate amount of the herbicide in ultra-pure water (18 MΩ cm) derived from a Milli-Q plus 185 water purifier. Batch adsorption isotherms were performed by shaking 500-ml amber Winchester bottles containing the required concentration of the herbicide in a Gallenkamp incubator shaker. The shaker was set at a temperature of 298 ± 1 K and a speed of 100 rpm. Initial solution concentration of 2–140 µg L⁻¹ was prepared by pipetting out the required amounts of the herbicide from the stock solution. The volume of solution in each bottle was maintained at 500 ml and the solutions were adjusted to pH 5. About 5 mg of each adsorbent were weighed accurately on aluminum foils using a Sartorius (Model BP 201D) analytical balance. The adsorbents were transferred carefully into the bottles using 10 ml solutions from the bottles. The bottles were shaken vigorously before shaking for 7 days in the incubator shaker (New Brunswick Scientific Model). Since the quantification of the equilibrium concentrations required a pre-concentration procedure, the samples had to be conditioned by filtering the adsorbent and adjusting the pH of the filtrate to 2, before preparing for a solid phase extraction (SPE) technique. The herbicides equilibrium concentrations were measured using a Hewlett-Packard 1100 series HPLC system.

Table 1

<table>
<thead>
<tr>
<th>Procedures for solid phase extraction (SPE)</th>
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<tbody>
<tr>
<td>Conditioning</td>
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<td>Reconstitution</td>
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</table>

The detector was set at 222 nm and 205 nm for benazolin and 2,4-D respectively, and the flow rate and injection volume were set at 1.47 x 10⁻⁸ m³ s⁻¹ and 100 µl, respectively. This gave the retention time of benazolin at 2.01 min while for 2,4-D was at 3.86 min. The column temperature was also set at 311 K. The eluent consisted of a solution of 40% acetonitrile and 60% buffer (10 mmol KH₂PO₄ at pH 3.0). A solid phase extraction (SPE) technique was employed for the pre-concentration of benazolin and 2,4-D before analysis. The complete procedure for the SPE is given in Table 1.

2.4. Adsorption kinetic experiments

Sorption kinetic experiments were carried out using an experimental procedure that involved placing 2 L of known herbicide concentration in a round bottomed reactor which was immersed in a water bath. The adsorbents were placed inside a rotating basket made of perspex and plastic mesh (40 µm) and this basket was connected to a stirrer motor via a steel rod. The basket was placed in the round bottomed reactor and the stirrer motor was set at 250 rpm for all the experimental runs. Samples (0.4 ml) were pipetted out using a 1 ml syringe at 10 min intervals. The collected samples were placed in HPLC vials and the concentration of the herbicides were analysed using the HPLC method described in Section 2.3.1.

3. Results and discussion

3.1. Characterisation

Fig. 2 shows the pore size distribution of the as-received and engineered samples. The results show that the annealing process did not affect the pore size distribution in the meso- and macropore regions. Both samples have significant amount of micropores with a maximum at around 8 Å and mesopores in the range 20–800 Å. However, heat treatment seems to have increased the micropores in the engineered sample, F400AN. This is expected since heat treatment eliminates some oxygen containing functional groups that are not stable at high temperatures. The higher BET surface area of F400AN and its lower
Table 2
Physical and chemical characterisation results of F400 and F400AN

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET surface area (m² g⁻¹)</th>
<th>pHpZC</th>
<th>pHIEP</th>
<th>Na⁺ capacity (mmol g⁻¹)</th>
<th>Elemental analysis (wt%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>F400</td>
<td>790</td>
<td>7.5</td>
<td>6.0</td>
<td>0.3</td>
<td>89.48</td>
</tr>
<tr>
<td>F400AN</td>
<td>960</td>
<td>8.0</td>
<td>7.8</td>
<td>0.004</td>
<td>92.73</td>
</tr>
</tbody>
</table>

Fig. 2. Pore size distributions of F400 and the engineered sample.

The elemental oxygen content (given in Table 2) also gives further evidence of the elimination of some surface functional groups due to heat treatment. A similar phenomenon has also been observed by other researchers [6–8]. The appearance on the graph of a ‘well’ in the region between 9 and 10 Å is caused by the DFT model which cannot model values in that region and it does not suggest a decrease in pore volume [9–11].

