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Adsorption of Selected Herbicides from Water using Activated Carbon and Polymeric Adsorbents

by

Daniel J. Horner

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

September 1999

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ABSTRACT

A range of adsorbents have been evaluated for the adsorption of selected herbicide compounds from aqueous solution. The adsorption performance of LF-1, a carbonised polymer produced in the laboratory, Amberlite XAD-4, a commercially available polymeric adsorbent produced by Rohm and Haas and MN-200, a Hypersol-Macronet polymer produced by Purolite, were compared with a commercial activated carbon, Chemviron F-400.

The pore size distributions of the adsorbents have been investigated using nitrogen adsorption. F-400, LF-1 and MN-200 were found to contain similar microporous structures. The carbons also possess a significant degree of mesoporous structure, which may enhance the diffusion of organic species into the micropores. The pore size distribution for XAD-4 shows an almost exclusive meso/macroporosity with very little microporous structure. Spectroscopic analysis and titration of the adsorbents indicated a number of different oxygen functional groups. XPS and elemental analysis suggested higher oxygen concentrations than those obtained using direct titration, which was attributed to bound oxygen within the structure of the adsorbents. The adsorption capacity of phenol was assessed as a characterisation technique. The capacity of the carbons was much greater than the polymeric adsorbents.

Analytical techniques were developed and validated for the determination of trace levels (0.1 parts per billion) of five herbicides; atrazine, benazolin, bentazone, imazapyr and triclopyr. Single and multi-component adsorption isotherms are presented for trace concentrations of the herbicides in aqueous solution. The effect of pH and fulvic acid upon the adsorption was also investigated. Mini-column experiments were performed using multi-component mixtures. In all cases, the uptake of herbicides on F-400 is greater than on the other adsorbents.

Regeneration of F-400 and MN-200 was investigated using solvent stripping techniques. Significant regeneration efficiencies were observed using ethanol at pH 12 and 50°C to make the technique a viable option.
ACKNOWLEDGEMENTS

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<td>X</td>
<td>association factor, water = 2.6</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>non-constant diffusivity factor</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>scaling factor</td>
<td></td>
</tr>
<tr>
<td>β_I</td>
<td>Redlich-Peterson heterogeneity factor</td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>characteristic free energy of adsorption</td>
<td>J/mol</td>
</tr>
<tr>
<td>γ</td>
<td>surface tension</td>
<td>dyn/cm</td>
</tr>
<tr>
<td>μ</td>
<td>viscosity</td>
<td>Ns/m², cp</td>
</tr>
<tr>
<td>v_{SC/LC}</td>
<td>velocity in small/large columns</td>
<td>e.g. m/s</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Section 1.1 General Introduction

The introduction and continuing tightening of legislation governing the levels of organic compounds in potable water have forced authorities in the European Union and United States to improve water treatment processes. The demand for higher water quality has initiated intensive examination and use of the process of adsorption.

Adsorption may be considered as the process of accumulating a substance at the interface between two phases, such as a liquid and a solid in the case of potable water treatment [Snoeyink, 1990]. The molecule that accumulates, or adsorbs, at the interface is called the adsorbate, and the solid on which the adsorption takes place is the adsorbent. Adsorbents of interest in water treatment include activated carbons; ion exchange resins; adsorbent resins; metal oxides, hydroxides and carbonates; activated alumina; clays; and other solids suspended in or in contact with water.

One of the first commercial adsorbents used in water treatment was Powdered Activated Carbon (PAC), primarily used for odour control. In 1977 the American Water Works Association (AWWA) showed that approximately 25 percent of 645 United States utilities used PAC as a control technology [AWWA, 1977]. In recent years more attention has focused on Granular Activated Carbon (GAC) as an alternative to PAC due to improved operating and handling characteristics, e.g. column operation at relatively high flow rates and off-site reactivation. Between 1977 and 1986, the number of plants in the US using GAC rose from 65 to 135 [Snoeyink, 1990].
Although GAC has proved to be an excellent adsorbent, the associated costs with its use are high. This has stimulated research into novel types of adsorbents, synthesised from cheap starting materials such as straw and waste rubber [Streat et al., 1995], to materials that may reduce the quantity of adsorbent required or enable cheap regeneration.
Section 1.2 Research Objectives

The objectives of this research were to investigate selected activated carbons and polymeric resins for the removal of 'key' organic pollutants, particularly herbicides, at various source concentrations from potable water. The adsorbents chosen for the study were;

1) F-400, a commercially available coal-based activated carbon produced by Chemviron. This carbon is currently the most widely used adsorbent for the treatment of potable water supplies,

2) LF-1, a novel carbonised polymeric resin derived from lignin, produced in the laboratory by Dr. Kozynchenko of The Institute of Sorption Problems and Endocology, Kiev, Ukraine,

3) XAD-4, a commercially available polymeric resin produced by Rohm and Haas which has been previously investigated for the removal of organic species,

4) MN-200, a Macronet™ polymer, developed by Purolite International Ltd and was the subject of extensive evaluation by Sweetland [Sweetland, 1997].

The adsorbates chosen for this study were the herbicides, atrazine, benazolin, bentazone, imazapyr and triclopyr. Atrazine is one of the most problematic herbicides to remove from potable water supplies and as a consequence was prohibited from non-agricultural uses in England and Wales in 1993. Since that time there has been increased use of a variety of alternative herbicide compounds for both agricultural and non-agricultural purposes. Relatively little information exists for many of these herbicides with regard to either their potential to pollute potable water supplies or their removal by water treatment processes.

Among the herbicides being increasingly used and of particular concern to Severn Trent Water Ltd are two agricultural herbicides, benazolin and bentazone, and two non-agricultural, atrazine-replacement herbicides, imazapyr and triclopyr. Particular attention has focused on these relatively new herbicides.
Adsorption using trace levels of the herbicides in the parts per billion range were performed to assess the adsorbents potential to remove the compounds of interest. Multi-component adsorption was investigated including the influence of naturally occurring organic matter on the adsorption to make the trials more realistic. Regeneration of the adsorbents was investigated using a variety of techniques.

Detailed studies of the physical and chemical surface characteristics using a variety of methods were undertaken, in an attempt to understand the mechanism of adsorption and regeneration of the sorbents.
Section 1.3  Activated Carbons

Activated carbon was used as an adsorbent in some of the earliest recorded examples of adsorption and continues to be the most widely used adsorbent for water treatment. It can be described as ‘a crude form of graphite, which is highly porous, over a broad range of pore sizes, from visible cracks and crevices to cracks and crevices of molecular dimensions’ [Chemviron]. It can be manufactured from a variety of starting materials, but the substances primarily used for drinking water treatment applications are wood, peat, lignite, sub-bituminous coal and bituminous coal [Hassler, 1967]. These materials are thermally decomposed to allow the volatile hydrocarbons to be removed. The resultant char is not particularly porous and therefore has a relatively low internal surface area. To increase the internal surface area, the carbon is “activated”, by exposure to oxidising gases such as steam or carbon dioxide at temperatures in excess of 1000K or by treatment before carbonisation with chemicals such as zinc chloride, nitric or phosphoric acid. Many variations of surface properties, pore-size distributions and regeneration characteristics can be generated depending on the source of the carbon and the preparation procedure used. Chemviron, the European branch of the Calgon Corporation, markets more than 100 different carbons [Chemviron].

Activated carbon was historically used for the removal of odours, tastes and colours caused by trace pollutants, but in recent years has been increasingly used in the treatment of potable water to remove compounds causing health concerns, such as herbicides and heavy metals. It has a low affinity for water and so is capable of preferential adsorption of hydrophobic organic components from aqueous solutions and moist gases. In drinking water treatment the carbon is used to remove dissolved organics. Generally, organics with a molecular weight greater than 45 will be adsorbed by activated carbon [Noll et al, 1992].

When exhausted, the activated carbon must either be replaced or regenerated. Regeneration is the process of removal of adsorbates from the surface of the activated
carbon so that it can be re-used. Regeneration is typically a three-step process. In the initial stage, thermal regeneration, volatiles and water are vapourised. Next, pyrolysis of the non-volatile organics and carbonisation occurs. Finally, a controlled reaction with water vapour, carbon dioxide or oxygen results in gasification of pyrolytic residues, and recovery of the pore structure. Due to the high costs of regeneration by carbon suppliers, water companies are increasingly installing on-site regeneration facilities, e.g. the Church Wilne site of Severn Trent Water Ltd.

Section 1.3.1 F-400

Calgon Carbon of which Chemviron is a subsidiary produce six activated carbons in the Filtrasorb range. F-400 is the most commercially used activated carbon available; to reflect this, a simple BIDS search produced over 50,000 articles. It is produced from bituminous coal, which is crushed, mixed with a binder, sized and processed in low-temperature ovens followed by high temperature furnaces.

Ayele et al [1998] investigated the removal of atrazine and diuron using three powdered activated carbons. They concluded that F-400 was the best for removing these herbicides. Mazet et al [1994] looked at the removal of a range of compounds including humic acids, phenols and atrazine using powdered F-400, heat treated powdered F-400 and acid treated powdered F-400. They showed that the adsorption capacity was in the order heat-treated>untreated>acid-treated and the same order was observed for the zeta potential and surface area. It was found that the amount of acidic groups on the surface retarded the adsorption of organic species, with the heat-treated carbon possessing the least amount of groups.

Section 1.3.2 LF-1

This carbon was prepared by Dr. Olegsander Kozynchenko (The Institute of Sorption Problems and Endocology, Kiev, Ukraine) from dry sodium lignosulphonate, phenol, paraformaldehyde in ethanediol solution in the presence of catalytic amounts of sulphuric acid. LF-1 was activated between 900-1100 °C and has a 48% burn-off. Lignin is a waste product from the manufacture of paper and it is claimed that the pore
size distribution of the resulting carbon is very narrow. Therefore it is hoped that LF-1 will provide a cheap alternative to activated carbon which is not as prone to fouling by Natural Organic Matter.
Section 1.4 Polymeric Adsorbents

Activated carbon continues to be recognised as the best available technology for the removal of organic compounds from potable water supplies. However, a large amount of research has been conducted using synthetic polymeric materials. The principal difference between activated carbons and polymeric adsorbents is the ease of regeneration of the latter. Whilst binding to activated carbon is often irreversible, the lower binding affinities to polymeric adsorbents often allows regeneration with acids, bases or water miscible organic solvents. This permits long-term cyclic operation and because of their physical durability, negligible attrition losses are encountered.

The Amberlite XAD series of polymeric adsorbents produced by Rohm and Haas have been widely studied in the literature as potential replacements for activated carbon. Thus far, however, they have only found successful application in the clean-up of wastewater streams, e.g. phenolic streams, due to their ability to be regenerated. Extraction of humic and fulvic acids from natural waters is commonly achieved by sorption onto XAD resins followed by elution using sodium hydroxide [Daignault et al, 1988].

In 1969, Davankov and Tsyurupa [1969] patented their new series of hypercrosslinked polymeric networks. Purolite International Ltd, in collaboration with Davankov and Tsyurupa, have developed an optimal series of ‘Hypersol Macronet™’ sorbent resins for industrial application. These polymers are based on a spherical styrene-divinylbenzene copolymer that is crosslinked while the polymer is in a swollen state. The polymers are produced with various pore structures and functionality.

Dow Chemical have also patented a series of methylene bridged styrene-divinylbenzene hypercrosslinked polymeric adsorbents, based on the Davankov-Tsyurupa technology [Schneider et al, 1992]. These polymers have been applied to areas where the use of activated carbon is futile, e.g. the adsorption and recovery of methyl-ethyl-ketone, MEK) [Blystone et al, 1994].
Chapter 1

Section 1.4.1 XAD-4

Amberlite polymeric adsorbents are hard, insoluble spheres of high surface area, porous polymers. They are provided in a variety of polarities and surface characteristics allowing them to be used in a wide range of adsorption applications. Amberlite XAD-2 and XAD-4 have been used in sensitive analytical procedures to detect, identify and measure the presence of herbicides and other organics in the environment [Rohm and Haas, 1978].

Amberlite XAD-4 was chosen from the range of Amberlite adsorbents due to its relatively high surface area and low pore diameter in the non-polar adsorbent range. XAD-4 is a copolymer of styrene and divinyl-benzene. Table 1-1 summarises the properties of the Amberlite polymeric adsorbents range.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Nature</th>
<th>Porosity %</th>
<th>True Wet Density g/cm³</th>
<th>Surface Area m²/g</th>
<th>Average Pore Dia. Å</th>
<th>Skeletal Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD-1</td>
<td>Polystyrene</td>
<td>37</td>
<td>1.02</td>
<td>100</td>
<td>100</td>
<td>1.07</td>
</tr>
<tr>
<td>XAD-2</td>
<td>Polystyrene</td>
<td>42</td>
<td>1.02</td>
<td>300</td>
<td>90</td>
<td>1.07</td>
</tr>
<tr>
<td>XAD-4</td>
<td>Polystyrene</td>
<td>45</td>
<td>1.02</td>
<td>725</td>
<td>40</td>
<td>1.08</td>
</tr>
<tr>
<td>XAD-7</td>
<td>Acrylic Ester</td>
<td>55</td>
<td>1.05</td>
<td>450</td>
<td>90</td>
<td>1.24</td>
</tr>
<tr>
<td>XAD-8</td>
<td>Acrylic Ester</td>
<td>52</td>
<td>1.09</td>
<td>160</td>
<td>225</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 1-1  Typical Properties of Amberlite polymeric adsorbents [Rohm and Haas, 1978]

Moore et al [1984] investigated its use as a Solid Phase Extraction (SPE) material for the extraction of several organic compounds. They found that at pH 7, XAD-2 and XAD-4 yielded recoveries of 90-100% in the 20-200ppb range. Woodrow et al [1986] investigated the recoveries of several herbicides and recorded acceptable recoveries in 10 and 0.1 ppb spiked samples. They concluded that XAD-4 was an attractive alternative to solvent extraction in terms of recoveries whilst offering
advantages in terms of recoveries, detection limits and sample handling. However, Blok et al [1983] preferred solvent extraction methods to Amberlite resins due to the high levels of impurities produced by the resins, even after clean-up.

Section 1.4.2 MN-200

The Hypersol-Macronet range of polymers are produced by Purolite International Limited, with a wide variety of pore sizes and chemical functionalities. The development of an optimal series of Macronets was performed in collaboration with Davankov and Tsyurupa [Davankov et al, 1969], the inventors of the polymeric networks. A full description of the method of preparation of the polymers is given in the thesis produced by Sweetland [1997].

Little work has been published on the characterisation and application of the Macronet polymers, with the notable exception of Sweetland [1997]. He investigated three of these polymeric adsorbents, MN-100, MN-150 and MN-200 (Table 1-2) for their ability to adsorb a variety of organic pollutants including phenol, chlorinated phenols and the herbicides atrazine, chlorotoluron, diuron, isoproturon and simazine. It was concluded that MN-200 offered a viable alternative to activated carbon for herbicide removal because of lower uptake of fulvic acid molecules and ease of regeneration.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>MN-100</th>
<th>MN-150</th>
<th>MN-200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionality</td>
<td>WBA</td>
<td>WBA</td>
<td>-</td>
</tr>
<tr>
<td>( d_{50}, \ \text{Å, mesopores} )</td>
<td>850-950</td>
<td>300-400</td>
<td>850-950</td>
</tr>
<tr>
<td>( d_{90}, \ \text{Å, micropores} )</td>
<td>15</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>Weight Capacity, eq/kg</td>
<td>0.6-0.8</td>
<td>0.4-0.7</td>
<td>-</td>
</tr>
<tr>
<td>BET surface area, m(^2)/g</td>
<td>800-1000</td>
<td>800-1000</td>
<td>800-1000</td>
</tr>
</tbody>
</table>

WBA = Weak Base Anion

Table 1-2 Hypersol Macronet\textsuperscript{TM} Sorbent Resins MN-100, MN-150 and MN-200
Section 1.5  Introduction to Adsorption Theory

Adsorption of a material occurs at the surface since it reduces the imbalance of attractive forces, and, therefore, the surface free energy of the heterogeneous system. The forces involved in the adsorption of either gases, liquids, or vapours may be non-specific (van der Waals) forces, termed physical adsorption, or stronger specific forces caused by the formation of chemical bonds, termed chemisorption.

Physical adsorption forces result from the electric charge density of individual atoms. Non-polar molecules are attracted to each other by weak induced dipole-dipole interactions called London forces (hydrophobic bonding). The hydrophobicity of organic pollutants is often measured by the logarithm of the octanol-water partition coefficient, $k_{ow}$. Most organic pollutants have positive values, gradually increasing as the compounds become more hydrophobic. The solubility of the compound is also an indication of hydrophobicity.

In polar substances there is an attraction between the positive end of one molecule and the negative end of another polar molecule. Such attractions are a result of dipole-dipole interactions. A special kind of dipole-dipole interactions are hydrogen bonds. Hydrogen bonding occurs with molecules containing fluorine, oxygen and nitrogen due to the concentrated negative charge of their small atoms.

Electrostatic bonding occurs through the process of ion exchange or coordination. In ion exchange, ions of a given charge (cations or anions) in a solution are sorbed onto the ion exchange material and are replaced by equivalent quantities of ions of the same charge, released by the ion exchange material. Ion exchange can only occur when the molecules are dissociated.

The capacity of adsorbents is generally proportional to the surface area within the pores which is accessible to the adsorbate, since hydrophobic molecules are dominant. As the organic pollutants become more hydrophobic in nature the hydrophobic
adsorbent interacts more strongly with the adsorbate, giving rise to increased capacity. The surface functional groups on the adsorbent can either increase or decrease the capacity. Adsorption can also be enhanced by hydrogen bonding and ion exchange. However, the dissociated or protonated functional groups on the surface of the adsorbent can cause the surface to have the same charge as the adsorbing species and thus repel the molecules.

Section 1.5.1 Diffusion

The adsorption process may be considered as three consecutive steps. Initially, external mass transfer of the solute from the bulk solution proceeds through the boundary layer to the particle surface, succeeded by diffusion within the particles (intraparticle diffusion), to the sorption sites where the solute molecules are adsorbed [McKay et al, 1986] as illustrated in Figure 1-1. The rate at which the molecules attach to the surface is normally sufficiently high so that it contributes no resistance in the transport process.

Intraparticle diffusion is dependent on many factors such as the structure of the adsorbent, and the physical and chemical properties of the adsorbent and adsorbate.
This has led to the development of many models to correlate the different adsorption mechanisms which can occur.

**Section 1.5.2 External Mass Transfer**

When mass transfer occurs between phases, it is necessary to take into account molecular diffusion and convection. Difficulty in the analysis of conventional mechanisms has led to the use of approximate models to permit a solution, namely, film theory, boundary layer theory and penetration theory. However, a more rigorous treatment of external mass transfer is often necessary to define several mass transfer coefficients, each appropriate to a different situation [McKay and Bino, 1985].

**Section 1.5.2.1 External Mass Transfer Coefficients**

The mass transfer, or diffusional flux $N$ (mg/s) of sorbate molecules from the bulk solution to the sorbent particle is defined by:

$$N = A_p k_f (C_t - C_e)$$

where $A_p$ is the external surface area of the sorbent (cm$^2$), $k_f$ is the external mass transfer coefficient (cm/s), $C_t$ is the fluid phase concentration at time $t$ (mg/ml) and $C_e$ is the equilibrium fluid phase concentration (mg/ml). A differential mass balance of the adsorption rate is given by:

$$N = -V \frac{dC}{dt}$$

where $V$ is the volume of the solution in litres. A study of the concentration of the adsorbate in solution versus time enables a graphical differentiation which is proportional to the rate of mass transfer. At time $t=0$ all of the mass transfer resistance is restricted to the external layer on the particle, hence equating the above equations:

$$k_f = \frac{V}{A_p C_o} \left( \frac{dC}{dt} \right)_{t=0}$$

where $C_o$ is the initial adsorbate solution concentration (mg/l). Therefore the external mass transfer coefficient can be determined.
Alternatively, in a well agitated tank, the concentrations of the adsorbate in the liquid phase and the concentration of adsorbent particles in the liquid are essentially uniform throughout the vessel. Hence, for a linear isotherm, Furusawa and Smith [1974] developed an analytical solution for the adsorption process, enabling the external mass transfer coefficient to be evaluated from the gradient and intercept of the linearised form of the solution.

Section 1.5.2.2 External Mass Transfer Correlations

The mass transfer version of Reynolds Analogy can be derived for particulate adsorption in terms of the Sherwood (Sh), Schmidt (Sc), Reynolds (Re) numbers and the friction factor (f);

\[ f = \frac{\text{Sh}}{2 \text{Sc Re}} \]

This applies if: (i) there are constant physical properties; (ii) very small net bulk flow at the interface; (iii) no chemical reactions in the fluid; (iv) no viscous dissipation; (v) no radiant energy interchange; (vi) no pressure, thermal or forced diffusion.

The mean Sherwood number is defined by:

\[ \text{Sh} = \frac{k_f d_p}{D_{\text{mol}}} = 0.66 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}} \]

where \( d_p \) is the particle diameter and \( D_{\text{mol}} \) (m\(^2\)/s) is the molecular diffusivity of the adsorbate, often calculated from the Wilke-Chang expression [1955] as shown in equation 6;

\[ D_{\text{mol}} = \frac{7.4 \times 10^{-8} (X M_H)^{0.5} T}{\mu V_m^{0.6}} \]

The equation for Sherwood number (Eqn. 5), can be rearranged to enable mass transfer coefficients to be compared by the general equation:

\[ \frac{\text{Sh}}{\text{Sc}^{\frac{1}{3}}} = A(C)^B \]

where A and B are constants and the variable, C, is for example, adsorbent particle size, agitation speed, adsorbent mass, temperature, pH etc.
**Section 1.5.3 Intraparticle Mass Transfer**

After the molecules of adsorbate have passed through the boundary layer, they must diffuse through the complex structure of the adsorbent. Most commercial adsorbents contain a distribution of pore sizes from micropores through to macropores. The uptake rate may therefore be controlled by either pore or surface diffusion or by a combination of both. If the diffusing molecule is continually within the attractive forces of the surface, it is transported by "hopping" between adsorption sites. This process is described as diffusion; if this mechanism dominates, the concentration within the adsorbate will be essentially uniform and the adsorption rate will be independent of particle size.

With pore diffusion, however, the diffusing molecule can escape into the bulk liquid, thus causing a concentration profile within the particle. Therefore, the uptake rate will depend upon the particle size. Diffusion within porous particles has been found to follow pore, solid, or branched pore diffusion mechanisms. For a complete study of the diffusion models, including derivations, the reader is referred to the papers by Al-Duri and McKay [1990;1991;1992]. A brief overview of the theoretical application of each model is presented below.