Table 2 shows the comparison of the point of zero charge (PZC) and the iso-electric point (IEP) for the two samples. It is apparent from the results that heat treatment of the as-received sample produced a sample with higher PZC and IEP than the original sample F400. This result is expected since it is well documented that activated carbon contains some acidic functional groups (phenol, carboxylic, carbonyl, etc.) that are unstable at high temperatures [7,8,12]. Hence the subsequent removal of the acidic functional groups through heat treatment renders the carbon surface more basic. The basic nature of the annealed sample comes from the pyrone groups and the π electrons of the activated carbon aromatic system and this property is enhanced by the elimination of the acidic functional groups. Sodium capacity determination shows that F400 has a higher affinity for Na⁺ ions than F400AN. The sodium uptake is caused by the existence of carboxylic and phenolic functional groups on the adsorbent surfaces. In this case the sodium capacity is expected to be low in the annealed sample due to thermal treatment that subsequently destroys the carboxylic functional groups.

3.2. Sorption studies

Fig. 3 shows adsorption isotherms of 2,4-D and benazolin on F400 and F400AN at 298 K. Correlation of the data using empirical or theoretical equations is required in the analysis and design of an adsorption process. The two most common equations employed for such analysis are the Langmuir and the Freundlich equations. The Langmuir isotherm is mainly applied to monolayer adsorption while the Freundlich isotherm is widely employed for sorption surfaces with nonuniform energy distribution. In the present investigation, the experimental data were tested with respect to both these isotherms. The Langmuir isotherm is expressed as

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \]  

where \( q_e \) is the amount of solute adsorbed per gram of adsorbent and \( C_e \) is the equilibrium concentration of solute in the bulk of the solution. The constants \( K_a \) and \( q_m \) are characteristics of the Langmuir equation and they can be evaluated from the linearised form represented by the equation

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \]  

A plot of \( C_e/q_e \) against \( C_e \) would give a straight line with a slope of \( 1/q_m \) and an intercept of \( 1/q_m K_a \).

The Freundlich equation is given as

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

where \( K_F \) and \( n \) are constants. The linear form of the equation can be expressed as

\[ \log q_e = \log K_F - \frac{1}{n} \log C_e \]  

Thus the constants \( K_F \) and \( n \) which relate to sorption capacity and sorption intensity of the adsorbent can then be evaluated from the intercept and slope of \( \log q_e \) against \( \log C_e \) plot.

The linearised Langmuir and Freundlich isotherms for the adsorption of the two herbicides on F400 and F400AN were plotted, however, only Langmuir isotherms are presented in Fig. 3. The linear regression correlation coefficient values in
Table 3: Langmuir equilibrium isotherm constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>298 K</th>
<th>308 K</th>
<th>318 K</th>
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<tr>
<td></td>
<td>$q_m$</td>
<td>$K_R$</td>
<td>$R^2$</td>
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<td>Benazolin on F400</td>
<td>34.84</td>
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<td>2,4-D on F400AN</td>
<td>53.19</td>
<td>20.89</td>
<td>0.9826</td>
</tr>
</tbody>
</table>

Note. Constants based on units of $q_m$ (µmol g$^{-1}$) and µmol (L·t). pH constant at 5.0 for all determinations.

Table 4: Freundlich equilibrium isotherm constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>298 K</th>
<th>308 K</th>
<th>318 K</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$K_F$</td>
<td>$1/n$</td>
<td>$R^2$</td>
</tr>
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<td>Benazolin on F400</td>
<td>734</td>
<td>0.69</td>
<td>0.9852</td>
</tr>
<tr>
<td>Benazolin on F400AN</td>
<td>1009</td>
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<td>0.9736</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>790</td>
<td>0.79</td>
<td>0.9651</td>
</tr>
<tr>
<td>2,4-D on F400AN</td>
<td>921</td>
<td>0.75</td>
<td>0.9641</td>
</tr>
</tbody>
</table>

Note. Constants based on units of $q_m$ (µmol g$^{-1}$) and µmol (L·t). pH constant at 5.0 for all determinations.

Tables 3 and 4 show that the equilibrium data were well represented by the Langmuir isotherm model compared to the Freundlich model. Results on the Langmuir monolayer adsorption capacity $q_m$ for both 2,4-D and benazolin was higher for the annealed carbon F400AN than the as-received sample F400. This is expected since the characterisation results showed that the BET surface area of F400AN was higher than that of F400 sample. Also, pore size distribution results in Fig. 2 show that sample F400AN had higher proportion of micropores than F400. The high proportion of micropores is desirable for the sorption of low molecular weight organic molecules because adsorption in this region is enhanced significantly by overlap of potential forces which ultimately leads to increased adsorption forces. In this study, the molecular width of benazolin and 2,4-D, which is 2.074 and 3.113 Å, respectively, shows that the molecules can easily be accommodated in the micropores (width of micropores <20 Å) of the adsorbents. From Fig. 3 the sorption capacity follows the sequence F400AN (2,4-D) > F400AN (benazolin) > F400 (2,4-D) > F400 (benazolin). It would normally be expected that benazolin should be adsorbed more than 2,4-D because of its low solubility (600 mg L$^{-1}$) in water compared to 2,4-D (890 mg L$^{-1}$). Also, benazolin possesses a greater functional variability which normally favours increased adsorption. The lower adsorption capacity of benazolin in sample F400AN may be a result of steric hindrances in its structure. One source of the steric hindrances in the two molecules is the existence of the carboxylic functional groups which are out of plane with the aromatic ring. However, the benazolin molecule consists of the heterocyclic ring adjacent to an aromatic ring and the heterocyclic ring consists of hetero-atoms nitrogen and sulfur. It is well known that during chemical bonding involving a nitrogen atom, the resultant molecules with a nitrogen atom usually form out of plane configurations. The nitrogen atom during bonding is known to form four pairs of σ electrons which adopt a tetrahedral distribution in order to minimise electron pair repulsions. One of the four tetrahedral positions is occupied by a lone pair while the other three are involved in bonding pairs [13,14]. Hence the nitrogen atom ultimately forms molecules structured in the form of a trigonal pyramid. Therefore, if the same notion is applied to the benazolin molecule, it would imply that the two ring systems that are linked to the nitrogen molecule are not in the same plane and this makes the molecule less linear and more bulky than the 2,4-D molecule. This is further evidenced by the side view of the spatial arrangement of the atoms of 2,4-D and benazolin shown in Fig. 1. Figs. 1c and 1d show a leaner 2,4-D molecule (width of 2.074 Å) than the benazolin molecule (width of 3.113 Å).

The effect of temperature on the adsorption of the two herbicides is clearly illustrated in Figs. 4-7. The results show that an increase in temperature results in a corresponding increase in the uptake of the herbicides. An increase in adsorption with temperature is usually associated with adsorption systems that are endothermic in nature. Aksu and Kabasakal [3] made similar observations when they adsorbed 2,4-D on a conventional activated carbon and results from the thermodynamic parameter calculations confirmed their observations. In this study, the thermodynamic parameters of adsorption, namely free energy
change, $\Delta G^0$, enthalpy change, $\Delta H^0$, and change in entropy, $\Delta S^0$, were evaluated using the following equation:

$$\Delta G^0 = -RT \ln K_0,$$

(5)

where $R$ is the universal gas constant ($8.314 \, \text{J K}^{-1} \, \text{mol}^{-1}$) and $T$ is the temperature in K. $K_0$ can be evaluated using a method described by Niwas et al. [15] and Li et al. [16]. In this method, $K_0$ can be defined as

$$K_0 = \frac{a_s}{a_e} = \frac{v_s}{v_e} \frac{C_s}{C_e},$$

(6)

where $a_s$ and $a_e$ are the activities of the adsorbed solute and the solute in solution at equilibrium, respectively, while $v_s$ and $v_e$ represent the activity coefficients of the adsorbed solute and the solute present in solution, respectively. When the concentration of the solute in solution approaches zero, the activity coefficient will approach unity and subsequently $K_0$ can be evaluated by plotting $\ln(C_s/C_e)$ against $C_s$ and extrapolating to zero. Subsequently, the intercept with the $Y$-axis gives the value of $K_0$.

The enthalpy change, $\Delta H^0$, and entropy change, $\Delta S^0$, were calculated using the following equation:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0.$$  

(7)

A plot of $\Delta G^0$ against temperature $T$ was found to be linear, hence the values of $\Delta S^0$ and $\Delta H^0$ were obtained from the gradient and intercept of the plot [17]. Table 5 shows the thermodynamic parameters derived from adsorption isotherms shown in Figs. 4-7. The standard free energy change, $\Delta G^0$, was found to be in the region of $-16.650$ to $-19.414 \, \text{kJ mol}^{-1}$. A negative standard free energy change indicates that benazolin and 2,4-D adsorption onto F400 and F400AN is a spontaneous process. Silva et al. [18] mentioned that such low values of free energy change were an indication of a spontaneous physisorption process. Akcay et al. [4] obtained molar free energy change of $-2.831 \, \text{kJ mol}^{-1}$ at 298 K and $-1.863 \, \text{kJ mol}^{-1}$ at 313 K while adsorbing 2,4-D on organophilic sepiolite. Aksu and Kabasakal [3] obtained a free energy value of $-6.8 \, \text{kJ mol}^{-1}$ when they were investigating batch adsorption of 2,4-D on granular activated carbon. This difference is mainly attributed to the difference in experimental conditions, however in all cases it was noted that the adsorption of 2,4-D was a spontaneous process. The positive values of the enthalpy change suggest that the adsorption process is endothermic, a phenomenon that was observed by Akçay et al. [4] and Aksu and Kabasakal [3]. Bhattacharyya and Sharma [19] reported that such small values in enthalpy change are not consistent with the formation of strong chemical bonds between the adsorbent and the adsorbate. The positive value of the entropy is an indication of increased ran-