**Section 1.5.3.1 Film-Pore Diffusion Model**

This model is characterised by intraparticle diffusion occurring through the liquid filled voids of the sorbent particles. Diffusion occurs through the boundary layer, followed by diffusion through the liquid filled pores onto the sorption sites. Transfer of adsorbate molecules from site to site is also via the liquid filled pores, that is, an adsorbed sorbate molecule moving from a site desorbs into the pore before the site is taken up by another molecule.

**Section 1.5.3.2 Film-Solid Diffusion Model**

In this model, intraparticle diffusion occurs by the surface hopping mechanism. It is also called the homogeneous model as it assumes that the sorbent has a homogeneous surface with a uniform structure; this implies that the adsorption sites are energetically identical. The transfer of sorbate from one site to another occurs by the hopping of
molecules on the solid surface without desorption, as in pore diffusion. Adsorption occurs at the outside surface of the sorbent particles and at the inner pore walls. Surface heterogeneity can be accounted for by the selection of a heterogeneous equilibrium isotherm model.

Section 1.5.3.3 Branched Pore Model

The branched pore model is based on a detailed analysis of the structure of activated carbon as a heterogeneous adsorbent. Carbon particles contain many pores with wide size ranges forming a dispersed network throughout the particle. To facilitate the study of the complex structure, Peel et al [1981] approximated the pore size distribution into two regions, namely the macropore region, where diffusion occurs by the surface hopping mechanism and the micropore region where multiple directional interactions between the sorbate molecules and the pore walls are significant. However, four parameters have been combined to express the rate of adsorption as described by this mechanism. These are $k_f$ (cm.$s^{-1}$), the external mass transfer coefficient, $D_s$ (cm.$^2$.s.$^{-1}$), the solid diffusivity that measures the diffusion in macropores, $k_b$ (cm.$s^{-1}$), the micropore mass transfer coefficient that approximates the rate of diffusion in the micropores and $f$, the fraction of macropores in the carbon particle.

Section 1.5.4 Isotherms

Adsorption of molecules may be represented as a chemical reaction:

$$A + B \leftrightarrow A.B$$

where $A$ represents the adsorbate, $B$ the adsorbent and $A.B$ the adsorbed compound. Assuming the reaction is reversible the adsorbate molecules will accumulate at the surface until the rate of the forward reaction (adsorption) is equal to the rate of the reverse reaction (desorption). When this condition exists equilibrium has been achieved and no further accumulation will occur. The time taken to reach equilibrium can vary considerably depending upon the adsorbate and adsorbent in question. The adsorbate may be held on the surface by various types of forces, such as hydrogen bonds, dipole-dipole interactions, van der Waals, ion exchange and co-ordination.
One important characteristic of any adsorbent is the quantity of adsorbate that can accumulate on the surface at a given temperature. The relationship between the quantity of adsorbate per unit of adsorbent, $q_e$, and the equilibrium concentration of adsorbate in solution, $C_e$, is called an adsorption isotherm. Experimental data is most accurately described by the general isotherm equation developed by Fritz and Schlunder [1981]:

$$ q_e = \frac{K_o C_e}{A + B C_e^D} $$

where, $K_o$, $A$, $B$ and $D$ are isotherm constants. Many studies have been carried out to simplify this equation and facilitate the evaluation of the isotherm constants based upon theoretically sound and thermodynamically consistent assumptions. This has resulted in some well known and established formulae, namely the Langmuir, Freundlich and Redlich-Peterson isotherms.

**Section 1.5.4.1 Langmuir Isotherm**

The Langmuir equation assumes an energetically homogeneous sorbent surface and hence the energy of adsorption is constant for all sites. This results in monolayer adsorption on the sorbent surface and the formation of a "plateau" or a constant sorbent capacity. Mathematically the Langmuir equation is obtained by setting $A=D=1$ in Equation 9, i.e.:

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

where $b$ and $q_{\text{max}}$ are the Langmuir constants. The constant $q_{\text{max}}$ corresponds to the surface concentration at monolayer coverage and represents the maximum value of $q_e$ that can be achieved as $C_e$ is increased. The constant $b$ is related to the energy of adsorption and increases as the strength of the adsorption bond increases. To evaluate the Langmuir constants, a linearised form of equation 10 is used:

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

and a plot of $1/q_e$ versus $1/C_e$ will yield a straight line for data which fits the Langmuir expression. Hence, from the gradient ($1/q_{\text{max}} b$) and intercept ($1/q_{\text{max}}$) the Langmuir constants can be calculated. However, it is often the case that the Langmuir plot does
not produce a linear relationship, due to the assumption of a homogeneous surface, zero interaction between the adsorbed molecules and other factors.

Section 1.5.4.2 Freundlich Isotherm

The Freundlich equation describes equilibrium at heterogeneous surfaces, and therefore the monolayer assumption is no longer valid. Although the Freundlich equation was developed empirically, a theory of adsorption which leads to the Freundlich equation was later developed. The equation is obtained by setting \( A=0 \) in Equation 9, yielding the formula:

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

where \( K \) and \( \frac{1}{n} \) are the Freundlich constants, which can be obtained by linearising equation 12:

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

The constant \( K \) is primarily related to the capacity of the adsorbent for the adsorbate, and \( \frac{1}{n} \) is a function of the strength of adsorption, i.e. the mechanism of adsorption. Low values of \( \frac{1}{n} \) suggest strong bonding leading to an irreversible isotherm and vice versa. The Freundlich isotherm has a wide range of application and a high degree of accuracy, yet it does not converge to Henry’s law at low surface coverage (\( q_e \rightarrow 0 \)). This problem has been overcome by an extrapolation technique developed by Al-Duri and McKay [1990].

Section 1.5.4.3. Redlich-Peterson Isotherm

The Redlich Peterson formula is applicable to both heterogeneous and homogenous surfaces and therefore it is suitable for a wide range of systems with a good accuracy. It also converges to Henry’s Law at low surface coverage. The formula is obtained by setting \( A=1 \) in Equation 9:

\[ q_e = \frac{K_j C_e}{1 + b_j C_e^{\beta_j}} \]  

where \( K_j, b_j, \) and \( \beta_j \) are Redlich-Peterson constants. \( \beta_j \) is the heterogeneity factor. The constants can be calculated by linearising the equation and substituting the
Langmuir constant \( q_{\text{maxb}} \) as a first approximation for \( K_j \). \( K_j \) can then be calculated by back substitution of the other constants.

**Section 1.5.5 Rapid Small Scale Column Trials (RSSCT)**

A wide variety of methodologies have been investigated to assess the performance of new adsorbents, with respect to their adsorption capacity and kinetics. Pilot columns were widely used to provide accurate and reliable predictions of breakthrough behaviour in full scale columns. However, the extended times and costs of the trials have led to a number of researchers developing tests which obtain data in a fraction of the time. Frick [1982] presented the idea of scaling down full-scale adsorber parameters, by dimensional analysis, to enable the rapid determination of a GACs performance. Crittenden *et al* [1986] developed the idea, which resulted in the rapid small scale column test.

The scaling equations are derived on the basis of the dispersed flow, pore-surface diffusion model (DFPSDM), containing the dimensionless groups; surface solute distribution parameter, pore solute distribution parameter, Stanton Number, pore diffusion modulus, surface diffusion modulus and Peclet Number. The scaling equations are derived by setting the dimensionless groups of a small-scale column equal to those of the large-scale adsorber, since the six independent dimensionless groups should remain constant. Initial equations proposed by Crittenden assumed that the value of the surface diffusion constant remained constant. However, correlations were also presented in later publications for cases of non-constant diffusivities [Crittenden *et al*, 1987; Crittenden *et al*, 1991]. Due to the reduced experimental time, the RSSCT cannot assess the possibilities of biodegradation or the effect of changes in condition and concentration of the feed water. A review of the applications of RSSCT in the literature will be presented in Chapter 4.

The scaling equations of the RSSCT are as follows:

\[
\text{EBCT}_{\text{sc}} = \left( \frac{d_{\text{sc}}}{d_{\text{LC}}} \right)^{2-Z} \text{EBCT}_{\text{LC}}
\]
where \( t_{SC/LC} \) are the empty bed contact times of small/large particles; \( t_{SC/LC} \) is the operation time of the small/large column; \( d_{SC/LC} \) are the particle diameters used in the small/large columns and \( Z \) is the non-constant diffusivity factor, ranging from 0-1.

If surface diffusion is independent of the adsorbent particle size then the diffusivity factor is zero. However, for a number of carbons the coefficient will not remain constant. In these cases the diffusivity factor is determined by linearising the equation:

\[
D_{SC} = \left( \frac{d_{SC}}{d_{LC}} \right)^Z D_{LC}
\]

where \( D_{SC/LC} \) are the diffusion coefficients for the small/large particles (m\(^2\)/s). The Stanton and Peclet Numbers only remain equal between the full scale and small scale columns if the diffusion coefficient is constant. In this case the following equation is obtained;

\[
v_{SC} = \left( \frac{d_{LC}}{d_{SC}} \right) \frac{Re_{SC,\text{min}}}{Re_{LC}}
\]

where \( v_{SC/LC} \) are the velocities in the small/large columns, \( Re_{SC,\text{min}} \) is the minimum Reynolds Number in the small particle column and \( Re_{LC} \) is the Reynolds Number in the large-particle column.

\( Re_{SC,\text{min}} \) defines the minimum velocity which can be used in the operation of the RSSCT without overexaggerating the effects of dispersion and external mass transfer. A value of 0.13 is often used for organic micropollutants such as pesticides [Crittenden et al, 1991]. The length of the small particle column, \( L_{SC} \) can then be calculated from equation 19;

\[
L_{SC} = v_{SC}.EBCT_{SC}
\]
Section 1.6 References


AWWA Committee, “Measurement and Control of Organic Contaminants by Utilities”, AWWA, 69, s, p267, 1977


Chemviron Carbon, “Product Information Brochure, Laboratory Evaluation of Activated Carbon”


Noll, K.E., Couranis, V., Sin Hou W., “Adsorption Technology for Air and Water Pollution Control”, Lewis Publishers, pp. 3-8, 1992

Peel, R.G., Benedek, A. And Crowe, C.M., Journal of the American Institute of Chemical Engineers, 27, 1, 1981


CHAPTER 2

PHYSICAL CHARACTERISATION

Section 2.1 Introduction

The extent to which an adsorbent can adsorb large amounts of an adsorbate is directly proportional to its porous structure. To obtain a complete description of the porosity of a material several important characteristics must be investigated; the pore shape, pore volume, surface area and spatial distribution of pores.

Activated carbons and polymeric adsorbents generally possess large internal surface areas which make them suitable for the removal of organic species from aqueous solution. The nature of the porous structure influences the ability of the materials to adsorb compounds of different size. Several authors have investigated the relationships between the size of pores in carbons and the size of adsorbates, including Summers et al [1988], Newcombe et al [1996] and Hopman et al [1995]. This chapter characterises the materials under investigation using optical and nitrogen adsorption techniques to assess the possibility of size exclusion of adsorbates and to explain the kinetics of adsorption in the liquid phase.
Section 2.2 Literature Review

There is a wide spectrum of pore sizes available in activated carbons and polymeric materials, ranging from molecular dimensions to pores in the micron range. Broadly speaking there are three size classifications of pores; micropores have pore diameters of less than 2 nm (20 Å), mesopores have diameters of between 2 and 50 nm and macropores have diameters greater than 50 nm [Gregg and Sing, 1982]. These are the official classifications adopted by the International Union of Pure and Applied Chemistry (IUPAC).

The study of macro and mesopores is often performed using Scanning Electron Microscopy (SEM) or mercury intrusion porosimetry. However, both of these techniques are limited to the measurement of pores greater than approximately 30 Å. Low field NMR spin-lattice relaxation measurements have been used [Glaves et al, 1988] for the analysis of the pore structure of several coal samples. This method is applicable for pores greater than 50 Å. A number of techniques exist for the investigation of micropores.

Scanning Electron Microscopy (SEM) is one of a variety of techniques used to investigate the external surface of substances. SEM images can reveal information on the size and shape of pores greater than 50 Å, i.e. in the macropore region. Higher resolution can be obtained by Transmission Electron Microscopy. The pore structure of activated carbon fibres have been investigated by several authors [Endo et al, 1995; Innes et al, 1989; Oshida et al, 1995] using High Resolution Transmission Electron Spectroscopy (HRTEM), whilst Economy et al [1995] and Donnet et al [1993] used Scanning Tunnelling Microscopy (STM). In general it has been observed that activated carbons possess slit shaped micropores formed from the random arrangement of aromatic sheets and strips [Stoeckli, 1989]. Wang et al [1997], used TEM to show the presence of single-shell fullerenes in monodispersed nanosize carbon spheres. The technique was also used by Steckle et al [1996] to demonstrate the uniformity and pore structure of hypercrosslinked polymeric foams.
Ito and Fraissard [1987] used nuclear magnetic resonance, using a $^{129}$Xe probe, to correlate chemical shift to pore sizes in the adsorption of xenon onto zeolite NaY. An increase in chemical shift was observed as the pore size decreased, thus allowing a qualitative measure of the pore size distribution. Conner et al [1989], applied the method to mesoporous silica, which showed the opposite chemical shift dependency with pore size distribution. Ferreo et al [1992] used the technique to investigate the formation and development of structure in the polymerisation of ethylene, with some microporosity observed. Small angle X-ray scattering (SAXS) has been applied to the study of carbon adsorbents with limited success. This is due to the fact that it is difficult to distinguish between pore and micrographites with the present technology [Fujiwara et al, 1991]. Davankov and Tsyurupa [1980] studied Styrosorb polymers using SAXS but found little conclusive information on the microporous nature of the adsorbents.

Chromatographic methods have been used by several authors to characterise the porosity of adsorbent materials. Macronet Isoporous Styrene polymers were studied using gel permeation chromatography by Tsyurupa and Davankov [1980]. They concluded that the polymers possessed a narrow pore size distribution with a mean pore size of approximately 7Å. Studies into the structure of the polymers using cyclohexane revealed a bidisperse structure consisting of meso and micropores [Belyakova et al, 1986]. The polymers have also been studied by Jerábek et al [1989] using inverse steric exclusion chromatography, which allows the characterisation of pore sizes for swollen polymers. They used fifteen solutes with an effective molecular size of $<100$Å for the tetrahydrofuran environment and six solutes for the water trials. It was concluded that the polymers contained 10-15% of highly expandable polymer mass and the rest was formed by a much more dense polymer skeleton.

Thermoporosimetry is a technique which has applications in wet porous systems. The solidification temperature of liquid produced in pores depends upon the pore width,
and is measured using a scanning differential calorimeter. Quinson et al [1986] used the method to evaluate the pore size distribution of wet silica gels.

The adsorption of molecules such as benzene and nitrogen on to the surface of porous media is a well established technique and has been used extensively in the characterisation of porous materials by carbon and polymer scientists. The relationship between the amount of gas adsorbed and the pressure at constant temperature is termed the adsorption isotherm. The majority of isotherms which result from physical adsorption may be grouped into five classes, as shown in Fig. 2-1, which were originally classified by Brunauer, Deming, Deming and Teller [1940]. Reversible Type I isotherms are given by microporous solids, having relatively little external surface, the limited uptake being governed by the accessible micropore volume, rather than by the internal surface area. The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. The Type II isotherm represents unrestricted monolayer-multilayer adsorption. The reversible Type III isotherm is not common and is characteristic of non-porous systems where the adsorbent-adsorbate interaction is unusually weak. The characteristic features of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limited uptake over a range of high relative pressure. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of the Type II isotherm. The Type V isotherm is uncommon. It is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents.

Pore size distribution and surface area measurements can be extracted from adsorption isotherms by modelling. The most common method for evaluating the surface area and pore size distribution is the adsorption of nitrogen at its boiling point, 77K. However, the results are extremely dependent on the model used to derive the distribution, which has resulted in many different modelling techniques. Sweetland
[1997] provided an excellent review of the history of the models in use and I refer the reader to this for a detailed account. The following text briefly covers the relevant models to this study.

Fig. 2-1 Type I to V Isotherm Classification

Interpretation of the Type I isotherm must account for the fact that the uptake does not increase continuously as in the Type II isotherm. According to Langmuir [1918], this limit exists because the pores are so narrow that they can only accommodate a single molecular layer and thus the plateau corresponds to the completion of this monolayer. The shape of the isotherm was explained using the classical Langmuir model, although this had originally been set up for a non-porous surface;

$$\frac{n}{n_m} = \frac{c(p/p_o)}{1 + c(p/p_o)}$$

which is of the same form as Equation 10 (Chapter 1). The constant c is related to the adsorption energy and is dimensionless.
It was soon discovered that not all systems conformed to the monolayer theory. Brunauer, Emmett and Teller [1938] discovered Type II isotherms and assumed that multiple layers of gas were forming on the surface of the samples in order to account for the increased uptake at higher pressure. If the number of molecular layers, even at saturation pressure, is restricted to the finite number \( N \) (by the walls of the pore for example), the BET theory leads to the following equation:

\[
\frac{n}{n_m} = \frac{c(p/p_o)\left\{1-(N+1)(p/p_o)^N + N(p/p_o)^{N+1}\right\}}{1-(c-1)(p/p_o) - c(p/p_o)^{N+1}}
\]

which reduces to the Langmuir equation (20) by setting \( N=1 \). At relative pressures below 0.05, B.E.T. observed that their theory broke down, since at these pressures adsorption was occurring preferentially on the most active parts of the surface. They also observed that at relative pressure greater than 0.35 there was significant deviation from the model.

Although BET theory is the most widely used method for determining the surface area of samples, it should be noted that interpretation of the data is somewhat difficult when applied to the complex and disordered pore structure of activated carbons. Adsorption in micropores does not occur in molecular layers as assumed in the BET theory, but rather by micropore filling. Therefore, the reader should be aware that quoted values for BET surface areas will rarely be wholly accurate, but they do provide a means of comparison between materials.

The Kelvin equation, which describes capillary condensation in vapour-phase adsorption may be used to determine the volume and surface area distributions in the mesopore range from the adsorption of gases such as nitrogen, argon or krypton as mentioned above.

\[
\ln\frac{p}{p_o} = \frac{2\gamma V}{RT} \frac{1}{r_m}
\]
where \( V_L \) = molar volume of the adsorptive, \( \gamma \) = surface tension and \( r_m \) = radius of curvature of the meniscus at saturation pressure \( p_o \). The applicability of the Kelvin equation is limited to pores of less than 12-15 nm in radius, above which capillary condensation is no longer valid, and has a lower limit of about 1.5 nm, below which adsorption by volume filling of the pores occurs.

Adsorption in mesoporous samples frequently shows closed loop hysteresis in the relative pressure range 0.4-1.0. This is due to the fact that different mechanisms are controlling adsorption and desorption. Adsorption occurs at a relative pressure controlled by the radius of the bottom of the pore, but desorption occurs at a lower relative pressure controlled by the radius of the neck of the pore. Capillary condensation in porous adsorbents occurs on an adsorbate layer whose thickness varies with relative pressure, rather than adsorbing directly on the pore wall. To overcome this, the Kelvin radius can be combined with the statistical t-plot method [Gregg and Sing, 1982]. Thus, a mesopore size distribution can be constructed.

Numerous methods exist for producing the pore size distribution, the most common being the Barrett, Joyner and Halenda (BJH) method [Barrett, Joyner and Halenda, 1951]. The model was derived from the work of Wheeler [1945] who assumed that equilibrium between the gas phase and the adsorbed phase during desorption is determined by two mechanisms: (i) physical adsorption onto the pore walls, and (ii) capillary condensation, as modelled by the Kelvin equation and thereby limiting the range of pores which can be modelled accurately.

Micropore size distribution can also be extracted from the adsorption isotherm using one of several methods available. The MP method is derived from the statistical t-plot and has attracted criticism [McEnaney, 1995]. Dubinin proposed that microporous adsorbents undergo volume filling as opposed to the formation of successive adsorption layers on the pore walls. It was assumed that the adsorbed molecules have an adsorption potential which governed the fractional filling of micropores, based on Polanyi’s potential theory of adsorption.
\[ A = RT \ln(p^o/p) \]

where \( A \) was originally termed by Polyani as the adsorption potential, but Dubinin termed it as the differential free energy of adsorption. The Dubinin-Radushkevich (DR) [Dubinin, 1967] equation (equation 24) was used to describe the local isotherm, which provided an approximate description of pore filling for adsorbents composed of uniformly sized capillaries assuming the pore size distribution was Gaussian.

\[
\frac{W}{W_o} = \exp \left[ -B \left( \frac{T}{\beta} \right)^2 \log_{10}(p^o/p) \right]
\]

\[ B = 2.303R^2/k \]

where \( W_o \) is the total volume of the micropore system and \( W \) is the volume filled at relative pressure \( p/p_o \). \( \beta \) is a scaling factor which is used to bring the "characteristic curves" of \( \theta \) (defined as \( W/W_o \)) against \( A \) into coincidence with the curve for a chosen standard adsorbate (usually benzene). Parameter \( k \) is an expression of the breadth of the Gaussian distribution of the cumulative micropore volume \( W \) over the normalised work of adsorption \( A/\beta \), and is therefore determined by the pore structure. For plotting, equation 24 may be transformed into,

\[
\log_{10} W = \log_{10} W_o - D \log_{10}(p^o/p)
\]

\[ D = B \left( \frac{T}{\beta} \right)^2 \]

For some activated carbon isotherms, deviations from the DR equation were observed and lead to the derivation of the Dubinin-Astakov (DA) equation (Equation 28), incorporating an exponent power, \( m \), to transform the pressure.

\[
\log_{10} W = \log_{10} W_o - D' \log_{10}^m(p^o/p)
\]

\[ D' = 2.303^m \left( \frac{RT}{\varepsilon} \right)^2 \]
The parameter $\varepsilon$ is a characteristic free energy of adsorption, equivalent to the value of $A$ when $\theta = 1/e = 0.368$ ($e=2.718$). Thus the DR equation is a special case of the DA equation when $m=2$ and $\varepsilon$ for $m=2$ is related to the structural constant $B$ by,

$$B = (2.303R/\varepsilon)^2$$

The Horvath-Kawazoe (HK) method [Horvath and Kawazoe, 1983] is more widely used and relates the relative pressure to calculated adsorption potentials in model micropores. The model considered the micropores of molecular sieve materials to be slits between two graphitised carbon planes. Mathematical descriptions were developed for the potential function, the interaction energy between a gas molecule and an infinite surface between two parallel layers filled with adsorbates. The functions were dependent on the polarisability and the magnetic susceptibility of the adsorbent and the adsorbate molecule. After integration, they had an equation of the form,

$$\frac{W}{W_0} = f(1 - d_a)$$

where $d_a$ is the diameter of an adsorbent atom. However, this model gave poor values for larger pores and so the use of the Dollimore and Heal [1964] model was recommended for pores greater than 15Å. The HK method was developed to model cylindrical and spherical pore shapes by Saito and Foley [1991] and Cheng and Yang [1994] respectively.