![Fig. 5. Effect of temperature on the adsorption of benazolin on F400AN.](image)

![Fig. 6. Effect of temperature on the adsorption of 2,4-D on F400.](image)

![Fig. 7. Effect of temperature on the adsorption of 2,4-D on F400AN.](image)

Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$298$ K $308$ K $318$ K</td>
<td>$298$ K $308$ K $318$ K</td>
<td></td>
</tr>
<tr>
<td>Benazolin on F400</td>
<td>$-16.540$ $-17.217$ $-19.337$</td>
<td>$25.376$ $11.930$ $7.764$</td>
<td>$139.9$ $98.5$ $82.0$</td>
</tr>
<tr>
<td>Benazolin on F400AN</td>
<td>$-17.445$ $-18.319$ $-19.414$</td>
<td>$11.930$ $7.764$ $6.410$</td>
<td>$98.5$ $82.0$ $79.1$</td>
</tr>
<tr>
<td>2,4-D on F400</td>
<td>$-16.825$ $-17.231$ $-18.466$</td>
<td>$7.764$ $6.410$ $4.870$</td>
<td>$82.0$ $79.1$ $74.5$</td>
</tr>
<tr>
<td>2,4-D on F400AN</td>
<td>$-17.223$ $-17.832$ $-18.805$</td>
<td>$6.410$ $4.870$ $3.700$</td>
<td>$79.1$ $74.5$ $68.7$</td>
</tr>
</tbody>
</table>
domness at the solid–liquid interface and an affinity of the adsorbents for the herbicides.

3.3. Kinetic considerations

Various kinetic models were used to fit the experimental data, however a pseudo-second-order kinetic model gave the best correlation coefficient for this work. The first-order kinetic model could not be attempted because of solubility limitations of the herbicides. The pseudo-second-order equation is based on the sorption capacity of the solid phase and can be expressed using the equation employed by Ho [17] as

$$\frac{dq}{dt} = k_{2, ad}(q_{eq} - q)^2,$$

where $q_{eq}$ is the amount of solute adsorbed at equilibrium and $q$ is the amount of solute adsorbed at time $t$, while $k_{2, ad}$ is the rate constant for pseudo-second-order adsorption. For boundary conditions, $t = 0$ to $t = t$ and $q = 0$ and $q = q_{eq}$, the integrated form of the equation becomes

$$\frac{t}{q} = \frac{1}{k_{2, ad}q_{eq}} + \frac{1}{q_{eq}}.$$

If second-order kinetics are applicable, the plot of $t/q$ against $t$ should give a linear relationship, from which $q_{eq}$ and $k_{2, ad}$ can be determined.

![Fig. 8. Pseudo-second-order plot for benazolin on F400 and F400AN.](image)

Fig. 8. Pseudo-second-order plot for benazolin on F400 and F400AN.

The rate of herbicides sorption on F400 and F400AN was determined as a function of the initial herbicides concentrations 10, 4, and 2 mg L$^{-1}$. Figs. 10 and 11 show sorption kinetic results of benazolin and 2,4-D, respectively, onto the adsorbents in terms of solid phase accumulation versus time. From the results, it is clear that the herbicide uptake increases with an increase in initial concentration. Also it is apparent that the higher the initial concentration, the faster the adsorption rate. A closer look at the results also shows that the sorption rate is high at the initial period of the adsorption process. This may be due to the high concentration gradient existing between the solute in solution and that in the adsorbent phase in the initial stages of the process. The higher concentration gradient is promoted by an increased number of vacant active sites available at the initial stage of the experiment. As the adsorption process proceeds,

![Fig. 9. Pseudo-second-order plot for 2,4-D on F400 and F400AN.](image)