Recently, advancement in computing power has placed emphasis on molecular-based statistical thermodynamic theory which allows many more parameters to be included within the model, such as fluid-fluid and fluid-solid interaction energy parameters, the pore size, pore geometry and the temperature. This often allows the full pore size distributions to be calculated, from micropores to macropores. The Density Functional Theory developed by Micromeritics is a commercial example of such a model [Olivier, J.P. and Conklin, W.B., 1992; Olivier, J.P., 1995]
Section 2.3 Experimental

Section 2.3.1 Scanning Electron Microscopy
Scanning electron micrographs of the adsorbents were taken by Mr. F. Page, Institute of Polymer Technology and Materials Engineering, Loughborough University, using a Cambridge Stereoscan 360 scanning electron microscope at accelerating voltages of 10-20kV. All samples were dried in an oven at 100°C and stored over silica gel in a desiccating jar. The adsorbents were glued to aluminium platforms prior to gold coating. Investigations were made into supplied and crushed F-400, LF-1, XAD-4 and MN-200.

Section 2.3.2 Surface Area and Pore Size Distributions
Surface area and pore size distributions were produced using a Micromeritics ASAP 2010C automatic analyser fitted with an optional high stability 1 torr (1.33 mbar) pressure transducer. Samples of the adsorbents, in the particle size range 53-75μm, were prepared by drying overnight in an oven at 70°C followed by degassing for a minimum of 24 hours at 100°C on the degas ports of the analyser. The actual adsorbent mass was determined by subtracting the weight of the empty degassed nitrogen back-filled sample tube from the nitrogen degassed back-filled adsorbent/sample tube. Seal frits, inserted into the top of the sample tubes prevented the samples from being contaminated by exposure to air.

Adsorption isotherms were generated by dosing nitrogen (>99.99% purity) onto the adsorbent contained within a Dewar of liquid nitrogen at approximately 77K (-196°C). A Micromeritics patented isothermal jacket was placed on the sample tube to ensure accurate temperature within the sample tube during the analysis.

The ASAP 2010 software contains a number of input files which are used to define the instrument parameters, thus enabling a number of different types of analysis. A pressure table was created to measure 110 adsorption/desorption pressure points. An equilibration interval of 10 seconds was selected as this was the optimum time.
determined by Sweetland [1997]. The microporous nature of the adsorbents necessitated the free space measurements to be made upon completion of the nitrogen sorption isotherm, since helium can be retained in the pores. The molecular drag pump was switched on for all measurements. The data reduction parameters are described in Section 2.4.2.
Section 2.4 Results and Discussions

Section 2.4.1 Scanning Electron Microscopy

Figs. 2-2 - 2-10 present the scanning electron micrographs of the adsorbents in the study. At low magnifications of the supplied materials it can be seen that F-400 is composed of irregular granular particles; LF-1 and MN-200 are composed of mainly spherical particles whereas XAD-4 appears broken into irregular chunks. In order to use the materials in the 53-75μm size range, F-400, LF-1 and MN-200 had to be crushed. This caused irregular shaped particles to be produced, e.g. Fig. 2-9 for MN-200. A significant quantity of fine material was also produced in the crushing process, which was effectively removed from XAD-4 and MN-200 by washing with ultrapure water. However, Fig. 2-3 clearly demonstrates that fine materials remained bound to the surface of F-400 even after washing. The surface texture of F-400 appears to be graphitic, with flat planes of carbon connected together, whereas the surface texture of LF-1, XAD-4 and MN-200 appears more sponge-like in appearance, suggesting the presence of a more uniform pore structure.

Fig. 2-2 SEM of F-400 (62x magnification)
**Fig. 2-3**  
*SEM of crushed F-400 (16,500x magnification)*

**Fig. 2-4**  
*SEM of LF-1 (58x magnification)*
Fig. 2-5  
*SEM of LF-1 (8,400x magnification)*

Fig. 2-6  
*SEM of XAD-4 (92x magnification)*
Fig. 2-7  SEM of crushed XAD-4 (11,500x magnification)

Fig. 2-8  SEM of MN-200 (58x magnification)
Section 2.4.2 Surface Area and Pore Size Distributions

The nitrogen adsorption/desorption isotherms for F-400, LF-1, XAD-4 and MN-200 are shown in Fig. 2-11. All of the isotherms possess the classical Type I shape, indicating the microporous nature of the adsorbents, although XAD-4 has a much shallower 'knee' in the low pressure region, suggesting that it contains a lower amount of microporosity.

The hysteresis in the isotherms is characteristic of the mesoporous structure in the adsorbents. According to the IUPAC classification [Sing et al, 1985], the hysteresis of F-400 could best be classified as H₄ behaviour which is often associated with narrow slit-shaped pores or microporosity in the case of Type I isotherms, as confirmed by Linares-Solano et al [1984]. XAD-4 and MN-200 have H₁ hysteresis which is associated with porous materials which consist of agglomerates or compacts of approximately uniform spheres in a fairly regular array, which can be seen in Figs. 2-7 and 2-10. It is difficult to classify the hysteresis behaviour of LF-1. This is probably due to the fact that it is a carbonised polymer and possibly consists of characteristics of both polymeric and carbonaceous materials.

Figs. 2-12 and 2-13 present a comparison of the adsorption isotherms for all the adsorbents. Overall, XAD-4 has the greatest capacity for nitrogen with F-400 having the lowest. However, analysis of the low pressure region in Fig. 2-13 suggests that F-400, LF-1 and MN-200 have a much larger micropore capacity than XAD-4.

Characterisation of the macropores from the isotherm data near \( p/p_0 = 1 \) is not practical since condensation on the apparatus walls occurs near the saturated vapour pressure. The most common technique for the determination of macropores is mercury intrusion porosimetry which has not been studied here since the macropore structure of the adsorbents is not important.
Fig. 2-11  *Nitrogen Adsorption/Desorption Isotherms for F-400, LF-1, XAD-4 and MN-200*
Fig 2-12  Comparison of the Nitrogen Adsorption Isotherms for F-400, LF-1, XAD-4 and MN-200

Fig 2-13  Logarithmic Comparison of the Nitrogen Adsorption Isotherms for F-400, LF-1, XAD-4 and MN-200
Section 2.2 introduced some of the large number of models which can be used to determine the surface area and pore size distribution of the adsorbents. The most common methods used to calculate the surface area are the Langmuir and B.E.T models. Table 2-1 presents the Langmuir and B.E.T. surface areas that have been obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Langmuir Surface Area (m²/g)</th>
<th>Linear Relative Pressure Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>943.04</td>
<td>1108.85</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>LF-1</td>
<td>1330.48</td>
<td>1593.80</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>XAD-4</td>
<td>876.31</td>
<td>1072.34</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>MN-200</td>
<td>1065.48</td>
<td>1241.69</td>
<td>0.05-0.10</td>
</tr>
</tbody>
</table>

**Table 2-1 Surface Area Results for F-400, LF-1, XAD-4 and MN-200**

As mentioned previously, the B.E.T theory is only valid within the relative pressure range 0.05-0.30. However, the data obtained showed significant curvature over this range and therefore the pressure ranges were selected to provide a positive y-intercept and a correlation coefficient of at least 0.9999. In order that direct comparison can be made between the samples it was important to select identical pressure ranges, since this can have an effect on the calculated surface area. The range \( p/p_0 = 0.05-0.10 \) was selected to enhance the effect of the micropore surface area and to yield the required correlation coefficient. However, this resulted in large values of the B.E.T. ‘c’ coefficient (>200) which indicates that micropore filling occurred. The B.E.T. analysis does not take account of this and hence the values quoted may be false, although they do provide a means of comparison. The ‘c’ coefficient for XAD-4 was quite low, indicating a lower quantity of microporous structure. Rohm and Haas [1978] quote the surface area of XAD-4 to be 725 m²/g, although neither the model used or relative pressure range is given making it difficult to account for the difference. It can be seen that the Langmuir surface areas are greater than those.
obtained by the BET theory, which has been attributed to the formation of multilayers of nitrogen which is not accounted for in the Langmuir theory.

The B.J.H. equations enable the size of mesopores and small macropores to be modelled. Table 2-2 presents the average pore diameters for the adsorbents modelled using the B.J.H. adsorption/desorption data and the Harkins and Jura [1943] equation.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BJH Average Adsorption Pore Diameter (Å)</th>
<th>BJH Average Desorption Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>80.69</td>
<td>66.05</td>
</tr>
<tr>
<td>LF-1</td>
<td>79.40</td>
<td>54.67</td>
</tr>
<tr>
<td>XAD-4</td>
<td>84.07</td>
<td>72.17</td>
</tr>
<tr>
<td>MN-200</td>
<td>109.60</td>
<td>85.07</td>
</tr>
</tbody>
</table>

*Table 2-2 Average B.J.H. Pore Sizes for F-400, LF-1, XAD-4 and MN-200 modelled using the Harkins-Jura equation*

As previously mentioned, adsorption occurs at a relative pressure controlled by the radius of the bottom of the pore, but desorption occurs at a lower relative pressure controlled by the radius of the neck of the pore. The average pore diameters indicate that the pore entrances are narrower than the whole pore, which can be likened to a doorway into a room.

The main criticism of the t-plot is that the enhancement of the adsorptive interaction in small pores, due to interactions among molecules in the adsorbed films on opposing pore walls and the superposition of wall potentials, is not accounted for. Thus, at a given pressure the statistical thickness of the adsorbed layer is greater in the pore than on the nonporous material [Russell and LeVan, 1994]. The theory of volume filling of micropores (TVFM) introduced by Dubinin and described by the Dubinin-Radushkevich and Dubinin-Astakov equations have been generally accepted as suitable methods to describe pore filling of adsorbents. However, a number of authors
have disputed the assumption of a Gaussian pore size distribution. Jaroniec and Piotrowska [1986] suggested a gamma distribution and Wojsz and Rozwadowski [1989] suggested Rayleigh and exponential distributions as well as general equations for all types of isotherms. Table 2-3 presents the micropore surface area and mean pore size as modelled by the Dubinin-Astakov equations.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Micropore Surface Area (m²/g)</th>
<th>Mean Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>712.66</td>
<td>14.95</td>
</tr>
<tr>
<td>LF-1</td>
<td>924.10</td>
<td>15.11</td>
</tr>
<tr>
<td>XAD-4</td>
<td>721.44</td>
<td>20.12</td>
</tr>
<tr>
<td>MN-200</td>
<td>716.53</td>
<td>16.52</td>
</tr>
</tbody>
</table>

Table 2-3  
Micropore surface area and mean pore diameter of F-400, LF-1, XAD-4 and MN-200 as modelled by the Dubinin-Astakov equations

Sweetland [1997] demonstrated that although the Horvath and Kawazoe model has been widely accepted for the characterisation of micropores, it is highly dependent upon the parameters used; e.g. the interaction parameter and pore shape. For comparison reasons, the adsorbents were modelled using the slit-pore model and an intermediate interaction parameter of 2.84x10⁻⁴⁵ ergs.cm⁴ which is between the interaction energies of the carbons and the lower energies experienced by the polymers. Table 2-4 presents the mean pore sizes of the adsorbents and Fig. 2-13 shows the pore size distributions produced using the Horvath and Kawazoe model.

It can be seen that F-400, LF-1 and MN-200 possess similar pore size distributions, which is reflected by the mean pore sizes. The pore size distribution of XAD-4 confirms the earlier results showing a relative lack of microporosity. Unfortunately, these figures are not quantitative due to the estimations made using the interaction parameters and pore shape. It is well established that activated carbons are composed
of layers of graphite, forming slit-shaped pores, however, this is not necessarily the case for the polymers. Ogston [1958] postulated that the pores in swollen polymer gels were spherical in shape.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Horvath and Kawazoe Mean Pore Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>4.6</td>
</tr>
<tr>
<td>LF-1</td>
<td>4.8</td>
</tr>
<tr>
<td>XAD-4</td>
<td>6.2</td>
</tr>
<tr>
<td>MN-200</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 2-4 Mean Pore Sizes of F-400, LF-1, XAD-4 and MN-200 modelled by the Horvath and Kawazoe slit pore model (interaction parameter: 2.84 ergs.cm$^4$)

Fig 2-14 Pore Size Distributions of F-400, LF-1, XAD-4 and MN-200 modelled by the Horvath and Kawazoe slit-pore model
Density Functional Theory (DFT) is a new technique which is based upon the adsorbate-adsorbate interactions, similar to the Horvath-Kawazoe model. However, unlike HK, DFT models the density of the fluid near the walls of the micropores. DFT is applicable over a much wider size range than any other model. However, at present the model is based upon slit pores and carbon-graphite interaction energies, making quantitative modelling of the polymers impossible. Fig. 2-15 presents the DFT pore size distributions for F-400, LF-1, XAD-4 and MN-200. The pore size distributions for F-400, LF-1 and MN-200 are reasonably similar in the micropore region, with MN-200 perhaps having a narrower distribution. However, in the meso/macropore region there are significant differences. The carbons have pores in the range 20-500 Å, which may enhance the diffusion of organic species into the micropores. However, these pores may also suffer from being blocked by large organic molecules such as fulvic and humic acids. The pore size distribution for XAD-4 shows an almost exclusive meso/macroporous structure. This structure may well be suited to the adsorption of large molecular weight organics but the adsorption of low molecular weight herbicides may be impaired.

The apparent bimodal distribution of pores in the microporous region is caused by deficiencies in the DFT model. The theory is incapable of modelling pores in the 8-10Å region, which causes the data to have a slight ‘dip’ in the distribution.
Fig 2-15  
*DFT Pore Size Distributions of F-400, LF-1, XAD-4 and MN-200*
Section 2.5 Conclusions

The pore size distributions of the adsorbents have been investigated using nitrogen adsorption. A number of models have been applied to the data in order to model the micro- and meso- pore structures. However, quantitative estimates of the pore sizes cannot be made due to the dependency of the models on pore shape and interaction parameters. Despite these problems, the models allow reasonable comparisons to be made between the adsorbents.

F-400, LF-1 and MN-200 possess similar microporous structure. The carbons also contain a reasonable degree of mesoporosity, which may enhance the diffusion of organic species into the micropores. The pore size distribution for XAD-4 shows an almost exclusive meso/macroporosity with very little microporous structure.
Section 2.6 References


Endo, M., Oshida, K., Kogiso, K., Matsubayashi, K., Takeuchi, K., Kobayashi, S., Dresselhaus, M.S., “Pore Analysis of Activated Carbon Fibres by High Resolution...


Langmuir, I., "The Evaporation, Condensation and Reflection of Molecules and The Mechanism of Adsorption", Journal of the American Chemical Society, 40, pp. 1361-1403, 1918


Wheeler, A. discussed at American Association for the Advancement of Science Conference on Catalysis, Gibson Island, 1945 (cited in Barrett, Joyner and Halenda, 1951)

CHAPTER 3

CHEMICAL CHARACTERISATION

Section 3.1 Introduction

The functional groups present on the surface of an adsorbent can have an influence on the adsorption of organic species. Functional groups give rise to adsorption mechanisms such as ion exchange or hydrogen bonding as opposed to the weaker mechanism of van der Waals forces. The surface charge of adsorbents caused by the acidic or basic nature of the functional groups allows for the attraction or repulsion of charged species. Numerous studies of the surface of activated carbons, and their modification by oxidation and heat treatment have been presented. Most activated carbons contain carbon atoms arranged in aromatic rings which build up basal planes of various size and stacking height. The aromatic layers are not structurally perfect, resulting in defects. At the surface, these defects cause the carbon atoms to be highly reactive, allowing the chemisorption of various atoms such as oxygen, hydrogen and halogens, producing surface complexes or functional groups [Ehrburger, 1994]. As much as 5-20% by weight of the material can be composed of other elements, which are mainly oxygen and hydrogen, although depending on the precursor and production method, elemental nitrogen, sulphur and metal atoms may also be found. These foreign elements, in particular oxygen can have a profound effect on the uptake of organic species [Sorial et al, 1993; Coughlin and Ezra, 1968; Boehm, 1994]. Coughlin and Ezra [1968] demonstrated that extensive oxidation of activated carbon led to large decreases in the adsorption capacity of phenol, nitrobenzene and benzene sulphonate. Kipling and Shooter [1966] observed similar results for carbon black, a material with similar properties to activated carbon. Oxidation of the surface of activated carbon with chlorine has also been shown to increase the number of oxygen containing surface groups, and thereby decrease the capacity for phenol [Snoeyink,
The negative functionality will however enhance the adsorption of cationic species, such as amine groups.

Davankov and Tsyurupa [No Date] studied the chemical functionality of their hypercrosslinked polymers and concluded that the polymers contained no polar or halogen functional groups. However, Law et al [1996] observed that 10% of aromatic groups of the hypercrosslinked resins they analysed using $^{13}\text{C}$ CP/MAS NMR, retained a chloromethyl group. These groups can be hydrolysed, thus enabling hydrogen bonding with suitable organics. Streat and Sweetland [1998] investigated MN-200 using a variety of techniques and found that it contains between 5 and 6% by weight of oxygen. The major functional groups present were ketones, ethers and alcohols.

The chemical characteristics of the surface of the adsorbents used in this study have been investigated using a variety of techniques in an attempt to understand the mechanisms for the adsorption of adsorbates.
Section 3.2 Literature Review

The determination of surface functional groups and bulk composition of adsorbents can now be achieved by a wide variety of techniques and the technology is continually improving. The following discussion is restricted to the techniques which have been applied in this study.

Section 3.2.1 Direct Titration

Although there are many types of acidic surface oxides, the most common fall into one of four groups which can be classified as carboxyl, lactones, phenolic and carbonyl, as shown in Fig. 3-1. The existence of these groups has been confirmed by classical chemical detection methods [Boehm, 1994], FT-IR and XPS [Ehrburger, 1994]. The acidity constants of these four groups differ by several orders of magnitude and therefore it is possible to estimate their relative amounts by titration with bases of differing strength. The method of Boehm and co-workers [Boehm et al., 1964] consists of using alkaline solutions of increasing strength; sodium hydrogen carbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH) and sodium ethoxide (NaOC₂H₅). Thus, carboxylic groups are titrated by NaHCO₃, lactones with Na₂CO₃, phenols with NaOH and carbonyls with NaOC₂H₅. This is achieved in practice by contacting the activated carbon with the bases and subsequently titrating the remaining sodium ions present with an acid such as HCl. Boehm [1966] verified the types of functional groups by using chemical derivatisation and confirmed the accuracy and assumptions used in the titration method.

Basic oxides are always present on the surface of an activated carbon. They are formed when carbon is exposed to dry oxygen on cooling to room temperature after heat treatment during production [Boehm, 1994; Ehrburger, 1994]. There is disagreement as to the form of these basic groups. Garten and Weis [1957] proposed a chromene structure in order to account for the uptake of acids but Voll and Boehm [1971] suggest that \(\gamma\)-pyrone-like structures are more plausible. There is also evidence that acids can be adsorbed due to the \(\pi\) electron system of the basal planes.
[Leon et al, 1992] and so both mechanisms must be considered. Although acidic and basic groups are simultaneously present on the surface of carbons, it is generally observed that the amount of oxygen detected as functional groups is only a fraction, typically 1/3 to 2/3 of the total oxygen content of the carbon [Ehrburger, 1994]. Mazet et al [1994] and Hazourli [1991] have investigated the surface functional groups of F-400 by Boehm’s titration, the concentrations of which are presented in Table 3-1. The results of Streat and Sweetland [1998] for F-400 and MN-200 are also presented in Table 3-1. The differences observed by Streat and Sweetland for F-400 were attributed to batch variances.

![Diagram of functional groups]

**Fig. 3-1** *Acidic Surface Oxide Groups*

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Carboxylic</th>
<th>Lactone</th>
<th>Phenolic</th>
<th>Carbonyl</th>
<th>Total Acidic Groups</th>
<th>Total Basic Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mazet et al (F-400)</td>
<td>0.33</td>
<td>0.23</td>
<td>0.10</td>
<td>0.49</td>
<td>1.05</td>
<td>0.26</td>
</tr>
<tr>
<td>Hazourli (F-400)</td>
<td>0.13</td>
<td>0.19</td>
<td>0.10</td>
<td>0.87</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>Streat et al (F-400)</td>
<td>0.05</td>
<td>0.07</td>
<td>0.00</td>
<td>0.24</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Streat et al (MN-200)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
<td>0.13</td>
<td>0.23</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3-1** *Concentration of Surface Functional Groups (meq/g)*
Section 3.2.2 Spectroscopic methods

It is difficult to achieve meaningful results using infra-red spectroscopy due to the strong IR absorption of carbon. Mattson et al. [1969;1970] identified surface functional groups using a technique known as Attenuated Total Reflection infra-red (ATR) spectroscopy. Direct Transmission has also been applied for the study of carbonaceous materials [Freidel and Hofer, 1970; Freidel and Carlson, 1972; Ishizaki and Marti, 1981]. However, varying degrees of success have been achieved, depending on the nature of the sample. Recently, Diffuse Reflectance FT-IR (DRIFT) spectroscopy has been used for the determination of carbon spectra [Fanning and Vannice, 1993; Meldrum and Rochester, 1990]. The technique overcomes some of the contamination and reflection problems experienced with the other techniques and is simpler in operation. With the advent of Fourier Transform spectrometers the analysis has improved and peaks corresponding to single C-O bonds, carboxyl groups, esters, lactone and carbonyl groups have been identified [Sellitti et al., 1990].

Infra-red studies have suggested a wide variety of functional groups on the surface of carbonaceous materials, since bands tend to be broad and unresolved. Also the graphitic planes tend to shift the frequencies of vibrations of various functional groups which cause uncertainty in their assignment. Fanning and Vannice [1993] conducted a survey of the literature regarding functional groups on activated carbon and found 14 different groups. The IR spectra of MN-200 was studied by Streat and Sweetland [1998]. They observed characteristic bands attributable to -CH, -CH₂, substituted benzene rings and oxygen functionality, mainly in the form of aryl and alkyl ketones.

Improvements in the resolution of X-Ray Photoelectron Spectrometers has led to better quantification of functional groups. Briggs et al. [1992] studied the spectra of 43 aliphatic homopolymers containing C, H and O plus two co-polymers (styrene/maleic anhydride and ethylene/maleic anhydride). They presented the primary and secondary shift data for the C1s envelope associated with the different types of oxygen functionality. Detailed studies into the surface functional groups on
oxidised polyolefins were performed by Popat [1995]. Variable take-off angles were used to enable depth profiling of the functional groups. Bradley et al [1996] used XPS to investigate the surface functionality of two carbon blacks and two porous carbons. They were able to correlate the concentration of oxygen on the surface of carbon to the heat of immersion of the carbons for n-heptane and water. Jansen et al [1995] used XPS to determine nitrogen functional groups on several nitrogen containing activated carbons. They observed that the nitrogen content of a series of modified carbons varied from 2.9 to 7.9% with a range in oxygen concentration of 4.2-16.0%. Elemental analysis produced compositions of nitrogen and oxygen that were generally higher than obtained from XPS, which was attributed to a non-uniform distribution of surface groups throughout the carbons. XPS has been used to study oxidised carbons but has been found to be inaccurate for quantitative determinations. The technique has been mainly applied in studies of carbons with low surface areas.

Section 3.2.3 Surface Charge

The surface of a particle will carry an inherent charge which is highly dependent on mobile ions present in the suspending medium. The distribution of ions close to the surface of a particle may be dominated by the effects of shape and size of the surface and solution groups, whereas electrostatic forces are responsible further away. These differences give rise to the idea of a double layer, the so-called inner and diffuse regions being characterised by different ionic behaviour.

At some distance from the surface the so called shear plane, the ions do not travel with a moving (or diffusing) particle, but remain in the bulk solution. The potential at this distance is, by definition, the zeta potential, $\zeta$. Zeta potential is often defined as a remote effect of the surface charge, related to the latter, but not directly.

The surface charge of an adsorbent affects the adsorption of charged molecules such as humic substances, phenols, herbicides and metals. At charged interfaces the distribution of ions in the solution surrounding the surface is influenced by the surface charge. The pH value at which the densities of the charge determining ions at the
surface are equal is referred to as the point of zero charge (PZC). At pH values below the PZC the surface is positively charged, and at pH values greater than the PZC the surface is negatively charged. Huang et al [1985], and Summers and Roberts [1988] have reported pH\textsubscript{PZC} values of 4.0 to 10.6, which would result in both positively and negatively charged surfaces at pH values typically found in water treatment, i.e. pH 6 to 8. Streat and Sweetland [1998] reported pH\textsubscript{PZC} of MN-200 to be 4.3, indicating a negatively charged surface at the pH of natural waters.

Section 3.2.4 Adsorption Characteristics

Most of the standard methods developed thus far evaluate the equilibrium adsorption capacity of an adsorbent as opposed to the kinetics. The tests were originally developed for use with powdered activated carbon or pulverised granular activated carbon, but it has since been shown that the adsorption capacity of granular activated carbon does not vary upon pulverisation, allowing the capacities can be compared. The following paragraphs give a brief overview of the most commonly used test methods [Sontheimer et al 1988].

The molasses test is mainly used for de-colourisation applications, such as sugar processing. It has found little applicability in potable water treatment due to the large molecular weight of the colour producing substances in molasses, although some application has been found in wastewater treatment. A standard source of molasses or carbon should be used in order that the results can be compared. However, the methods of conducting the test and reporting the results vary. Hassler [1967] developed a test using diluted molasses solution to which different amounts of carbon are added. The results are based on the amount of carbon required to reduce the colour by 90-95%.

Methylene Blue is an aromatic dye of intermediate size, for which activated carbon has a high adsorption capacity. It is commonly used in testing, but because of its high affinity for activated carbon, the results are difficult to apply in practical water treatment conditions. Paprowicz [1986] provided an extensive review of the test
methods for a wide range of carbons. All the test methods yield results that are proportional to the amount adsorbed under defined conditions. However, due to the number of different methods available, comparison with carbons from other studies is somewhat limited.

The iodine number is defined as the amount of iodine (mg) adsorbed by 1.0 g of carbon at a residual concentration of 0.02 N [AWWA 1974;1978]. The test results give a good indication of the microporosity and are often correlated to the surface area values. Other test methods include the alkylbenzene sulphonate test for adsorption of large molecular weight detergents; the tannin test [AWWA, 1978] used to give an indication of the removal of compounds added to water by decaying vegetation; the dechlorination column test and the threshold odour number [AWWA, 1978].

The high aqueous solubility of phenol and its presence as a pollutant led to the development of the phenol test. It gives an indication of an adsorbents ability to remove some types of chemical taste and odour. The presentation of the results varies, from the amount of phenol adsorbed per mass of carbon at an equilibrium concentration of 1.0 g/m³ (1.0 mg/l) or 0.1 g/m³, to the weight of phenol adsorbed per 100 g of carbon [AWWA, 1978].

The adsorption of phenolic pollutants has been studied extensively. Sweetland [1997] presented a table showing the Freundlich parameters for phenol adsorption on F-400 as presented by six different authors. van Vliet et al [1980] compared the adsorption capacity for phenol of eight commercial synthetic adsorbents with F-400 activated carbon. In general, the activated carbons offered the highest capacity, followed by the carbonised polymers and the polymeric adsorbent resins. At high concentrations, the capacity of the XAD polymeric adsorbents were similar to that of activated carbon, suggesting possible uses in waste water treatment. Fox [1978], discussed the advantages of using XAD resins for the recovery of phenolic compounds from waste streams, due to their ease of regeneration. Kim et al [1996] investigated the
adsorption of phenols onto macroreticular resins produced with various surface areas and functionalities. Experiments using p-chlorophenol showed that a linear relationship existed between the surface area of the adsorbent and its adsorption capacity. Differences in the adsorption of phenol and phenolic compounds containing substituted groups of -NO\(_2\) and -Cl were explained by the resonance effect of the functional group and the compounds solubility. Existence of functional groups at the ortho position appeared to enhance the adsorption capacity and accelerated intraparticle mass transfer. Itaya et al [1984] investigated the adsorption of phenol, p-chlorophenol and p-cresol onto two macroporous resins, XAD-4 and XAD-7. They investigated a number of adsorption isotherm correlations and concluded that the equation of Jossens et al [1978] proved to be the most satisfactory over the entire range of concentration. In all systems, the Freundlich and Langmuir equations showed a poor fit to the data. Tsyurupa et al [1995; 1995] compared the sorption of phenols onto Macronet Polymers to that of XAD-4 and observed that the Macronet polymers could treat 4 times that of the XAD-4.
Section 3.3 Experimental

Section 3.3.1 Infra-Red Spectroscopy
All spectra were recorded on a Nicolet 20-DXC FT-IR spectrometer with a dry air purge, liquid nitrogen cooled MCT (mercury-cadmium-telluride) detector, and a Spectra-Tech diffuse reflectance accessory. The diffuse reflectance accessory consisted of a hemispherical mirror which split into two halves, with the sample mounted on the central platform. The accessory was aligned to provide maximum infra-red signal intensity using a stainless steel mirrored platform. The height of the sample on the platform was adjusted to minimise the gain of the detector. Samples were dispersed in ground spectroscopic grade KBr prior to analysis. The sample loading was 1% by weight in the KBr. The same batch of ground KBr was used for all samples to keep particle size consistent. The average particle size was in the region of 20 microns.

Diffuse reflection spectra can be used quantitatively, but samples must be prepared and the results interpreted with care. The infra-red spectra obtained depend strongly on the shape and size of the powder particles used and the size of the diluent particles. One practical problem is that it can be difficult to achieve the same degree of dispersion of the adsorbents in the KBr. To achieve a sufficient level of dispersion, samples were shaken for six periods of 5 minutes.

Interpretation and spectra manipulation was achieved using the Nicolet OMNIC software. Water vapour detected in the sample spectra was subtracted, using water vapour standards created using the background KBr. All spectra have been obtained in absorbance units, and converted to Kubelka-Munk units after water vapour subtraction.

Section 3.3.2 X-ray Photoelectron Spectroscopy
A VG ESCALAB MK 1 spectrometer employing a monoenergetic Al kα X-ray source (1486.6 eV) at a pressure of ~10^{-7} mbar was used for the analysis of F-400 and LF-1,
XAD-4 and MN-200. Survey spectra were obtained at a pass energy of 100eV using a 0-1100 eV scan (5 eV step size) and a dwell time of 20 ms. All spectra were obtained using an anode power of 200 W (10 kV, 20 mA).

Section 3.3.3 Direct Titration

In order to quantify the amount of acidic surface oxides present in the carbons, the method of Boehm et al [1964] was used. 0.1 M solutions of sodium hydrogen carbonate, sodium carbonate, sodium hydroxide were prepared in ultra-pure water. A 0.1 M solution of sodium ethoxide was prepared in HPLC grade ethanol since sodium ethoxide reacts with water. The sodium hydroxide and sodium carbonate were volumetric standards supplied by Aldrich Chemicals. The sodium hydrogen carbonate and sodium ethoxide were prepared from analytical reagents, also supplied by Aldrich. 15 ml of each solution was measured with a pipette and placed into separate 25 ml conical flasks. Approximately 150 mg of carbon was added to each conical flask, the weight being accurately recorded by a Sartorious BP210D balance. The flasks were subsequently covered with Parafilm and shaken for five days to equilibrate. Control experiments which featured no carbon were also prepared for comparison.

At the end of the equilibration period 5ml aliquots of each solution were extracted, filtered using 0.22 μm PVDF filters, supplied by Whatman, and titrated with a volumetric standard of HCl using a 5ml burette marked with 0.05 ml divisions. Methyl Red was used as indicator which changed from yellow to red at the end point. Each sample was produced in triplicate to reduce the error associated with the titration.

Section 3.3.4 Elemental Analysis

An elemental analysis of F-400, LF-1, XAD-4 and MN-200 was performed in the polymer chemistry department at the University of Strathclyde. The samples were analysed on a Perkin Elmer Series II 2400 elemental micro analyser. The estimated error for each element analysed was ±0.5%.
Section 3.3.5 Zeta Potential Analysis

The zeta potential of F-400, LF-1 XAD-4 and MN-200 was determined using a Zetamaster from Malvern Instruments. The measurements were based on a Laser Doppler Electrophoresis technique. The technique operates by measuring the interference fringes of two laser beams at the point where the beams cross. Particles that cross the beams will cause the interference fringes to shift and this can be related back to their velocity and hence to the electrophoretic mobility. This technique offers several advantages over traditional microscope methods. It averages the measurement over thousands of readings, generating an intensity distribution, greatly reducing the statistical errors. Very low or zero zeta potential can also be measured accurately by virtue of an optical modulator which causes a Doppler shift in one of the beams.

The materials were crushed using an agate mortar and pestle and added to ultrapure water to allow the larger particles to sediment. The suspended particles were recovered and dried in an oven at 378 K for 24 hours before subsequently being stored in a desiccator. Each curve was generated using twelve individual samples consisting of 20 mg adsorbent suspended in 30 ml of 0.1 M NaCl. The pH of the solutions were adjusted using 0.05 M NaOH and 0.05 M HCl solutions such that the pH ranged from 2-12. The conical flasks were sealed with Parafilm and shaken for 24 hours to equilibrate. The equilibrium pH of each sample was measured prior to analysis on the zetamaster.

The calibration of the zetamaster was checked by measuring a standard latex solution which gave a zeta potential of -55 mV. Between all samples the cell was flushed with 30 ml of a 1% Decon solution followed by 30 ml of ultrapure water. The samples were injected and the zeta potential measured five times to provide an average. If the zeta potential varied by more than 0.5 mV over the five measurements the cell was flushed and the sample introduced again. Large variations in measurements are
indicative of contamination or more frequently, air bubbles obstructing the electric field and laser.

Section 3.3.6 Phenol Capacity Measurements

In order to calculate the Phenol number, adsorption isotherms were produced. A stock solution of 1000 mg/l phenol was made and diluted to provide the individual solution concentrations. The bottles used were brown glass 500 ml capacity with PTFE lined caps to eliminate organic leaching. The concentrations of phenol used were 20, 50, 100, 200 and 300 mg/l, made up to 500 ml, into which 100 mg of the adsorbent of interest was placed. The size range of adsorbent used was 53-75 μm to minimise the reaction time. The bottles were shaken at 25°C in a New Brunswick C series incubator shaker.

At specified time intervals, a 5ml aliquot was taken from each bottle, filtered using a 0.22 μm PVDF filter and the concentration of phenol measured using a Perkin Elmer UV Lambda 12 spectrophotometer at a wavelength of 269.4nm. The aliquot was subsequently returned to the reaction bottle to ensure the solid/liquid ratio remained constant. Analysing the concentrations at suitable time intervals ensured that equilibrium had been achieved at the end of the reaction.
Section 3.4 Results and Discussion

Section 3.4.1 Infra-Red Spectroscopy

The spectra of F-400 and LF-1, presented in Figs. 3-2 and 3-3 do not indicate any sharp peaks that are caused by the carbon absorbing the infra-red beam. Transmission FT-IR as well as attenuated transmission spectroscopy have been attempted with little improvement in the results. Improved spectra can be obtained using a photo acoustic spectrometer but this equipment is currently not available. Infra-red spectra of XAD-4 and MN-200 can be seen in Figs. 3-4 and 3-5, respectively.

Both polymers, XAD-4 and MN-200 have characteristic bands attributable to the vibrations of -CH, -CH$_2$ and benzene rings. The aromatic out-of-plane C-H vibrations and ring out-of-plane vibrations in the region 900-650 cm$^{-1}$ provide a means of determining the type of aromatic substitution [Socrates, 1994]. Most mononuclear and polynuclear aromatic compounds have three or four peaks in the region 3080-3010 cm$^{-1}$, these being due to the stretching vibrations of the ring -CH bonds. Ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm$^{-1}$.

![Diffuse Reflectance FT-IR Spectra of F-400](image_url)
The medium intensity absorption bands on the spectra of XAD-4 at 904 cm\(^{-1}\) and 836 cm\(^{-1}\) as well as the strong band at 700 cm\(^{-1}\) suggests the presence of meta-disubstituted benzene rings. These wavelengths are also represented in the spectra of para-substituted benzene rings. However, the strong bands at 796 cm\(^{-1}\) and 700 cm\(^{-1}\) with the first band being less intense than the second also provides evidence for the presence of 1,2,3 tri-substituted benzene rings. The evidence for all these groups is confirmed by the C=C stretching vibrations between 1625 and 1430 cm\(^{-1}\).

There is very little to suggest the presence of oxygen functionality on the surface of XAD-4. The characteristic bands for hydroxyl, C-O, C=O or ether groups are not observed. There is also no evidence of amine functionality. This is to be expected since XAD-4 is marketed as a non-polar adsorbent. MN-200 shows strong absorption bands at 816 cm\(^{-1}\) and 700 cm\(^{-1}\) which are indicative of p-substituted benzene rings suggesting that most of the crosslinking bridges are in the para position. Evidence of mono-substituted rings, e.g. uncrosslinked polystyrene is shown by the two medium absorptions, one at 760 cm\(^{-1}\) and the other at 700 cm\(^{-1}\). However, the first band is smaller than the second which is usually vice versa for mono-substituted rings. These two absorption bands are also represented in the spectra of 1,2,3-tri- and 1,2,4-tri-
substituted benzene rings. The absence of a strong band in the 720-685 cm\(^{-1}\) region would tend to eliminate the possibility of 1,2,3-tri-substituted rings.

![Diffuse Reflectance FT-IR Spectra of XAD-4](image)

**Fig. 3-4 Diffuse Reflectance FT-IR Spectra of XAD-4**

The strong peak at 1706 cm\(^{-1}\) suggests the presence of carbonyl (C=O) functional groups. Carbonyl peaks are observed in a wide variety of compounds including ketones, aldehydes, carboxylic acids, esters, peroxides etc. Evidence of aryl ketones is presented by the absorption band at 1210 cm\(^{-1}\), the phenyl-carbon stretch, and several medium intensity bands around 1300 cm\(^{-1}\), due to C-O-C bending and C-CO-C. Similarly, bands at 1304 cm\(^{-1}\) and several bands around 1100 cm\(^{-1}\) suggest the possible presence of an alkyl ketone. The methylene scissoring vibration of the -CH\(_2\)-CO- group occurs in the range 1435-1405 cm\(^{-1}\) which is lower than that for CH\(_2\) in aliphatic hydrocarbons which occurs in the range 1480-1440 cm\(^{-1}\). The lack of a sharp band at 2720 cm\(^{-1}\) eliminates the possibility of aldehyde groups. Aryl ethers
absorb strongly in the region 1270-1230 cm\(^{-1}\) whereas alkyl aryl ethers have two strong absorptions, the most intense of which is at 1270-1230 cm\(^{-1}\), and the other being at 1120-1020 cm\(^{-1}\). However, bands due to ketonic compounds also occur in this region, preventing positive determination [Streat and Sweetland, 1998].

**Fig. 3-5**  *Diffuse Reflectance FT-IR Spectra of MN-200*

Section 3.4.2  *X-ray Photoelectron Spectroscopy*

X-ray photoelectron spectroscopy (XPS) was performed on F-400, LF-1, XAD-4 and MN-200 to identify the surface concentration of the oxygen in the adsorbents. Table 3-2 presents the atomic compositions of the adsorbents.

Surface bonded oxygen molecules in the form of C-O-C or C=O usually arises from strongly bonded water. Analysis of the C\(_1\)s peak was performed by D.P. Maton of the
Department of Chemistry, Loughborough University for XAD-4 and MN-200 and served to confirm that the polymers have low levels of surface functionalities.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Carbon (%)</th>
<th>Oxygen(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>93.8</td>
<td>6.2</td>
</tr>
<tr>
<td>LF-1</td>
<td>96.7</td>
<td>3.3</td>
</tr>
<tr>
<td>XAD-4</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>MN-200</td>
<td>90.4</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*Table 3-2 Atomic composition of the adsorbents determined by X-Ray photoelectron spectroscopy*

**Section 3.4.3 Direct Titration**

The quantities of base consumed and the concentration of functional groups on the surface of the adsorbents are presented in Tables 3-3 and 3-4 respectively. The adsorbents under investigation do not contain appreciable amounts of acidic surface oxide groups. The capacity of the carbons is significantly greater than that for the polymers. However, the capacity observed for F-400 is lower than that presented by Mazet *et al* [1994], of 1.05 meq/g. This titration has been performed by several members of the laboratory with similar results and the differences are attributed to differing chemical composition of the two samples. F-400 which had been subjected to an oxidation process within the laboratory by V. Strelko Jr. showed a total acidic surface oxide group capacity of 2.94 meq/g.

The predominant surface groups on LF-1 are phenolic in nature, whereas for F-400 the predominant groups are carbonyls. This contrast may explain differences observed in the adsorption characteristics of various materials.

The results indicate that XAD-4 and MN-200 contain almost identical amounts of strongly and weakly acidic functional groups. However, XAD-4 possesses
significantly more phenolic type groups than MN-200 and shows no carbonyl functionality. Again, these differences may explain the adsorption characteristics of these two polymers.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Base Consumption (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaOC$_2$H$_5$</td>
</tr>
<tr>
<td>F-400</td>
<td>0.358</td>
</tr>
<tr>
<td>LF-1</td>
<td>0.514</td>
</tr>
<tr>
<td>XAD-4</td>
<td>0.155</td>
</tr>
<tr>
<td>MN-200</td>
<td>0.220</td>
</tr>
</tbody>
</table>

**Table 3-3 Base Consumption of F-400, LF-1, XAD-4 and MN-200**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Concentration of Surface Groups (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carboxylic</td>
</tr>
<tr>
<td>F-400</td>
<td>0.047</td>
</tr>
<tr>
<td>LF-1</td>
<td>0.027</td>
</tr>
<tr>
<td>XAD-4</td>
<td>0.061</td>
</tr>
<tr>
<td>MN-200</td>
<td>0.060</td>
</tr>
</tbody>
</table>

**Table 3-4 Concentration of Surface Functional Groups on F-400, LF-1, XAD-4 and MN-200**

**Section 3.4.4 Elemental Analysis**

The elemental analysis results for F-400, LF-1, XAD-4 and MN-200 can be seen in Table 3-5. The analytical technique prevents the accurate determination of oxygen and so it is calculated by the residual.
The results show that F-400 and LF-1 have a significantly higher ratio of carbon to hydrogen in their structure, when compared to XAD-4 and MN-200, which is to be expected. The carbons also possess a small amount of nitrogen, suggesting the possibility of amine functionality. F-400 also contains sulphur, which may also contribute to the surface functionality. However, the nitrogen and sulphur present in the carbons may be bound into the structure and therefore not contribute to the functionality.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Carbon %</th>
<th>Hydrogen %</th>
<th>Nitrogen %</th>
<th>Sulphur %</th>
<th>Chlorine %</th>
<th>Oxygen %*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>89.37</td>
<td>0.40</td>
<td>0.44</td>
<td>0.74</td>
<td>Trace or Nil</td>
<td>9.05</td>
</tr>
<tr>
<td>LF-1</td>
<td>93.27</td>
<td>0.37</td>
<td>1.11</td>
<td>Trace or Nil</td>
<td>Trace or Nil</td>
<td>5.25</td>
</tr>
<tr>
<td>XAD-4</td>
<td>88.86</td>
<td>7.82</td>
<td>Trace or Nil</td>
<td>Trace or Nil</td>
<td>Trace or Nil</td>
<td>3.32</td>
</tr>
<tr>
<td>MN-200</td>
<td>84.10</td>
<td>5.81</td>
<td>Trace or Nil</td>
<td>Trace or Nil</td>
<td>0.97</td>
<td>9.12</td>
</tr>
</tbody>
</table>

Data given in mass percent *oxygen determined by residual

Table 3-5  Elemental Analysis of F-400, LF-1, XAD-4 and MN-200

The chlorine present in MN-200 may be attributed to chloromethyl groups which did not undergo crosslinking or a chlorinated solvent used in the Macronet production or residuals of the Freidel-Crafts reaction [Streat and Sweetland, 1998].

Section 3.4.5  Zeta Potential Analysis

The zeta potential curves of F-400, LF-1, XAD-4 and MN-200 at different pH values are illustrated below in Fig. 3-6, indicating zero crossover points at a pH of 4.8, 3.8, 6.4 and 4.4 for F-400, LF-1 XAD-4 and MN-200 respectively. The surface charge of the materials at a pH of around those of natural water (pH 6-7) indicates that they will have negatively charged surfaces except for XAD-4, which will probably have a neutral surface.
Section 3.4.6 Phenol Capacity Measurements

The adsorption isotherms for phenol are presented in Fig. 3-7. Tables 3-6 and 3-7 presents the Freundlich coefficients and Phenol Number of each material, respectively.