Table 6

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration (mg L$^{-1}$)</th>
<th>$q$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>Correlation coefficient</th>
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<tr>
<td>Benazolin on F400</td>
<td>10</td>
<td>43.86</td>
<td>$5.44 \times 10^{-4}$</td>
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<tr>
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<td>4</td>
<td>17.57</td>
<td>$1.79 \times 10^{-3}$</td>
<td>0.9962</td>
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<tr>
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<td>2</td>
<td>9.97</td>
<td>$1.42 \times 10^{-3}$</td>
<td>0.9955</td>
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<td>Benazolin on F400AN</td>
<td>10</td>
<td>47.17</td>
<td>$3.01 \times 10^{-4}$</td>
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<td>4</td>
<td>19.46</td>
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<td>2</td>
<td>9.84</td>
<td>$1.96 \times 10^{-3}$</td>
<td>0.9969</td>
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<tr>
<td>2,4-D on F400</td>
<td>10</td>
<td>50.00</td>
<td>$3.29 \times 10^{-4}$</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.87</td>
<td>$1.71 \times 10^{-3}$</td>
<td>0.9981</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18.02</td>
<td>$2.74 \times 10^{-4}$</td>
<td>0.9809</td>
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<td>2,4-D on F400AN</td>
<td>10</td>
<td>48.54</td>
<td>$5.35 \times 10^{-4}$</td>
<td>0.9989</td>
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<tr>
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<td>20.79</td>
<td>$9.11 \times 10^{-4}$</td>
<td>0.9977</td>
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<td></td>
<td>2</td>
<td>15.53</td>
<td>$4.03 \times 10^{-4}$</td>
<td>0.9938</td>
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the gradual filling of the vacant sites takes place resulting in the
decrease of the concentration gradient. This leads to the grad-
ual decrease in the sorption rate in the final stages from 50 to
\( \approx 150 \) min. Figs. 10 and 11 show the fits between the predicted
(using pseudo-second-order model) curves and the experimen-
tal values.

Solid-liquid sorption processes are usually characterized by
three consecutive steps, namely external diffusion, internal dif-
fusion, and the adsorption stage. The adsorption stage is usually
fast and can be considered negligible. External diffusion in-
volves the movement of adsorbate molecules from the bulk of
the solution toward the surface of the adsorbent. This is fol-
lowed by movement of molecules through the boundary layer
while internal diffusion involves the movement of molecules
in the interior of the particles. In the solid-liquid adsorption
processes, there is always the involvement of the two mech-
anisms. For example, the first stage of the process is usually
dominated by external diffusion which facilitates loading of the
solute to the adsorbent before internal diffusion takes place.

In order to identify the slowest steps in the adsorption
process, the Boyd kinetic equation [20] was applied and it is
represented as

\[
F = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_l}{r_0^2} t \right) = 1 - \frac{6}{\pi^2} \exp(-Bt), \tag{10}
\]

where \( F \) is the fractional approach to equilibrium at time \( t \) and
\( B \) is given as

\[
B = \frac{\pi^2 D_l}{r_0^2}, \tag{11}
\]

\( D_l \) is the effective diffusion coefficient of solute in the adsor-
bot phase and \( r_0 \) is the radius of the adsorbent particles.

Equation (10) can be re-arranged while taking natural loga-
rithm to obtain the equation

\[
Bt = -0.4977 - \ln(1 - F). \tag{12}
\]

The values of \( Bt \) can be evaluated for different time intervals
using Eq. (12). A plot of \( Bt \) against time \( t \) can be employed to
test the linearity of the experimental values [21]. If the plots are linear and passing through the origin, then the slowest step in the adsorption process is the internal diffusion and vice versa. The $B_t$ against $t$ plots for benazolin and 2,4-D for different initial concentrations are shown in Figs. 12 and 13. It is apparent from the graphs that the $B_t$ against $t$ plots do not pass through the origin, hence the adsorption process is mainly controlled by film diffusion. The calculated effective diffusion coefficient ($D_i$) values at different initial herbicide concentrations are given in Table 7. The average $D_i$ values were found to be $1.63 \times 10^{-12}$ and $1.66 \times 10^{-12}$ $m^2 s^{-1}$ for benazolin on F400 and F400AN, respectively, while for 2,4-D, the average values were $1.55 \times 10^{-12}$ and $1.40 \times 10^{-12}$ $m^2 s^{-1}$ in samples F400 and F400AN, respectively. Similar $D_i$ values were obtained by Gupta et al. [22] when they were investigating the removal of herbicides (i.e., lindane and malathion) from wastewater using bagasse fly ash derived from waste from the sugar industry.

4. Conclusions

The present study showed that engineered activated carbon (F400AN) has a superior micropore content than its parent sample. When the two samples were challenged for the sorption of benazolin and 2,4-D, the modified sample marginally outperformed the conventional sample and structural differences of the herbicides play a crucial role for their sorption capacity. The equilibrium data followed the Langmuir isotherm, and the thermodynamic parameters showed that the adsorption process was spontaneous and endothermic. The sorption kinetic data fitted the pseudo-second order kinetics very well while the Boyd plot confirmed that external mass transfer was the slowest step in the sorption process.

Acknowledgments

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References