The results indicate that LF-1 has a larger capacity for phenol than F-400 which can be attributed to the larger surface area of LF-1. The Freundlich coefficients for F-400 compare well with those presented by Seidel et al [1985] (K=2.32, 1/n=0.216) and Sorial et al [1993] (K=2.28, 1/n=0.177). The carbons have a much higher capacity for phenol than the polymeric adsorbents which may be due to delocalised electrons in the carbons forming strong interactions with the π electrons in the phenol. From Table 3-7, MN-200 has approximately 4 times the capacity of XAD-4, confirming the results reported by Tsyurupa et al [1995].

The strength of the bond between the adsorbate molecule and the surface of the carbons is similar, as indicated by the value of 1/n. The same is true of the polymeric
adsorbents, although the larger values of the $1/n$ coefficient suggests weaker adsorption forces.

![Adsorption Isotherms for Phenol Adsorption onto F-400, LF-1, XAD-4 and MN-200](image)

**Fig. 3-7** *Adsorption Isotherms for Phenol Adsorption onto F-400, LF-1, XAD-4 and MN-200*

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$K$</th>
<th>$1/n$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>2.400</td>
<td>0.183</td>
<td>0.993</td>
</tr>
<tr>
<td>LF-1</td>
<td>3.415</td>
<td>0.196</td>
<td>0.993</td>
</tr>
<tr>
<td>XAD-4</td>
<td>0.386</td>
<td>0.618</td>
<td>0.996</td>
</tr>
<tr>
<td>MN-200*</td>
<td>1.087</td>
<td>0.547</td>
<td>0.998</td>
</tr>
</tbody>
</table>

coefficients based on units of $q_c$ (mmol/g) and $C_e$ (mmol/l)

* data from Sweetland [1997]

**Table 3-6** *Freundlich Coefficients for F-400, LF-1, XAD-4 and MN-200 Sorbing Phenol*
<table>
<thead>
<tr>
<th>Carbon</th>
<th>Phenol Number at $C_e$ of 1 mg/l (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>98.26</td>
</tr>
<tr>
<td>LF-1</td>
<td>131.94</td>
</tr>
<tr>
<td>XAD-4</td>
<td>2.19</td>
</tr>
<tr>
<td>MN-200</td>
<td>8.53</td>
</tr>
</tbody>
</table>

*Table 3-7*  Phenol numbers for F-400, LF-1, XAD-4 and MN-200
Section 3.5 Conclusions

Spectroscopic analysis and titration of the adsorbents has indicated a number of different oxygen functional groups. A limited investigation into the surface chemistry of F-400 and LF-1 suggested a mixture of oxygen functional groups, which were determined using direct titration. The groups which could be identified using this technique were carboxylic, lactone, carbonyl and phenolic. The concentration of these groups was greater than those present on the surface of the polymers. However, a more detailed study of the surface of the polymers revealed a complicated mixture of oxygen containing functional groups, such as, ketones, ethers, alcohols and carboxylic acids. XPS and elemental analysis suggested higher oxygen concentrations than those obtained using direct titration. This could be due to bound oxygen within the structures of the adsorbents, which is not accessible to adsorbates.

The oxygen functional groups will enable sorption of organic species by a variety of mechanisms. Carboxylic and phenolic groups may allow sorption by an ion exchange mechanism, as long as the pH of the solution enables dissociation of the functional groups. Other functionality, such as ketones, quinones, ethers, etc may enhance sorption due to hydrogen bonding with the oxygen.

The adsorption capacity of phenol was also assessed. The capacity of the carbons was much greater than the polymeric adsorbents. The capacity of MN-200 was shown to be greater than XAD-4.
Section 3.6 References


Davankov, V.A., Tsyurupa, M.P., “Rigid Hypercrosslinked Polystyrene Networks with Unexpected Mobility”, Paper provided by M.P. Tsyurupa


Chapter 3


CHAPTER 4

HERBICIDE ADSORPTION

Section 4.1 Introduction

Throughout history, civilisations developed around regions with abundant water supplies. Water quality was judged by taste or appearance, paying little attention to disease. The first drinking water standards originated about 4000 years ago for the purification of foul water. Only in the 19th century was it realised that various epidemics were caused by or spread by contaminated water e.g. cholera and typhoid. It became obvious that the quality of water could not be judged by sensory perception alone, and in 1852 a law was passed in London stating that all water should be filtered [AWWA, 1990]. In the late 1880's, William Pasteur presented the particulate germ theory of disease which reinforced the requirement for water treatment. The rapid increase in understanding the effects of and the ability to analyse for pollutants in water has led to the introduction of more rigorous legislation.

Pesticides enter water supplies from several sources, including, careless overspraying; washing down of contaminated equipment and leaching through soils. It is well known that triazines, particularly atrazine, have been found in several supplies derived from both ground-water and surface-water sources. The control of pesticides is effected by means of domestic legislation, some of which is required by the European Community, and by the adoption of good practice promoted through the use of codes, advice and publicity. Fig. 4-1 summarises the usage of pesticides within England and Wales in terms of crop areas and shows that the vast majority of pesticides in use are in fact herbicides. Therefore the potential for leaching in to water courses is enormous. The statutory control of pesticides in the UK was established with the Food and Environment Protection Act (FEPA), 1985, together with the Control of Pesticides Regulations (COPR) made under the act. Under FEPA, an
independent Advisory Committee advises the government on pesticides regulation and approval [DoE, 1996]. In England and Wales, the quality of controlled waters, including inland waters, such as rivers, canals, lakes, groundwater, estuarine and coastal waters is regulated by the Environment Agency. Regulation is achieved by setting standards on discharges to controlled waters. Monitoring of discharges used to be carried out by the National Rivers Authority (NRA) and the results are held in public registers. In May 1994 a new scheme was introduced to classify river quality, termed the statutory water quality objective (SWQO). The SWQO defines the water quality standard to be achieved and sets a date by which it must be met for a given stretch of river.

Fig. 4-1  Pesticide Usage within England and Wales

An EC Directive exists on Dangerous Substances in Water (76/464/EEC) designed to control dangerous substances specified in two groups (List I and List II). Under the
terms of the directive, List I substance pollution should be eliminated and List II pollution significantly reduced. Legislation within the UK is set to demonstrate compliance with respect to List I pollution on the basis of Environmental Quality Objectives (EQO), which is defined as the acceptable concentration of a specific dangerous substance for the protection of aquatic life. A total of 129 substances have List I status, of which 23 substances or groups of substances have been classified by the UK as priority pollutants, the so-called Red List.

With regard to drinking water, the EC Drinking Water directive (80/778/EEC) sets the limit for individual pesticides at 0.1 µg/l, with a total for all pesticides of 0.5 µg/l. These limits were devised on the basis of detectable limits and not necessarily on the toxicity of the pesticides. In many cases the World Health Organisation (WHO) guideline values are higher than the EC regulations. A proposal to eliminate the "total" pesticide limit was published in 1995 but has thus far not been implemented. Individual water companies are required under the Water Act of 1989 to devise a monitoring strategy based upon the usage of pesticides within the water catchment area and the possibility of entering water sources. These monitoring schemes are regulated by the Drinking Water Inspectorate (DWI).

The Department of the Environment and the National Rivers Authority publish reports detailing the occurrence of pesticides in water [DoE, 1996; NRA, 1995]. Table 4-1 shows selected data from the Department of the Environment, covering the period 1990-1993 regarding pesticides exceeding the limit of 0.1µg/l during routine monitoring of drinking water. The first six entries in the table represent the most frequently detected herbicides in the UK over the period in question. A recent moratorium on the non-agricultural use of atrazine and simazine has been reflected in the monitoring results for 1992 and 1993. However, it would also appear that diuron, which is widely accepted as an effective alternative to atrazine has been recorded with increasing frequency. These observations are confirmed by NRA monitoring results for 1992 and 1993 of all controlled waters, as summarised in Table 4-2.
<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Number of samples in which 0.1μg/l was exceeded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total no. of samples</td>
<td>2536</td>
</tr>
<tr>
<td>Atrazine</td>
<td>695</td>
</tr>
<tr>
<td>Simazine</td>
<td>479</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>281</td>
</tr>
<tr>
<td>Chlorotoluron</td>
<td>249</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>201</td>
</tr>
<tr>
<td>Diuron</td>
<td>133</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>-</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4-1 Number of samples in which pesticide concentration exceeded acceptable limit in drinking water [DoE, 1996]

Imazapyr and triclopyr are two of a group of four herbicides (benazolin, bentazone, imazapyr and triclopyr) which Severn Trent Water Ltd have identified as atrazine replacements and therefore possible future pollutants [Upton, 1996]. Research work is being undertaken to investigate their removal from water using a variety of techniques such as ozonation and adsorption [Lambert et al, 1996]. As can be seen in Table 4-2, bentazone and benazolin were detected frequently in 1993, mainly in fresh and groundwater, which represent the majority of drinking water sources in the UK. In fact, of the groundwater samples taken in 1993, bentazone was the most frequently detected pesticide exceeding 0.1 μg/l, ahead of atrazine [NRA, 1995].
**Table 4-2 Summary of Pesticides which exceeded 0.1µg/l in Controlled Waters**

The presence of Natural Organic Matter (NOM) in drinking water supplies results in premature breakthrough of pollutants, which is probably due to the NOM blocking access to the micropores. This results in a reduction in the life of carbon beds to about 3-6 months, compared with a typical life of up to two years for taste and odour removal [Smetham, 1994]. Hence, more frequent regeneration of the adsorbed species is required, increasing the cost of the treatment process.

This chapter investigates the adsorption of atrazine, benazolin, bentazone, imazapyr and triclopyr in single-component and multi-component solutions to assess the potential of the adsorbents for drinking water purification. The influence of NOM on the adsorption of the pesticides is also investigated.
Section 4.2 Literature Review

Section 4.2.1 Herbicides

Atrazine is one of the most problematic herbicides to remove from potable water supplies and as a consequence was prohibited from non-agricultural uses in England and Wales in 1993. Since that time there has been increased use of a variety of alternative herbicide compounds for both agricultural and non-agricultural purposes. Relatively little information exists for many of these herbicides with regard to either their potential to pollute potable water supplies or their removal by water treatment processes. The average concentrations of herbicides in water are generally below the legal limit. However, the seasonal variations in the usage of pesticides can result in concentrations which significantly exceed the legal limit. Recent data, which is summarised in Table 4-3 was provided by the Environment Agency and shows the maximum concentration of each herbicide under investigation during sampling in 1995, 1996 and 1997. It can be seen that only Imazapyr has not exceeded the legal limit in the three years in question.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>1.37</td>
<td>1.8</td>
<td>5.42</td>
</tr>
<tr>
<td>Benazolin</td>
<td>0.093</td>
<td>0.525</td>
<td>0.331</td>
</tr>
<tr>
<td>Bentazone</td>
<td>1.12</td>
<td>0.423</td>
<td>1.84</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>0.058</td>
<td>0.074</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>0.122</td>
<td>0.988</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*Table 4-3 Maximum concentration of herbicides in water during 1995, 1996 and 1997 [Environment Agency]*
Table 4-4 shows the structural formulae and properties of atrazine, benazolin, bentazone, imazapyr and triclopyr. Analogous to atrazine, the other herbicides under investigation are all nitrogen heterocyclic compounds. In addition, all of the herbicides are significantly more soluble than atrazine. Benazolin, bentazone, imazapyr and triclopyr are significantly more soluble than atrazine, which could enhance their ability to leach into the water course. They also contain several reactive functional groups which may enhance adsorption by electrostatic attractions on the surface of an adsorbent.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Chemical Formula</th>
<th>Structural Formula</th>
<th>Solubility in H₂O (mg/l)</th>
<th>pKa</th>
<th>log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>C₈H₁₄ClN₅</td>
<td><img src="image" alt="Atrazine structural formula" /></td>
<td>33</td>
<td>1.7</td>
<td>2.5 (25°C)</td>
</tr>
<tr>
<td>Benazolin</td>
<td>C₆H₆ClNO₃S</td>
<td><img src="image" alt="Benazolin structural formula" /></td>
<td>600</td>
<td>3.04</td>
<td>1.34 (20°C)</td>
</tr>
<tr>
<td>Bentazone</td>
<td>C₁₀H₁₂N₂O₃S</td>
<td><img src="image" alt="Bentazone structural formula" /></td>
<td>500</td>
<td>3.30</td>
<td>0.77 (pH 5) -0.55 (pH 9)</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>C₁₃H₁₅N₃O₃</td>
<td><img src="image" alt="Imazapyr structural formula" /></td>
<td>11,300</td>
<td>1.9,3.6, 10.6</td>
<td>0.11</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>C₃H₄Cl₂NO₃</td>
<td><img src="image" alt="Triclopyr structural formula" /></td>
<td>440</td>
<td>2.68</td>
<td>0.42 (pH 5) -0.96 (pH 9)</td>
</tr>
</tbody>
</table>

Table 4-4 Structural formulae and properties of selected herbicides

Kruithof et al [1994] reported >94% degradation of bentazone by 2.2 mg O₃/l and 60% degradation for atrazine. They also showed that pesticides could be removed by nanofiltration and low pressure reverse osmosis membranes. Lambert et al [1996] looked at the efficiency of ozone and ozone in conjunction with hydrogen peroxide
for the degradation of atrazine, benazolin, bentazone, imazapyr and triclopyr in lowland water supplies. It was found that bentazone was completely degraded at a consumed ozone dose of 1 mg O\textsubscript{3}/l. Benazolin was reduced by 55%, 68% and 88% with consumed doses of 1.0, 2.0 and 3.1 mg O\textsubscript{3}/l. However, much lower removals of imazapyr and triclopyr of 66% and 45% respectively at a consumed dose of 3.1 mg O\textsubscript{3}/l were reported. The addition of hydrogen peroxide improved the removal, although the residual concentrations of atrazine, imazapyr and triclopyr still exceeded the legal limit of 0.1\mu g/l from an initial concentration of 2\mu g/l. They concluded that although ozone was effective in degrading the compounds, a complementary technique such as adsorption must be employed in order to attain legally compliant concentrations of atrazine, imazapyr and triclopyr. To the authors knowledge, this is the only study to solely use the herbicides under consideration in this project.

Section 4.2.2 Natural Organic Matter

Natural Organic Matter (NOM) is the term used to describe the complex matrix of organic compounds present in natural waters. The largest portion of organic matter in the aquatic environment is comprised of humic substances which are formed by the breakdown of animal and vegetable matter in the environment. Although the term "humic substances" describes a complex, ill-defined mixture, some generalisations can be made about their molecular structure [Newcombe, 1994; Summers and Roberts, 1988];

(i) they possess high molecular weights, typically between 500 and 250,000,
(ii) display both aliphatic and aromatic character,
(iii) contain functional groups such as carboxyl and phenolic groups
(iv) behave as polyelectrolytes in solution; therefore, the degree of dissociation of the functional groups is dependent on pH.

Humic substances are operationally defined on the basis of their solubility in water; humin substances are insoluble at any pH value; humic acid is insoluble below a pH value of 2; fulvic acid is soluble over the whole pH range. Numerous techniques have
been applied to the fractionation and characterisation of humic substances including
titration, spectrometry, mass spectrometry, adsorption, etc. Stevenson [1994] provides an excellent review of humus chemistry and the reader is referred to this book for further information.

The molecular size and chemistry of humic and fulvic acid significantly affects their ability to be adsorbed. Humic acids are generally large molecules, equivalent to spherical particles with diameters of 60-100Å whereas fulvic acids generally have a molecular size of 20-30Å. At high sample concentrations, low pH and high amounts of neutral electrolytes, humic and fulvic acids behave like rigid “spherocolloids”. In contrast, flexible linear chains are observed at low sample concentration, neutral pH or low ionic strengths. The large molecular size will generally prevent the substances from entering the micropores of the adsorbents. However, many granular activated carbons possess mesopores (20-100Å), which quicken their adsorption kinetics but also allow humic and fulvic acids to be adsorbed. The highly acidic functionality of humic and fulvic acid means that they often exist as negatively charged molecules at the pH of natural waters. The pK_a of soil humic acid depends on the ionic strength of the background. At an ionic strength of 0.001M the average pK_a is 5.7, whereas at a strength of 0.1M the pK_a decreases to 4.7. Hence for negatively charged surfaces, humic and fulvic acid will be repelled. Although humic and fulvic acids are hydrophilic in nature, they can contain areas that are hydrophobic. Hence, many organic molecules bind to the humic substances either through hydrophobic interactions or ion exchange and coordination.

The concentrations of humic and fulvic substances in natural waters are generally in the low parts per million range which is 1000 times greater than the herbicide concentrations.

It is well recognised that humic substances decrease the effectiveness of granular activated carbon due to several factors, including, a decrease in the number of
available adsorption sites, a decrease in surface area caused by pore blockage, and an increase in negative surface charge caused by adsorption of humic material.

The conventional drinking water treatment processes of coagulation, settling, and sand filtration remove between 20 and 50% of dissolved humic substances. Humic acids are generally preferentially removed, leaving the smaller, more highly charged fulvic acids in solution.

The RSSCT has been widely applied to the adsorption of humic acid to determine capacity and kinetics parameters. Lee et al [1983] used the HSDM to determine the surface diffusion coefficients for the adsorption of humic and fulvic acid using F-400. Analysis of the batch kinetic data gave values of $6.0 \times 10^{-12}$ and $2.7 \times 10^{-11} \text{cm}^2/\text{s}$ for commercial humic and fulvic acid, respectively. Summers et al [1988] investigated the size exclusion and electrostatic interactions of humic substances on F-400 and four other activated carbons. The adsorption performance generally showed a 3 to 10-fold increase when the concentration of NaCl was increased from 0 to 0.1M NaCl. The behaviour was explained by the humic macromolecule changing size with the background electrolyte concentration. At low ionic strengths the functional groups become dissociated which causes an expansion of the macromolecule due to the mutual repulsion of like charges. As the ionic strength is increased, the counter ions in solution suppress the double layer forces, allowing the molecule to coil and reduce its size effect. They correlated the available surface area of F-300 and F-400 with the approximate size of different molecular weight fractions of humic and fulvic acid.

Lafrance et al [1989] investigated the adsorption of humic substances, in the presence of sodium salts, for F-400. They also observed that the increase in capacity was due to the neutralisation of the negative charges on the humate molecules and carbon surface functional groups, thus reducing the electrostatic repulsion. Newcombe [1994] investigated the adsorption of the fulvic acid fraction, since humic acids were generally removed by conventional water treatment processes of coagulation, settling
and sand filtration. Langmuir type isotherms were observed, suggesting that F-300 had a high affinity for fulvic acid. At low surface concentrations it was concluded that the molecules were adsorbed by ion pair formation between the carboxyl groups of the humic material and positive groups on the surface of the carbon. The adsorption performance of activated carbon fibres for the removal of humic substances has been presented by a number of authors [Štarek et al, 1994; Brasquet et al, 1997; Tamai et al, 1997]. The fibres have a large capacity for small organic species, however, humic acid was size excluded from the micropores.

Frederick et al [1997] correlated the adsorption of calcium on F-400 by pre-loading the carbon with NOM. A linear relationship was observed between the NOM loading and calcium uptake. During the thermal regeneration of the carbon, calcium tends to catalyse burn off resulting in a reduction of the carbon mass and surface area. Karanfil et al [1997] suggested that surface oxidation of F-400 reduced the uptake of NOM. Heat treatment of the carbon surface did not increase the uptake suggesting that the low degree of oxygen functionality did not interfere with the removal.

Crittenden et al [1993] attempted to model the adsorption of humic acid onto F-400 by breaking the NOM into five fictitious components. The Freundlich isotherm equation was used to describe the single component equilibrium of the individual components. The ideal adsorbed solution theory (IAST) was applied to describe the competitive interactions between the components. They found that neither the HSDM nor the pore diffusion model could be used to predict NOM pilot column data using batch determined intraparticle diffusivities and isotherm parameters. Pore diffusion controlled the mass transfer rate for the pilot column. Smith [1994] also used the IAST to model the adsorption of NOM onto F-400.

Bulloch et al [1997] presented a model to predict the influence of NOM on the adsorption of synthetic organic compounds (SOC). They used the pore and surface diffusion model (PSDM), which includes the effects of external mass transfer and
intraparticle mass transfer due to both pore and surface diffusion, to model the breakthrough. The Polanyi potential theory was used to predict single solute isotherms for some of the SOC's with the competitive interactions estimated using the IAST. Crittenden and coworkers have presented many studies on the application of the IAST for the multi-component adsorption of organic species onto F-400 [Crittenden et al., 1985; Crittenden et al., 1985; Crittenden et al., 1987]. Five basic equations are used in the model, which after mathematical manipulation result in an expression which calculates the equilibrium state in an isotherm bottle if the single solute Freundlich parameters, (assuming that the Freundlich isotherm can describe the equilibrium relationship over the full concentration range), the initial concentration of each solute and carbon dose is known. However, for a solution containing N components, N non-linear simultaneous equations with N unknowns must be solved. The Newton-Raphson equation is often applied.

The Ideal Adsorbed Solution Theory (IAST), originally proposed by Myers and Prausnitz [1965] for gas mixtures and later developed by Radke and Prausnitz [1972] for dilute liquid systems, has the most thermodynamically accepted foundation. Numerous authors have investigated the IAST theories for a wide variety of systems [Knettig et al., 1986; Xing et al., 1996].

Section 4.2.3 Adsorption Studies

Mazet et al [1994] investigated the influence of heat and chemical treatment on Chemviron F-400 activated carbon for the adsorption of atrazine. Heat treatment of the carbon, which reduced the concentration of oxygenated functional groups, increased the capacity for atrazine adsorption by 60%. Ayele et al [1996] investigated the adsorption of four triazine herbicides, including atrazine, onto powdered F-400. Langmuir capacities of between 1.1 and 1.5 mmol/g were obtained, based on initial solution concentrations of 10-20 mg/l. Adams and Watson [1996] investigated the adsorption of triazine herbicides and their metabolites using powdered F-200. They observed that the adsorption capacity of the carbon for the metabolites was generally lower than that for the herbicides, due to the increased solubility of the metabolites in
water. Qi et al [1994] determined the adsorption capacity and kinetics for the adsorption of atrazine onto WPH powdered activated carbon produced by the Calgon Carbon Corporation. The surface diffusion coefficient, calculated using the homogeneous surface diffusion model was \(7.9 \times 10^{-11} \text{ cm}^2/\text{min}\). The pure water Freundlich isotherm parameters, \(1/n\) and \(K\), were 0.335 and 797 \((\mu\text{mole/g})(\text{L}/\mu\text{mole})^{1/n}\) respectively. Speth and Miltner [1980] observed similar values of \(1/n=0.291\) and \(K=858\) for pulverised F-400. Hopman et al [1994] conducted isotherm tests on ROW 0.8 S activated carbon for a variety of pesticides in ultrapure water. Bentazone had a capacity of 47 mg/g at an equilibrium concentration of 1\(\mu\text{g/l}\). In theory, this capacity would correspond to a bed-life of 600 years, but under certain conditions the bed-life was found to be just 200 days. This was attributed to the presence of NOM and the adsorption kinetics.

Streat and Sweetland [1998] presented single and multi-component adsorption isotherms for the sorption of atrazine, simazine, chlorotoluron, isoproturon and diuron on a range of Macronet polymers, including MN-200. The single component Freundlich parameters, \(K\) and \(1/n\) for atrazine adsorption on MN-200 were 2073 \((\mu\text{mole/g})(\text{L}/\mu\text{mole})^{1/n}\) and 0.718, respectively. They compared the results with those of Speth and Miltner [1980] for the adsorption of atrazine on F-400 and concluded that the capacity of the carbon was approximately three times higher than that of the polymer at low concentrations. However, the larger \(1/n\) coefficient indicated that the strength of interaction was lower on the polymer, resulting in more amenable regeneration/stripping of the herbicides. Streat et al [1998] presented adsorption isotherms for humic and fulvic acid on F-400 and MN-200 which show that the uptake of humic acid is extremely low at high adsorbent masses. This indicates that size exclusion of the humic acid molecules is taking place. The adsorption capacity of F-400 was slightly higher than that of MN-200 which was attributed to the larger accessible surface area due to mesopores in F-400. MN-200 had a significantly lower capacity for fulvic acid than F-400.
Mini-column experiments are presented for the adsorption of atrazine, simazine, chlorotoluron, isoproturon and diuron in ultrapure water. There was no breakthrough of the herbicides on F-400 after 800,000 bed volumes. Breakthrough of atrazine to 0.1 μg/l on MN-200 occurred after 140,000 bed volumes. However, in the presence of fulvic acid, breakthrough of atrazine on F-400 occurred after approximately 160,000 bed volumes, whereas for MN-200 it was only reduced to 105,000 bed volumes.

Bernazeau et al [1996] investigated the competitive adsorption of atrazine with natural organic matter on F-400. They observed that the atrazine capacity decreased from 0.6 mg/g to 0.2 mg/g (for C_{e}=0.1 μg/l) when the concentration of natural organic matter increased from 2 to 8 mg/l. Matsui et al [1994] used a range of pesticides with varying solubilities, including simazine and bentazone, to investigate the effects of intermittent loading and natural organic matter. They found that pre-loading the adsorbent beds with natural organic matter deteriorated the removal efficiency of the pesticides. The breakthrough curves for intermittently and continuously loaded pesticides were almost identical. A later study by Matsui et al [1996] presented RSSCT data, assuming constant diffusivity, for the adsorption of a range of hydrophobic (including simazine) and hydrophilic (including bentazone) pesticides. The mini-columns used consisted of F-400 with an EBCT of approximately 0.3s. The hydrophobic pesticides showed similar breakthrough and adsorptive capacities. However, the hydrophilic group showed much shorter breakthrough times and lower adsorption capacities, which could also be categorised in terms of the solubility of each of the pesticides. In the presence of humic acid all the pesticides showed a reduction in capacity and breakthrough time; the hydrophilic group showed a more pronounced reduction than the hydrophobic group. For example, the simazine capacity was reduced to 1/10th of its original capacity, whereas bentazone was reduced to 1/35.
Pusino et al. [1994] investigated the adsorption of triclopyr onto various clays and soils. It was found that the adsorption capacity decreased with increasing pH of the solution. Although at the pH range in question (pH 4.4 to 7.2) the percentage of protonated herbicide would be low, the surface of the clays could be 2-3 pH units lower, thereby increasing the amount of protonated groups. They suggested that the adsorption mechanism could be due to physical forces, hydrogen bonding or cationic binding, between the protonated pyridine moiety of the herbicide molecule and the negative surface of the clay. As the solution pH increased, triclopyr exists in anionic form, leading to a repulsion interaction with the surface. Adsorption on soil was found to also decrease with increasing pH as well as with decreasing organic matter. They also investigated the adsorption of imazapyr on soil [Pusino et al., 1996] and found a similar negative dependence on pH for the adsorption of imazapyr on organic matter. Imazapyr exhibits two protonation sites, the carboxylate and the pyridine type nitrogen of the imidazolinone ring. It can exist in cationic, neutral and anionic forms, depending on the pH, as shown in Fig. 4-2.

![Cationic, Neutral and Anionic Forms of Imazapyr](image)

They also investigated the adsorption of imazapyr on iron oxides which had a pH$_{pzc}$ of 8.5, thus a positively charged surface at the pH of natural waters. The interaction
was described as a Ligand exchange, leading to an inner sphere complex upon displacement of a hydroxyl group or water molecule bound to an Fe ion by an organic functional group, such as the carboxylate. It was postulated that this mechanism was responsible for the stronger binding properties of soils with a high iron content.
Section 4.3 Analysis Method Development

The requirement of the analysis technique is to determine the concentration of atrazine, benazolin, bentazone, imazapyr and triclopyr in water at levels of 0.1 ppb or below. The method had to be suitable for both ultrapure water and water containing humic or fulvic acid. A Hewlett Packard 1100 series HPLC system consisting of a binary pump, autosampler, column thermostat and diode array detector was available and had been shown to be suitable for the analysis of herbicides in a previous project [Streat and Sweetland, 1998].

Section 4.3.1 HPLC Method Development

A previous method developed by Sweetland [Streat and Sweetland, 1998] had been used in the laboratory to analyse the herbicides atrazine, simazine, isoproturon, chlorotoluron and diuron. A Genesis C18 column (4µm, 150 x 3 mm) combined with a 1 cm Genesis guard column, supplied by Jones Chromatography was used. Separation of the compounds was achieved using isocratic elution at a flow of 0.8 ml/min, thermostatically controlled at 40 °C. The eluent consisted of 29% acetonitrile/THF (60:40 v/v) and 71% buffer (10 mmol KH₂PO₄ at pH 4.5). The injection volume was 100 µl and detection was performed at 230 nm and 245 nm.

Using these conditions, atrazine, benazolin, bentazone, imazapyr and triclopyr were analysed. However, inadequate separation of the compounds occurred, with co-elution and short retention times experienced. A new HPLC method for the determination of atrazine, benazolin, bentazone, and triclopyr at trace concentrations was required.

Lambert et al [1996] presented a method for the determination of the herbicides of interest. Two separate analysis conditions were required due to the low retention of imazapyr. They used a reversed-phase phenyl column and a THF:KH₂PO₄:HPO₃ mobile phase. Table 4-5 summarises the analysis conditions and retention times. It can be seen that the retention times for atrazine and benazolin are almost identical.
However, co-elution was avoided since the liquid-liquid extraction pre-concentration step required separate extraction and therefore analysis of atrazine. Since the mobile phase composition for the analysis of imazapyr is different, this would result in a total of three injections per sample to analyse for all five compounds, which was deemed unacceptable.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (ml/min)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Injection Volume (µl)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Detection Wavelength (nm)</td>
<td>221</td>
<td>221</td>
<td>221</td>
<td>230</td>
<td>293</td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>11.84±0.07</td>
<td>11.16±0.06</td>
<td>14.70±0.20</td>
<td>2.23±0.03</td>
<td>26.72±0.25</td>
</tr>
</tbody>
</table>

Table 4-5 HPLC Analysis of atrazine, benazolin, bentazone, imazapyr and triclopyr [Lambert et al, 1996]

A gradient elution over 20 minutes, starting from 5% MeOH/95% H₂O to 100% MeOH suggested that an isocratic elution of atrazine, benazolin, bentazone and triclopyr could be achieved. However, the retention time of imazapyr was extremely short. The gradient elution was optimised for all five herbicides, but it resulted in an unstable base-line, which reduced the limit of detection of the compounds. As Lambert [1996] had experienced, two separate methods were required.

The composition of the mobile phase was optimised for the elution of atrazine, benazolin, bentazone and triclopyr using a methanol/water isocratic elution. An equivalent strength acetonitrile/water and tetrahydrofuran/water mobile phase was then tried. Analysis of the chromatograms suggested that the acetonitrile/water phase provided the cleanest separation. The relative percentage of acetonitrile to water was varied until a compromise between sensitivity and resolution was achieved. A variety of pH values for the buffer were used. At pH 4.0, it appeared that the four compounds separated adequately. However, analysis of the isoabsorbance plot showed that there was a peak which was co-eluting with bentazone. Further analysis elucidated the
interfering compound to be simazine, which is an impurity in atrazine and therefore
can not be avoided. The retention times of atrazine and simazine were unaffected by
changes in mobile phase pH whereas the retention time for bentazone increased as the
pH decreased. The pH of the mobile phase was reduced to 3.0 and adequate
separation of the five compounds was achieved. The temperature of the column was
also varied to optimise the separation. The flow rate was selected such that the
pressure in the system did not exceed 150 bar.

The final method for the separation of atrazine, benazolin, bentazone and triclopyr
used an isocratic elution at a flow of 0.88 ml/min, thermostatically controlled at 38°C.
The eluent consisted of 30% acetonitrile and 70% buffer (10 mmol KH₂PO₄ at pH
3.2). The injection volume was 100 µl. Detection was performed at 204 nm and 222
nm, which is near to the absorption maxima of the compounds (see Fig 4-3).

Due to the equipment available, the method for the detection of imazapyr had to use
the same solvents and column. However, the ratio of the two components of the
mobile phase and the flow rate could be changed. It was observed that imazapyr had a
retention time of approximately 1.5 minutes, thus forming part of the solvent peak, in
the method developed for atrazine, benazolin, bentazone and triclopyr. In order to
increase the retention time of imazapyr, the mobile phase flow rate and composition
were adjusted until the retention of imazapyr was adequate. It was found that an
isocratic elution at a flow rate of 0.40 ml/min, thermostatically controlled at 38°C
consisting of 20% acetonitrile and 80% buffer gave a sufficient retention time.
Detection was performed at 204 nm. Fig. 4-3 shows the UV absorption spectra of
each compound. Both methods were calibrated using standards obtained from Qmx
Laboratories. Typical chromatograms produced using the methods outlined above are
shown in Fig 4-4.
UV Absorption Spectra of atrazine, benazolin, bentazone, imazapyr and triclopyr
Fig. 4-4  **HPLC Chromatograms for atrazine, benazolin, bentazone, imazapyr and triclopyr**

The interference of fulvic acid on the chromatograms is shown in Fig. 4-5. Fulvic acid contains a complex mixture of organic compounds which strongly absorb in the UV region. Separation of the fulvic acid and the herbicides is achieved due to their more hydrophilic nature, which causes early elution in the chromatogram. However, the concentrations of the fulvic acid are approximately 1000 times higher than those of the pesticides and interferences are caused by tailing of the elution peak. Multi-component samples spiked with 20mg/l fulvic acid were analysed using both methods to check that calibration was still valid. The results confirmed that the instrument was just as sensitive in the presence of fulvic acid.

The methods are linear over the range 0-10 ng/μl with correlation coefficients of 1.000 for all the herbicides. The calibration graph, produced by multiple injections of different concentration of each herbicide is shown in Fig. 4-6.

The HPLC pump was purged on each channel prior to analysis and the system allowed to stabilise for at least one hour before analysis commenced. The guard column was changed when the stable pressure rose by 10% of the normal operating pressure.
Chapter 4

Benazolin
RT 3.53 min

Bentazone
RT 5.73 min

Atrazine
RT 9.16 min

Imazapyr
RT 5.50 min

Triclopyr
RT 11.49 min

--- 222nm
......
204nm

Fig. 4-5  **HPLC Chromatograms for atrazine, benazolin, bentazone, imazapyr and triclopyr in the presence of fulvic acid**

![HPLC Chromatograms](image)

Fig. 4-6  **HPLC calibration graph for atrazine, benazolin, bentazone, imazapyr and triclopyr**

![HPLC Calibration Graph](image)
Section 4.3.2 Solid Phase Extraction Method Development

In order that the concentration of the herbicides can be determined at levels of 0.1 ppb or below, a pre-concentration step is required before analysis on the HPLC. Lambert et al [1996] used a liquid-liquid extraction technique, but the recoveries achieved and time required to process the number of samples generated by the present project deemed this method unsuitable. Solid-phase extraction (SPE) is a relatively new technique which offers a number of advantages over liquid-liquid extraction, including the following:

- high recoveries of the analytes
- concentration of the analytes
- highly purified extracts
- ability to simultaneously extract analytes of wide polarity range
- ease of automation
- compatibility with instrumental analysis
- reduction in organic solvent consumption

In principle, SPE is analogous to liquid-liquid extraction. As a liquid is passed through the SPE column, compounds are ‘extracted’ from the sample onto the sorbent material in the column. The desired analytes may then be recovered from the column by an elution solvent, resulting in a highly purified extract.

A wide variety of packing materials have been and continue to be developed which are increasingly suitable for particular applications to provide high recoveries. Samples of 500 ml can be re-constituted in 0.5 ml of solvent, providing a concentration factor of 1000. The method can easily be expanded to process several samples at the same time through the use of multi-port manifolds.

A sixteen port manifold with PTFE valves, made in the Department of Chemical Engineering at Loughborough University, was used for solid-phase extraction. The
method previously developed by Sweetland [Streat and Sweetland, 1998] using Isolute C8 (Jones Chromatography) columns was initially investigated. This method was proven to recover atrazine, simazine, chlorotoluron, isoproturon and diuron with 100% efficiency. It was discovered that benazolin, bentazone, imazapyr and triclopyr were not retained on the hydrophilic C8 columns. Several authors [Balinova, 1993; Chiron et al, 1995; Johnson and Hall, 1996] used C18 cartridges and samples acidified to pH 1.5-2.0 using H₂SO₄ to improve the retention of the herbicides.

S-Triazine SPE columns were obtained from Jones Chromatography which are based on a C18 packing, but have been enhanced specifically for the retention of s-triazine type compounds. 500 ml samples of ultrapure water were spiked with 0.5 ml of a 10 mg solution containing 2 mg/l of each herbicide to produce a solution concentration of 2 μg/l of each herbicide. The samples were acidified with 150 μl of conc. H₂SO₄, supplied by Fisher Scientific, which reduced the pH to around 2.0. The columns were solvated using 10 ml methanol passed under gravity followed by 10 ml of a 2% methanol/98% ultrapure water solution. A Masterflex peristaltic pump connected to the manifold was used to draw the samples through the columns at a rate of 5 ml/min. Oxygen free nitrogen was used to dry the columns before being eluted with solvent. A range of solvents were investigated: methanol, ethanol, acetonitrile, THF, acetone, ethyl acetate. Solvents modified with 10% formic acid were also investigated since atrazine has been shown to be difficult to remove with pure solvent [Sweetland, 1997].

Acetone was found to split the benazolin peak on the subsequent HPLC analysis, which rendered it unsuitable for further investigation. Ethanol, THF and solvents modified with formic acid produced interfering peaks on the chromatogram which could not be eliminated. Acetonitrile was found to give the “cleanest” chromatogram and was selected as the extraction solvent. Initial trials using a sample flow rate of 5 ml/min gave recoveries of around 65-75%, which may have been caused either by breakthrough of the SPE columns or the compounds being retained on the silica.
Experiments performed with two columns in series suggested that breakthrough was occurring. This was eliminated by reducing the sample flow rate to 1ml/min. However, the recovery efficiencies were still approximately 80%, indicating that the compounds were also being retained on the silica. The eluent was subsequently allowed to soak on the column for 20 minutes before being passed through the column at a controlled flow of approximately 0.5 ml/min. Varying amounts of eluent were used and it was found that 6 ml provided the optimum recovery. The recovery efficiencies improved to between 85 and 100%.

Following extensive experimental trials it was found that a single SPE method to extract and recover all five herbicides was not possible. This was due to the hydrophilic nature of benazolin, bentazone, imazapyr and triclopyr compared to the more hydrophobic nature of atrazine. Various column packings were investigated with no improvement. For single-component work, two SPE methods were employed, as detailed in Table 4-6. However, atrazine could not be included in multi-component work since the volume of samples and the analysis time required was too high. It was felt that this was acceptable since the focus of the project was upon the adsorption of benazolin, bentazone, imazapyr and triclopyr due to the relative lack of knowledge in the literature.

The concentrations expected for analysis were in the range 0-20 ppb and so the methods were validated up to 30 ppb of each herbicide in solution. The reproducibility of the method was tested by conducting 40 separate determinations of 0.1 ppb of each herbicide in ultrapure water. Table 4-7 summarises the results. Fig. 4-7 represents the recovery of each compound with the mean indicated by a solid line and the standard deviation shown by the dotted lines.

Table 4-8 presents the recovery efficiencies for the analysis of the pesticides in the range 1-30 µg/l based on five determinations for each concentration. The recovery
Table 4-6  Procedures for solid phase extraction

<table>
<thead>
<tr>
<th></th>
<th>Mean (µg/l)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine*</td>
<td>0.100</td>
<td>4.3</td>
<td>98</td>
</tr>
<tr>
<td>Benazolin</td>
<td>0.100</td>
<td>3.0</td>
<td>97</td>
</tr>
<tr>
<td>Bentazone</td>
<td>0.098</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>0.082</td>
<td>5.0</td>
<td>85</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>0.104</td>
<td>4.0</td>
<td>100</td>
</tr>
</tbody>
</table>

* Atrazine results from Sweetland [1997]

Table 4-7  Means, relative standard deviations and recoveries for the determination of herbicides at a concentration level of 0.1µg/l

efficiencies of the herbicides are not affected by increasing the concentration of the herbicides.
Fig. 4-7  
Recovery efficiency of herbicides at a concentration of 0.1 ppb

<table>
<thead>
<tr>
<th>Concentration of each herbicide (µg/l)</th>
<th>Atrazine</th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.0</td>
<td>99.5</td>
<td>101.2</td>
<td>84.2</td>
<td>102.3</td>
</tr>
<tr>
<td>2</td>
<td>99.5</td>
<td>99.8</td>
<td>100.6</td>
<td>84.1</td>
<td>100.2</td>
</tr>
<tr>
<td>5</td>
<td>100.3</td>
<td>99.2</td>
<td>101.4</td>
<td>85.9</td>
<td>101.4</td>
</tr>
<tr>
<td>8</td>
<td>100.5</td>
<td>98.4</td>
<td>101.3</td>
<td>85.2</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>100.1</td>
<td>99.3</td>
<td>100.4</td>
<td>87.0</td>
<td>100.6</td>
</tr>
<tr>
<td>15</td>
<td>99.2</td>
<td>98.7</td>
<td>100.2</td>
<td>85.9</td>
<td>101.4</td>
</tr>
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<td>20</td>
<td>100.7</td>
<td>98.5</td>
<td>100.9</td>
<td>84.5</td>
<td>102.6</td>
</tr>
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<td>25</td>
<td>100.3</td>
<td>98.9</td>
<td>102.0</td>
<td>86.3</td>
<td>100.8</td>
</tr>
<tr>
<td>30</td>
<td>100.6</td>
<td>98.7</td>
<td>101.8</td>
<td>85.4</td>
<td>101.1</td>
</tr>
</tbody>
</table>

Table 4-8  
Recovery efficiencies for the determination of atrazine, benazolin, bentazone, imazapyr and triclopyr at a concentration range of 1-30 µg/l
The limit of detection for each compound was determined directly by solid phase extraction and subsequent HPLC analysis of low concentration of the herbicides benazolin, bentazone, imazapyr and triclopyr and are presented in Table 4-9. The result presented by Sweetland [1997] was used for atrazine.

<table>
<thead>
<tr>
<th></th>
<th>Atrazine*</th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (μg/l)</td>
<td>0.004</td>
<td>0.008</td>
<td>0.005</td>
<td>0.010</td>
<td>0.004</td>
</tr>
</tbody>
</table>

* from Sweetland [1997]

Table 4-9  Limits of Detection for the Analytical Method
Section 4.4 Experimental

All reagents were used as received. The herbicide compounds were supplied by Qm\textsubscript{x} Laboratories with respective purities as follows: atrazine: 97.0\%, benazolin: 99.3\%, bentazone: 99.1\%, imazapyr: 99.2 and triclopyr: 98.8. Stock solutions of 20 mg/l of the individual herbicides were prepared in ultrapure water (18 M\text{\Omega}cm) supplied from a Milli-Q 185 Plus water purification system. These solutions were then used for the preparation of working solutions by dilution. All organic solvents were supplied by Sigma-Aldrich (UK) and were of HPLC grade. All other reagents (except where specified) were supplied by Fisher Scientific (UK) and of AnalaR grade.

The polymeric adsorbents, MN-200 and XAD-4 had to be "wetted" prior to use. Dry weights of the adsorbents were measured and then soaked in methanol for 10 minutes, followed by washing with ultra-pure water before immediate transfer to the experiment.

The fulvic acid used in the experiments was produced from Aldrich humic acid, sodium salt, using the method outlined by Streat et al [1998]. 100 g of the sodium salt was dissolved in 2.5 litres of ultrapure water and filtered using a 0.12 \textmu m microfiltration membrane to remove the humin substances. The permeate was adjusted to pH 1 using concentrated hydrochloric acid. After two hours, the fulvic acid solution containing the precipitated humic acid was filtered using a Buchner flask to separate the two fractions. The fulvic acid solution was adjusted to pH 7 using sodium hydroxide prior to rotary evaporation. The concentrated solution was then freeze dried to obtain solid fulvic acid.

All glassware was soaked in a 1\% Decon solution overnight before washing with copious amounts of ultra pure water. The glassware was subsequently rinsed with HPLC grade methanol and dried in an oven at 350 °C prior to use. All other apparatus which came into contact with herbicide solutions was either manufactured from PTFE or stainless steel to minimise the risk of organic leaching.
Section 4.4.1 Batch Adsorption Isotherms

Batch adsorption isotherms were performed by shaking 500 ml amber Winchester bottles, with PTFE liners, in a New Brunswick C Series incubator shaker. The shaker was set to 100 rpm and thermostatically controlled to 25±0.1 °C. Initial solution concentrations were chosen according to the adsorbent based upon experimental capacity trials. Each solution was prepared by pipetting different volumetric amounts of the stock herbicide solution, into ultrapure water in the bottles. The total volume of solution in each bottle was 500 ml. A Sartorious, model BP201D, analytical balance was used to weigh 5.00 mg quantities of each adsorbent onto foil dishes. The adsorbent was washed into the bottles using 5 ml of solution extracted from the bottle. The bottles were agitated vigorously before shaking for 7 days. Prior to analysis, each solution was filtered using an all glass vacuum filter system and 0.2 μm Anopore membranes supplied by Whatman, to remove the adsorbent before acidification to pH 2.0 for the solid phase extraction process. This eliminated the possibility of the equilibrium being changed due to the addition of the acid during the course of the analytical process.

Section 4.4.1.1 Pure Herbicides

Single component isotherms were produced for F-400 and MN-200 sorbing atrazine, benazolin, bentazone, imazapyr and triclopyr. Adsorption isotherms for LF-1 and MN-200 sorbing atrazine were also produced. Multi-component isotherms using benazolin, bentazone, imazapyr and triclopyr were completed on all the adsorbents.

Section 4.4.1.2 Fulvic Acid Contaminated Herbicide Solutions

The effect of fulvic acid interference was investigated by sorbing multi-component mixtures of the herbicides in the presence of a 20 mg/l fulvic acid solution on F-400 and MN-200. The experimental procedure was the same as before except the herbicide solutions were prepared in a 20 mg/l solution of fulvic acid instead of ultrapure water.
Section 4.4.1.3 Adjusted pH

Multi-component adsorption isotherms were produced for F-400 and MN-200 at pH 3.0 and 10.0. The herbicide solutions were adjusted using 0.1 M hydrochloric acid and sodium hydroxide prior to the addition of adsorbent.

Section 4.4.1.4 Fulvic Acid

Adsorption isotherms for all the adsorbents sorbing fulvic acid were produced at a concentration of 20 mg/l. The solutions were prepared by dissolving 220 mg of fulvic acid in 11 litres of ultra-pure water. The pH of the solution was adjusted to 6.8 using 0.1 M sodium hydroxide. The mass of the adsorbent added to each 500 ml solution was varied from 2.5 mg up to 320 mg. The concentration in solution was analysed using a Perkin Elmer Lambda 12 UV-Vis spectrophotometer at a wavelength of 254 nm and a matched pair of Hellma silica cuvettes. The pH of the solution was measured before and after the experiment.

Section 4.4.2 Batch Temperature Kinetic Trials

An on-line batch reactor set-up was used to investigate the effect of temperature on the adsorption kinetics of atrazine, benazolin, bentazone, imazapyr and triclopyr sorbing onto F-400, LF-1, XAD-4 and MN-200.

The experimental apparatus consisted of an agitated batch reactor, with a capacity of 1 litre, from which fluid was extracted and pumped through a flow cell in a Perkin Elmer Lambda 12 UV-Vis spectrophotometer before return to the vessel. Fig. 4-8 shows a schematic of the set-up. The spectrophotometer was controlled by UVWinlab software. The fluid was extracted from the flask through a 10 μm stainless steel solvent inlet filter and circulated using a Watson Marlow 505S peristaltic pump. The pump was operated at 60 rpm, corresponding to a flow rate of 30 ml/min, or a response time of ten seconds for the system. The vessel was agitated with a flat four-bladed stainless steel impeller at a constant rate. Experiments were conducted by contacting a 2 mg/l solution of the herbicide with 10 mg of the adsorbent at temperatures of 25, 50 and 80 °C. The temperature was controlled by means of a water bath and heater. Each experiment was monitored until the UV trace reached a
plateau, indicating that equilibrium had been reached. At 25 °C each experiment lasted approximately 7 days, whereas at 80 °C equilibrium was attained in less than 2 days.

Section 4.4.3 Mini-column experiments

The experimental rig for the mini-column experiments is illustrated in a simplified flow diagram in Fig. 4-9. It consists of three sections: The first is the preparation of spiked ultrapure water solution, followed by adsorption onto thermostatically controlled columns, with the effluent collected in sample bottles.

The feed solution used for the experiments was prepared on-line by dosing the concentrated pesticide solution into ultrapure water. The Milli-Q 185 purification unit
was connected directly to the column apparatus. It was supplied by a level controlled 30l buffer tank, which in turn was fed by a 200l tank containing grade 2 water. Water for the grade 2 tank was produced by a Millipore Elix 10 water purification unit. The total organic carbon (TOC) content of the water was monitored using an Anatel AI0 monitor capable of measuring a TOC range of 0-200 ppb with an accuracy of 2%. The use of the Anatel monitor also ensured the MilliQ 185 Plus system did not overheat, by providing a recycle stream back to the buffer tank.

![Simplified Flow Diagram of Column Apparatus](adapted from Sweetland, [1997])

A feed solution containing 20 µg/l of benazolin, bentazone, imazapyr and triclopyr was prepared on-line by dosing a flow of 0.1 ml/min of an 8 mg/l pesticide mix solution into a flow of 9.9 ml/min ultrapure water. The pumps were controlled by Masterflex drive controllers to enable accurate speed control. A Masterflex PTFE peristaltic pump head was used to deliver the ultrapure water with the concentrated pesticide dosed using a FMI ceramic metering pump head, having a maximum stroke volume of 50 µl. A stainless steel static in-line mixer was used to obtain a homogeneous solution. A Cole Parmer 0-10 ml/min flow controller was used to accurately control the flow through column 1 to 5 ml/min, with the remainder of
solution passing through column 2. The flow controller coupled with the accuracy of the pumps enabled accurate flow control through each column to 5 ml/min. The mini-columns were thermostatically controlled at 25±1°C using water circulated from a temperature controlled water bath. The effluent from the two columns was either directed to the sample collection bottles or to waste using three-way PTFE solenoid valves. All wetted parts of the experimental rig were either stainless steel, glass or PTFE to eliminate other organic contamination. Sample collection was controlled using a Mitsubishi FX0 14 I/O programmable logic controller (PLC) connected to a data access panel which enabled alteration of the timer constants.

Section 4.4.3.1 Pure Herbicide Mini-Column Trials

For the first experiment, mini-columns, with a bed volume of 0.35 ml (6.4 mm diameter, 11 mm height) were prepared using F-400 and MN-200 in the size range 53-75 μm (wet sieved). The adsorbents were wet packed into methanol washed polyethylene SPC columns using 10 μm stainless steel frits as bed supports. The columns were then washed using 1 litre of ultrapure water to eliminate any fines. Finally, the columns were soaked in ultrapure water and a vacuum applied to remove any air trapped inside the adsorbent pores.

From the results of this experiment it was apparent that the Empty Bed Contact Time (EBCT) of the columns had to be adjusted to provide satisfactory breakthrough curves within a reasonable time scale. For the second experiment the F-400 mini-column was prepared with a bed volume of 0.19 ml (6.4 mm diameter, 6 mm height) and the MN-200 column was prepared with a bed volume of 0.70 ml (9 mm diameter, 11 mm height).

Section 4.4.3.2 Fulvic Acid Contaminated Herbicide Solutions

Two mini-columns with bed volumes of 0.19 ml and 0.70 ml were prepared as before using F-400 and MN-200, respectively. The experiment was performed with a background of 10 mg/l fulvic acid. Fulvic acid was added to the concentrated pesticide solution at a concentration of 1 g/l to give the required concentration in the columns.
Section 4.5 Results and Discussion

Section 4.5.1 Batch Adsorption Isotherms

The results for the single component herbicide adsorption are presented in Figs. 4-10 - 4-13 for F-400, LF-1, XAD-4 and MN-200, respectively. Only atrazine curves were produced for LF-1 and XAD-4 since these adsorbents showed the least promise. Figs. 4-14 to 4-17 show the multi-component curves obtained for the same adsorbents adsorbing benazolin, bentazone, imazapyr and triclopyr. Tables 4-10 and 4-11 present the Freundlich coefficients for the single and multi-component adsorption isotherms, respectively. All correlation coefficients were 0.988 or greater. The Langmuir equation failed to model the data accurately. The pH was measured for every sample before and after equilibration, but no detectable changes were noticed, which is to be expected when working at such low concentrations.

The immediate conclusions which can be drawn from these results is that the activated carbons have a far superior adsorption performance compared to the polymeric adsorbents. It is also clear that single component systems show a greater adsorption capacity than multi-component, which is to be expected due to competition for adsorption sites in multi-component solutions, although the effect is not as profound for MN-200 as with F-400. Of the two classes of adsorbents, F-400 and MN-200 are the best carbon and polymeric adsorbents respectively. However, the adsorption capacity of benazolin, bentazone, imazapyr and triclopyr on MN-200 is significantly lower than that for atrazine. Sweetland [1997] postulated that the adsorption of atrazine on MN-200 was mainly due to hydrophobic bonding, with the potential for hydrogen bonding also present. The other herbicides are far more hydrophilic than atrazine which explains the lower adsorption capacity.

The octanol-water partition coefficient gives an indication of the hydrophobic-hydrophilic nature of the herbicides (see Table 4-4). If it is assumed that hydrophobic interactions dominate the adsorption process then the adsorbents should display selectivity according to descending log K_{ow} values. However, this does not occur in
practice and so using the log $K_{ow}$ values to predict adsorption is inaccurate in this case.

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$</td>
<td>$1/n$</td>
<td>$K$</td>
<td>$1/n$</td>
<td>$K$</td>
</tr>
<tr>
<td>F-400</td>
<td>2488.2</td>
<td>0.486</td>
<td>1618.9</td>
<td>0.307</td>
<td>1774.8</td>
</tr>
<tr>
<td>LF-1</td>
<td>608.6</td>
<td>0.444</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XAD-4</td>
<td>882.2</td>
<td>0.986</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MN-200</td>
<td>2072.7</td>
<td>0.718</td>
<td>66.5</td>
<td>0.941</td>
<td>105.7</td>
</tr>
</tbody>
</table>

Table 4-10  
Freundlich coefficients for single component adsorption of atrazine, benazolin, bentazone, imazapyr and triclopyr

<table>
<thead>
<tr>
<th></th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$</td>
<td>$1/n$</td>
<td>$K$</td>
<td>$1/n$</td>
</tr>
<tr>
<td>F-400</td>
<td>184.0</td>
<td>0.163</td>
<td>132.9</td>
<td>0.132</td>
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<tr>
<td>LF-1</td>
<td>236.4</td>
<td>0.273</td>
<td>98.3</td>
<td>0.171</td>
</tr>
<tr>
<td>XAD-4</td>
<td>241.4</td>
<td>1.713</td>
<td>83.5</td>
<td>1.512</td>
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<tr>
<td>MN-200</td>
<td>279.8</td>
<td>0.782</td>
<td>65.4</td>
<td>0.813</td>
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</table>

Constants based on units of $q_e$ (μmol/g) and units of $C_e$ (μmol/l)

Table 4-11  
Freundlich coefficients for multi-component adsorption of benazolin, bentazone, imazapyr and triclopyr

There is no clear indication of the selectivity of the herbicides with respect to the adsorbents. The multi-component results for F-400 and LF-1 show selectivity in the order benazolin>triclopyr>bentazone>imazapyr. At pH 3 and 10, the selectivity on F-400 follows the same trend, as shown in Figs. 4-18 and 4-19. However, the single component results for F-400 show selectivity in the order benazolin>(atrazine)>bentazone>triclopyr>imazapyr, implying that there are competing effects present in the multi-component systems. Triclopyr is a smaller
molecule than bentazone, therefore it may diffuse into the micropores more easily than bentazone, which could account for the difference.

The structural formulae of the herbicides reveal that apart from having nitrogen containing heterocyclic rings, benazolin and bentazone contain aromatic ring π electron systems in their structures (see Table 4-4). The surface of activated carbon can be described as a collection of organic functional groups containing oxygen, with these groups occurring primarily at the edges of broken graphitic planes, and basal planes consisting of large fused aromatic ring systems in a graphite-like structure. The dominant adsorption force for benazolin and bentazone molecules by F-400 will be dispersion in character, with the most likely orientation of the molecules being flat with the benzene rings of the adsorbate molecules parallel to the rings of the graphene structure of the carbon. The adsorption force would therefore arise from the dispersion interaction of the π electrons in the respective aromatic systems. This type of interaction of the aromatic ring with the surface of the activated carbon through the π electron system of the ring is considered as the formation of donor-acceptor complexes between the adsorbate molecules and several kinds of electron donors.

It is well known that the electron density of an aromatic ring is strongly influenced by the nature of the substituent groups. The chloro (-Cl) group on the aromatic ring of the benazolin acts as an electron-withdrawing group in reducing the overall electron density in the π system of the ring. Thus, benazolin acts as an acceptor in such complexes and forms stronger donor-acceptor complexes with a given donor than bentazone, because the latter has no low-lying acceptor orbitals to form complexes with very strong donors. Hence the adsorption capacity of bentazone is lower than that of benazolin.

It is also known that the oxygen group dipole moment is the determining factor in the strength of the donor-acceptor complex formed. Carbonyl oxygen has a larger dipole moment than carboxylic acid oxygen, and would therefore be expected to act as a
stronger donor. Thus, it is suggested that benazolin and bentazone molecules adsorb on F-400 by a donor-acceptor complex mechanism involving carbonyl oxygen on the carbon surface acting as the electron donor and the aromatic ring of the solute acting as the acceptor. Because of the \( \pi \) system interaction, it is expected that the solute molecules will adsorb in the planar direction. Similar arguments can be proposed for the adsorption of imazapyr and triclopyr which contain aromatic rings with a single nitrogen substitution.

The selectivity of adsorption is less clear on MN-200. At pH 6-7, the selectivity follows the order triclopyr>benazolin>imazapyr>bentazone. However, the order changes depending upon pH, as presented in Figs. 4-20 and 4-21. At pH 3, the selectivity order is triclopyr>bentazone>benazolin>imazapyr, whilst at pH 10 it is imazapyr>benazolin>triclopyr>bentazone, suggesting that the mechanism of adsorption on MN-200 is dependent on pH. Triclopyr and benazolin are smaller molecules than bentazone and imazapyr, which is thought to be the reason for comparatively better adsorption of these molecules in the multi-component system than the single-component system.

Tables 4-12 and 4-13 show the Freundlich coefficients for adsorption at pH 3 and pH 10, respectively on F-400 and MN-200. The herbicides adsorb to a greater extent on F-400 with decreasing pH, which suggests that the surface charge has a significant role in the adsorption of these particular herbicides. The same trend is generally observed with MN-200, but to a lesser extent, with the selectivity of adsorption also affected by pH.

At pH 3, the surface of MN-200 will be positively charged, whilst the adsorbates will be neutral or partially dissociated which will promote adsorption. With increasing pH, the surface of MN-200 becomes negatively charged and the functional groups on the adsorbates will be almost completely dissociated, giving rise to a repulsion effect and thus diminished adsorption. In addition to carboxylic acid functionality, triclopyr
and benazolin also contain chlorine groups which enhance the negative charge of the molecules. As a result, the adsorption capacity of these two molecules shows the greatest decline with increasing pH, which explains the changes in the order of selectivity with pH of solution. Therefore, electrostatic interactions such as dipole-dipole or hydrogen bonding are likely to play a significant role in the adsorption of benazolin, bentazone, imazapyr and triclopyr onto MN-200.

Fig. 4-10  Single component adsorption isotherms for F-400
Fig. 4-11  Single component adsorption isotherm for LF-1

Fig. 4-12  Single component adsorption isotherm for XAD-4
**Fig. 4-13**  *Single component adsorption isotherm for MN-200*

**Fig. 4-14**  *Multi-component adsorption isotherms for F-400*
Fig. 4-15  Multi-component adsorption isotherms for LF-1

Fig. 4-16  Multi-component adsorption isotherms for XAD-4
Fig. 4-17  Multi-component adsorption isotherms for MN-200

Fig. 4-18  Multi-component adsorption isotherms for F-400 at pH 3
Fig. 4-19  
**Multi-component adsorption isotherms for F-400 at pH 10**

Fig. 4-20  
**Multi-component adsorption isotherms for MN-200 at pH 3**
Fig. 4-21  Multi-component adsorption isotherms for MN-200 at pH 10

<table>
<thead>
<tr>
<th></th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K</strong></td>
<td>295.6</td>
<td>178.1</td>
<td>161.1</td>
<td>214.8</td>
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<tr>
<td><strong>1/n</strong></td>
<td>0.198</td>
<td>0.157</td>
<td>0.190</td>
<td>0.147</td>
</tr>
<tr>
<td><strong>F-400</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MN-200</strong></td>
<td>8941.3</td>
<td>93718.0</td>
<td>392.6</td>
<td>81617.1</td>
</tr>
<tr>
<td><strong>K</strong></td>
<td>1.140</td>
<td>1.455</td>
<td>0.667</td>
<td>1.247</td>
</tr>
<tr>
<td><strong>1/n</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-12  Freundlich coefficients for multi-component adsorption of benazolin, bentazone, imazapyr and triclopyr at pH 3

<table>
<thead>
<tr>
<th></th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>K</strong></td>
<td>184.3</td>
<td>233.8</td>
<td>289.6</td>
<td>90.2</td>
</tr>
<tr>
<td><strong>1/n</strong></td>
<td>0.319</td>
<td>0.581</td>
<td>0.924</td>
<td>0.165</td>
</tr>
<tr>
<td><strong>F-400</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MN-200</strong></td>
<td>40.80</td>
<td>47.6</td>
<td>104.1</td>
<td>30.8</td>
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<td><strong>K</strong></td>
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<td>1.019</td>
<td>0.845</td>
<td>0.704</td>
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<tr>
<td><strong>1/n</strong></td>
<td></td>
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<td></td>
<td></td>
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</tbody>
</table>

Constants based on units of $q_e$ (μmol/g) and units of $C_e$ (μmol/l)

Table 4-13  Freundlich coefficients for multi-component adsorption of benazolin, bentazone, imazapyr and triclopyr at pH 10
The Freundlich \(1/n\) coefficient, derived from the isotherm data, is indicative of the strength of adsorption. No clear trends can be observed from the data, although it is clear that the values for F-400 are consistently lower than those for MN-200, indicating stronger adsorption on F-400.

The influence of a high concentration of fulvic acid on the adsorption of trace levels of the herbicides for F-400 and MN-200 is presented in Figs. 4-22 and 4-23, respectively. Fulvic acid reduces the capacity of the adsorbents for all the herbicides, although the isotherms are not of the traditional shape which can be modelled by Freundlich or other isotherm equations. The isotherms are of Type II, according to the classical definition. Initially it was assumed that this was due to a pore filling mechanism, as occurs with nitrogen adsorption isotherms and so the pure multi-component isotherms were repeated to obtain higher equilibrium solution concentrations. However, the extra data fit the curves already presented in Figs. 4-14 to 4-17 and the plateau and sharp rises observed in Figs. 4-22 and 4-23 were not observed. Therefore, it is assumed that the fulvic acid molecules are responsible for sorption. In the first stage of adsorption (up to the plateau) it is assumed that the mechanism of adsorption is as before, albeit reduced due to the effects of pore blockage occurring in the presence of fulvic acid molecules. After the plateau, it is postulated that the fulvic acid molecules adsorbed to the surface of the adsorbents are also acting as adsorption sites or that the fulvic acid molecules influence the surface charge of the adsorbents. Further investigation is required to elucidate this phenomenon.

Adsorption isotherms for fulvic acid adsorption on F-400, LF-1, XAD-4 and MN-200 are presented in Fig. 4-24. The uptake of fulvic acid on LF-1, XAD-4, and MN-200 is lower than that for F-400. The results for XAD-4 are a little surprising since it has a large meso/macropore structure which is accessible to fulvic acid molecules. However, LF-1 and MN-200 have comparable surface area and pore size distributions when compared with F-400 and so it is thought that the pore structure in LF-1 and MN-200 is more ordered, thus promoting a molecular sieving effect, restricting access
to large molecular weight species. Fulvic acids behave as weak acid polyelectrolytes, with pKₐ's in the range 3-6 [Summers and Roberts, 1988].

The adsorption experiments were carried out at pH 6.8 which suggests that the molecules are negatively charged. The pH\textsubscript{pzc} of the adsorbents are 4.8, 3.8, 6.4 and 4.4 for F-400, LF-1 XAD-4 and MN-200 respectively. This would indicate that the surfaces of F-400, LF-1, and MN-200 will be negatively charged, thus repelling the fulvic acid molecules. The surface of XAD-4 will be neutral and it can be seen from the gradient of the isotherm that at high fulvic acid concentrations it will adsorb larger quantities.

![Multi-component adsorption isotherms for F-400 in the presence of 20 mg/l fulvic acid](Fig. 4-22)
**Fig. 4-23**  Multi-component adsorption isotherms for MN-200 in the presence of 20 mg/l fulvic acid

**Fig. 4-24**  Adsorption isotherms of fulvic acid on F-400, LF-1, XAD-4 and MN-200
There is little data in the literature with which to compare the adsorption capacity data. The Freundlich coefficients presented by Speth and Miltner [1980] for atrazine adsorption on pulverised F-400 of $1/n=0.291$ and $K=858$ do not appear to compare to those presented in Table 4-10 of 0.486 and 2488.2 for F-400 and 0.718 and 2072.7 for $1/n$ and $K$, respectively. However, the value of $K$ is strongly dependent upon the $1/n$ coefficient making comparison of the figures irrelevant. Table 4-14 compares the equilibrium adsorption capacities at solution concentrations of $5 \times 10^{-4}$ $\mu$mol/l (approximately 0.1 $\mu$g/l) and 0.01 $\mu$mol/l (approximately 2.2 $\mu$g/l). The data shows reasonable comparison for F-400. The differences are probably due to the particle size ranges used in the two studies, as well as batch variances in the carbon. The capacity of MN-200 is around 7 times lower than F-400 at an equilibrium solution concentration of 0.1 $\mu$g/l.

The only other relevant adsorption capacity data located in the literature was presented by Hopman et al [1994] for bentazone adsorption on ROW 0.8S carbon. At a solution capacity of 1$\mu$g/l the carbon showed a capacity of 47 mg/g. The relative molecular mass of bentazone is 240.3, which gives a comparable capacity of 41.3 mg/g for bentazone adsorption on F-400 at a solution concentration of 1$\mu$g/l. However, the capacity of MN-200 is just 0.197 mg/g at this solution concentration.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_e$ at $C_e = 5 \times 10^{-4}$ $\mu$mol/l</th>
<th>$q_e$ at $C_e = 0.01$ $\mu$mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>61.9</td>
<td>265.4</td>
</tr>
<tr>
<td>MN-200</td>
<td>8.8</td>
<td>76.0</td>
</tr>
<tr>
<td>Speth and Miltner [1980]</td>
<td>94.0</td>
<td>224.6</td>
</tr>
</tbody>
</table>

Table 4-14  Adsorption capacities for atrazine adsorption on F-400

The Ideal Adsorbed Solution Theory (IAST) was applied to the data without success. The single component Freundlich coefficients are used to predict multi-component adsorption. However, at the low concentrations used there is a reasonable scatter in the data which creates uncertainty in the Freundlich coefficients. Also the theory does
not account for phenomena such as size competing effects as occurs with triclopyr and so using the model is not worthwhile.

Section 4.5.2 Batch Temperature Kinetic Trials

The effect of temperature on the adsorption equilibria and kinetics for the adsorbents was investigated for atrazine, benazolin, bentazone, imazapyr and triclopyr. Approximate overall rate coefficients can be calculated using a linear driving force (Equation 32) or, the sometimes preferred “quadratic driving force” approach proposed by Vermeulen (Equation 33) [Harland, 1994].

\[
F(t) = 1 - \exp(-kt) \tag{32}
\]

\[
F(t) = [1 - \exp(-kt)]^{0.5} \tag{33}
\]

where \( F(t) \) is the fractional approach to equilibrium, \( k \) is the overall rate constant (s\(^{-1}\)) and \( t \) is the time (s). An Arrehenius type relationship was observed in the data, indicated by a straight line obtained on a plot of \( \ln k \) versus \( 1/T \). Table 4-15 presents the activation energies obtained using this method. Appendix 1 presents examples of the kinetic data and Arrehenius plots.

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>Benazolin</th>
<th>Bentazone</th>
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<tr>
<td>F-400</td>
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<td>25.57</td>
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<tr>
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<td>30.92</td>
<td>31.36</td>
<td>27.07</td>
</tr>
<tr>
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<td>41.16</td>
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<tr>
<td>MN-200</td>
<td>29.12</td>
<td>41.71</td>
<td>37.61</td>
<td>36.57</td>
<td>42.23</td>
</tr>
</tbody>
</table>

Table 4-15 Activation energies for adsorption of atrazine, benazolin, bentazone, imazapyr and triclopyr on F-400, LF-1, XAD-4 and MN-200

These low values suggest that the attractive forces between the adsorbent and adsorbates are predominantly physical in nature. However, it is shown that the activation energies for the polymeric adsorbents, XAD-4 and MN-200 are
significantly higher than those for F-400 and LF-1, suggesting that dipole-dipole interactions play an important role in the adsorption process.

The Biot number (Equation 34) can be used to assess whether the adsorption is film or pore diffusion controlled, with a large value indicating the latter.

$$Bi = \frac{k_f r_p}{D_{eff}}$$  \hspace{1cm} (34)

where $k_f$ is the external mass transfer coefficient (m/s) as defined in Equation 3, $r_p$ is the adsorbent particle radius, and $D_{eff}$ is the effective particle diffusivity, defined by,

$$k = \frac{D_{eff} \pi^2}{r_p^2}$$  \hspace{1cm} (35)

The external mass transfer coefficients were calculated using Equation 3. $dC/dt$ was calculated by determining the gradient of the concentration decay curve in the time range 0-3 minutes. This technique has been used extensively in the literature. The overall particle mass transfer coefficients at 25°C were used to calculate the effective diffusivities. Table 4-16 shows the resultant Biot numbers. The low numbers indicate that the adsorption is film-diffusion controlled in all cases.

<table>
<thead>
<tr>
<th></th>
<th>F-400</th>
<th>LF-1</th>
<th>XAD-4</th>
<th>MN-200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.454</td>
<td>0.294</td>
<td>0.003</td>
<td>0.091</td>
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<tr>
<td>Benazolin</td>
<td>0.652</td>
<td>0.285</td>
<td>0.079</td>
<td>0.038</td>
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<td>Bentazone</td>
<td>0.389</td>
<td>0.188</td>
<td>0.016</td>
<td>0.108</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>0.216</td>
<td>0.120</td>
<td>0.003</td>
<td>0.031</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>0.332</td>
<td>0.199</td>
<td>0.007</td>
<td>0.112</td>
</tr>
</tbody>
</table>

Table 4-16  Biot numbers for atrazine, benazolin, bentazone, imazapyr and triclopyr adsorption on F-400, LF-1, XAD-4 and MN-200 ($C_o=2$ mg/l)
Section 4.5.3 Mini-column experiments

Section 4.5.3.1 Pure Herbicide Mini-Column Trials

The first mini-column experiment was performed using an EBCT of approximately 4.3 seconds for both the F-400 and MN-200 beds. Figs. 4-25 and 4-26 present the breakthrough curves for F-400 and MN-200 respectively, sorbing benazolin, bentazone, imazapyr and triclopyr. It is clear that the capacity of F-400 is far superior to MN-200 since no breakthrough occurred on the carbon column after 28 days service and nearly 200 l of water treated. However, the polymeric column showed instant breakthrough, indicating that the EBCT was too low.

In order to reduce the time required to complete an experiment whilst producing satisfactory breakthrough curves, the EBCT of the carbon column was reduced and that of the polymeric column increased. The breakthrough curves obtained from the second experiment are shown in Figs. 4-27 to 4-29. The experiment was stopped after 35 days, with each column having processed 214 l of water.

Breakthrough of the carbon column to the EU legal limit (Fig. 4-28) occurs between 50,000 and 160,000 bed volumes, in the sequence imazapyr, bentazone, benazolin and finally triclopyr. The selectivity sequence for benazolin and triclopyr is reversed compared to the results obtained in the batch isotherm experiments. This may be due to the kinetic effects encountered during the batch equilibrium of 7 days. During the long duration of the column experiment, triclopyr may be able to diffuse into the pores to a greater extent than benazolin. The adsorption capacity for benazolin, bentazone, imazapyr and triclopyr is 34.20, 22.84, 15.22, 38.01 mg/g respectively. Chromatographic elution is observed for the herbicides which caused the imazapyr and bentazone concentrations to reach 25 and 23 μg/l respectively. Once again, the MN-200 adsorption bed showed breakthrough almost instantly, which is reflected in the low adsorption capacities of 0.48, 0.42, 0.26, 1.28 mg/g for benazolin, bentazone, imazapyr and triclopyr respectively.
Fig. 4-25  Mini-column breakthrough curves for F-400 sorbing benazolin, bentazone, imazapyr and triclopyr (EBCT ≈ 4.3 seconds)

Fig. 4-26  Mini-column breakthrough curves for MN-200 sorbing benazolin, bentazone, imazapyr and triclopyr (EBCT ≈ 4.3 seconds)
Fig. 4-27  \textit{Mini-column breakthrough curves for F-400 sorbing benazolin, bentazone, imazapyr and triclopyr (EBCT \approx 2.3 \text{ seconds})}

Fig. 4-28  \textit{Mini-column breakthrough curves for F-400 sorbing benazolin, bentazone, imazapyr and triclopyr (EBCT \approx 2.3 \text{ seconds}) - expanded view}
The breakthrough curves are shallow in shape which suggests that the flow rate through the column was too high, thus spreading the mass transfer zone. A slower flow rate and hence EBCT will probably result in a greater life time for the columns. In practice, an EBCT of 15 minutes is standard. The concentration used for the breakthrough curves was also exceptionally high, approximately 20 times those found in surface waters. However, the large capacity of the adsorbents and the limited time for experiments necessitated their use.

Section 4.5.3.2 Fulvic Acid Contaminated Herbicide Solutions

The mini-column breakthrough curves in the presence of fulvic acid are presented in Figs. 4-30 and 4-31. The introduction of fulvic acid into the herbicide mixture caused instant breakthrough on the F-400 column. MN-200 also showed instant breakthrough, although the reduction in capacity is not as profound.
Fig. 4-30  Mini-column breakthrough curves for F-400 in the presence of fulvic acid  (EBCT $\approx 2.3$ seconds)

Fig. 4-31  Mini-column breakthrough curves for MN-200 in the presence of fulvic acid  (EBCT $\approx 8.4$ seconds)
Fulvic acid adsorption isotherms presented in Fig. 4-24 show that F-400 has a much higher capacity for fulvic acid than MN-200, which is attributed to the mesoporous nature of the carbon. It is thought that the fulvic acid molecules adsorb in the mesopores, thus preventing diffusion of the herbicides into the micropore structure of the carbon.
Section 4.6 Conclusions

The adsorption of benazolin, bentazone, imazapyr and triclopyr in the parts per billion (ppb) range has been investigated in batch and mini-column modes. An analytical technique was developed for these herbicides comprising solid phase extraction followed by HPLC analysis of the extracts. Relative standard deviations of 5.0% and less were achieved for all the herbicides. Recoveries of benazolin, bentazone and triclopyr were 100%, whilst the recovery of imazapyr was 85%.

Adsorption of the herbicides on F-400 is thought to be by a donor-acceptor complex mechanism, involving carbonyl oxygen on the carbon surface acting as the electron donor and the aromatic rings of the solutes acting as the acceptors. The selectivity of adsorption on MN-200 was affect by pH and it is thought that electrostatic interactions such as dipole-dipole or hydrogen bonding play a significant role in the adsorption of benazolin, bentazone, imazapyr and triclopyr.

The activation energy of adsorption indicates that the adsorption bonds are mainly physical in nature. Kinetic analysis indicates that the adsorption is film-diffusion controlled.

F-400 has a significantly higher adsorption capacity for the herbicides in ultrapure water than MN-200. Breakthrough above the EU legal limit occurs between 50,000 and 160,000 bed volumes with an EBCT of 2.3 seconds. However, in the presence of fulvic acid, F-400 showed instant breakthrough.

Purolite International Ltd also manufacture polymeric hypercrosslinked adsorbents which contain weak base anion or cation exchange functional groups. It is possible that an adsorbent containing surface functional groups will adsorb these herbicides to a greater extent than MN-200.
Section 4.7 References


Chiron, S., Papilloud, S., Hærdi, W., Barcelo, D. “Automated online liquid-solid extraction followed by liquid chromatography high flow pneumatically assisted electrospray mass-spectrometry for the determination of acidic herbicides in environmental waters”, Analytical Chemistry, 67, 9, pp. 1637-1643, 1995


Environment Agency, “Water Sampling Data”, Correspondence by e-mail, June 1999


National Rivers Authority, "Pesticides in the Aquatic Environment", HMSO, 1995


CHAPTER 5

REGENERATION

Section 5.1 Introduction

Activated carbon possesses a finite capacity for adsorbates, that is, eventually the carbon will no longer be able to adsorb contaminants. Adsorption capacity is dependent on the physical and chemical characteristics of the activated carbon, the solutes and the operating temperature of the process. When the adsorptive capacity of the activated carbon is reached, or when the concentration of contaminant in the effluent exceeds allowable limits, it must either be replaced or regenerated, with the latter usually proving to be the more economical [Roller et al, 1982].

The most commonly used technique for the reactivation of exhausted activated carbon is by thermal regeneration. The carbon is transported to a furnace where it undergoes a three-step regeneration process: (i) the carbon is dried at about 100 °C; (ii) the adsorbed pollutants are pyrolysed at 260-840 °C and (iii) the carbon is reactivated with flue gas and steam at 870-930 °C. This process is extremely energy intensive, requiring large capital investment and results in carbon attrition rates of approximately 5-10% per cycle. A number of water utilities have installed reactivation furnaces on-site to minimise the costs.

This chapter investigates the solvent regeneration of F-400 and MN-200. The effect of solvent, pH and temperature upon regeneration efficiency is investigated. The literature review concentrates on liquid phase desorption and as such, microbiological and electrical regeneration have not been considered.
Section 5.2 Literature Review

A great deal of research has been conducted into liquid-phase desorption over the past few years. Three major processes have emerged as possible alternatives to thermal regeneration; chemical regeneration, solvent regeneration and supercritical extraction. Chemical regeneration usually involves adjusting the pH within the pores of the carbon to convert the organic adsorbates into an ionised form that has a less favourable adsorption equilibrium or ion exchanges for a preferred inorganic cation. This technique has found application in the removal of phenol via conversion to sodium phenate at high pH [McLaughlin, 1995]. Sontheimer et al [1988] recognised that an increase in solution pH can cause organics to desorb from the surface of carbon. It was concluded that this technique would only be viable if the desorbing solution could be recycled. Johnson et al [1988] indicated that partial regenerations using bases and/or acids may prolong carbon life between thermal reactivations. Newcombe and Drikas [1993] related chemical regeneration efficiency to the surface characterisation, surface charge and electrophoretic mobility to explain the high removal efficiencies of adsorbed organics when an acid wash followed by a base wash was employed to regenerate activated carbon. Several studies have concluded that regeneration efficiency declines as the molecular weight of the adsorbate increases [Martin and Ng, 1985; Chiang and Wu, 1989]. Martin and Ng [1985] also concluded that in the absence of chemical reaction between the regenerant and adsorbate the success of the regeneration process is governed by the mechanism of physical displacement of the adsorbate by the solvent. It is interesting to note that formic and acetic acids have been reported to remove essentially 100% of adsorbed commercial humic acid from the surface of activated carbon. In contrast, ethanol, methanol and acetone only remove, 39.8, 36.5 and 10.7% respectively, even though humic substances are highly soluble in the aforementioned solvents [Martin and Ng, 1987].

Solvent regeneration displaces the process fluid from the pores of the carbon and removes the adsorbate molecules in solution. The key to the success of the method is in choosing an effective solvent for which the contaminants of interest have a high
affinity for, and is also easily removed from the pores at the end of the regeneration step. This last point is of particular importance when considering potable water applications where trace levels of organic solvent are extremely undesirable. The solvent regeneration of phenol adsorbed on activated carbon has been the focus of several studies. Cooney et al [1983] investigated the effectiveness of nineteen solvents before concentrating efforts on methanol. During repeated adsorption-regeneration cycles, the regeneration efficiency reached a plateau of approximately 81%. It was proposed that this loss in adsorption capacity could be accounted for by providing extra activated carbon initially - an economically viable alternative to replacing 5-10% of the carbon after each thermal regeneration. Similar tests were performed by Tamon et al [1980]. High regeneration performance was again noted, except for those organic compounds substituted by electron donating groups, such as -NH$_2$, -OH and -OCH$_3$. Improved regeneration efficiencies were produced when electron donating solvents, such as dimethylformamide (DMF) were used.

Robertson and Lester [1995] achieved 95% atrazine desorption from activated carbon by a 16 hour Soxhlet extraction using acetone. Polar solvents, including ethanol and methanol, offered low recoveries, with only 50% of simazine extracted. Supercritical CO$_2$ fluid extraction recoveries of atrazine and simazine exceeded 90% using dynamic acetone modification (50 mol%). Static acetone modification and unmodified supercritical CO$_2$ provided significantly lower extraction efficiencies. Soxhlet extraction efficiency was reduced by approximately 25% when the solid phase concentration of the triazine herbicides on the carbon was reduced from 100μg/g to 1μg/g, although no appreciable difference was observed in the recovery efficiency using dynamic acetone modified supercritical CO$_2$.

Supercritical fluid extraction involves the use of a supercritical fluid, typically carbon dioxide, since its critical temperature is close to ambient (31.2 °C). The fluid extracts adsorbates from the surface of the carbon in a similar way to solvent regeneration. The adsorbates are separated from the solvent by reducing the pressure to sub-critical
conditions so that the solvent reverts to the vapour phase. The adsorbates are insoluble in the sub-critical phase and are separated as a liquid. Supercritical fluid extraction requires high capital and operating costs, which usually eliminates it from consideration as a viable regeneration technique.

Streat et al [1998] investigated the regeneration of atrazine, simazine, isoproturon, chlorotoluron and diuron sorbed onto MN-200. They used ethanol, methanol and 1-propanol and all showed similar elution profiles. However, ethanol was considered the safest solvent for use in the water industry. Regeneration was 99.95% complete within 3.2 bed volumes of ethanol passed. Limited regeneration of F-400 was shown, although less than 5% of diuron and chlorotoluron were recovered.

Horner et al [1998] used methanol and ethanol to remove atrazine from F-400. They reported recovery efficiencies of 94.4% and 90% for ethanol and methanol respectively.
Section 5.3 Experimental

Section 5.3.1 Trial Regeneration

Mini columns were prepared by wet packing 200 mg of F-400 and MN-200 into 3 ml solid phase extraction columns, which gave bed volumes of 0.55 and 0.92 ml respectively. 10μm stainless steel frits were used as bed supports. The columns were placed on the SPE manifold and 500ml samples containing 4 μg/l of each herbicide were passed through the columns at 1ml/min. One column of each adsorbent was loaded individually and the effluent retained to check for breakthrough using the methods outlined in Chapter 4. The loaded columns were then dried for 10 minutes using nitrogen prior to regeneration.

A Kontron 420 HPLC pump, capable of a flow rate of 0.05-5 ml/min, was used for the regeneration experiments. Fig. 5-1 shows a schematic of the apparatus. Autosampler vials with a capacity of 2ml, were numbered and weighed using the Sartorius balance. Regeneration of the columns was performed using a flow rate of 0.5 bed volumes per minute. The temperature of the bed was maintained using a water bath and heater, which circulated water in the column jacket.

![Regeneration Apparatus](image)

Fig. 5-1 Regeneration Apparatus

The solvents used were HPLC grade ethanol and acetonitrile. The effect of pH on regeneration was investigated by adjusting the solvent pH to 12 using 0.1 M NaOH.
The effect of temperature was also investigated by increasing the column jacket temperature to 50 °C. Samples, with gradually increasing volumes, were collected into the vials and then the vials were re-weighed to enable the volume of solvent to be calculated. The solvent was evaporated from the vials using a stream of nitrogen and the sample reconstituted using 500 µl of 15% acetonitrile, 85% 10 mmol KH₂PO₄ buffer at pH 3.0. Analysis of the vials was performed using the HPLC methods outlined in Chapter 4.

Section 5.3.2 Regeneration of mini-columns

The mini-columns which were saturated in the adsorption experiments, were dried using nitrogen for 10 minutes, prior to regeneration using HPLC grade ethanol at a pH of 12 and temperature of 50°C. Samples were collected and evaporated and reconstituted in 1ml of 15% acetonitrile, 85% 10 mmol KH₂PO₄ buffer at pH 3.0. The F-400 samples were then diluted by a factor of 10 for HPLC analysis. Regeneration was continued until the herbicides were no longer eluted. A second adsorption and regeneration cycle was performed using the F-400 column.
Section 5.4 Results and Discussion

Section 5.4.1 Trial Regeneration

Tables 5-1 and 5-2 show the results for the trial regenerations of F-400 and MN-200 respectively. Acetonitrile does not provide sufficient recovery of the herbicides for it to be considered a viable option. The elution profiles for the experiments involving ethanol can be seen in Figs. 5-2 - 5-7. Increased recoveries are observed when the pH and temperature are raised. The effect is most noticeable for MN-200, where recovery efficiencies of 102.9, 100.9, 101.4, 81.9 and 102.9% were observed for atrazine, benazolin, bentazone, imazapyr and triclopyr respectively. This was achieved in 10-15 bed volumes of eluent. For F-400, the pH swing produces approximately 50% recovery of bentazone and imazapyr without any significant enhancement in the recovery of atrazine. At 50°C, the recovery of atrazine increases from 22% to 81.8% whilst the recovery of bentazone and imazapyr remains at approximately 50%. Benazolin and triclopyr are not recovered within 80 bed volumes which is probably due to the adsorbates stronger interaction with the carbon surface than the other adsorbates.

<table>
<thead>
<tr>
<th>Regenerant</th>
<th>Regeneration Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atrazine</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>57.6</td>
</tr>
<tr>
<td>Acetonitrile @ pH 12</td>
<td>76.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>20.0</td>
</tr>
<tr>
<td>Ethanol @ pH 12</td>
<td>22.0</td>
</tr>
<tr>
<td>Ethanol @ pH 12, 50°C</td>
<td>81.8</td>
</tr>
</tbody>
</table>

Table 5-1 Trial regeneration results for F-400
### Chapter 5

**Regenerant Regeneration Efficiency (%)**

<table>
<thead>
<tr>
<th>Regenerant</th>
<th>Atrazine</th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>83.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>Acetonitrile @ pH 12</td>
<td>66.2</td>
<td>-</td>
<td>46.2</td>
<td>15.0</td>
<td>-</td>
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<tr>
<td>Ethanol</td>
<td>99.3</td>
<td>-</td>
<td>21.9</td>
<td>27.2</td>
<td>9.1</td>
</tr>
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<td>Ethanol @ pH 12</td>
<td>83.2</td>
<td>94.4</td>
<td>97.7</td>
<td>77.0</td>
<td>97.7</td>
</tr>
<tr>
<td>Ethanol @ pH 12, 50°C</td>
<td>102.9</td>
<td>100.9</td>
<td>101.4</td>
<td>81.9</td>
<td>102.8</td>
</tr>
</tbody>
</table>

**Table 5-2**  *Trial regeneration results for MN-200*

![Graph showing concentration in eluent vs. bed volumes of eluent passed](image)

**Fig. 5-2**  *Trial regeneration of F-400 with ethanol*
Fig. 5-3  Trial regeneration of F-400 with ethanol at pH 12

Fig. 5-4  Trial regeneration of F-400 with ethanol at pH 12 and 50°C
**Fig. 5-5**  *Trial regeneration of MN-200 with ethanol*

**Fig. 5-6**  *Trial regeneration of MN-200 with ethanol at pH 12*
Section 5.4.2 Regeneration of mini-columns

Table 5-3 presented the recoveries of herbicide from the mini-columns used in Chapter 4. Tables 5-4 and 5-5 show the concentrations of herbicides in each vial, together with the number of bed volumes of eluent passed through the F-400 and MN-200 column respectively. Figs. 5-8 and 5-9 show the elution curves for the F-400 and MN-200 columns respectively.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Regeneration Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benazolin</td>
<td>102.8</td>
</tr>
<tr>
<td>Bentazone</td>
<td>53.3</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>50.4</td>
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<tr>
<td>Triclopyr</td>
<td>103.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Regeneration Efficiency (%)</th>
</tr>
</thead>
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<tr>
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<td>98.9</td>
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<tr>
<td>Bentazone</td>
<td>100.3</td>
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<td>Imazapyr</td>
<td>79.5</td>
</tr>
<tr>
<td>Triclopyr</td>
<td>101.0</td>
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</table>

Table 5-3 Regeneration efficiencies for F-400 and MN-200 adsorption columns
<table>
<thead>
<tr>
<th>Bed Volumes Passed</th>
<th>Benazolin (mg/l)</th>
<th>Bentazone (mg/l)</th>
<th>Imazapyr (mg/l)</th>
<th>Triclopyr (mg/l)</th>
<th>Total Mass (mg/l)</th>
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<tr>
<td>0.00</td>
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<td>4.37</td>
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<td>91.767</td>
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<td>8.12</td>
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<td>8.566</td>
<td>13.624</td>
<td>81.422</td>
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<td>90.78</td>
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*Table 5-4  Concentration of herbicides in regenerant solution for F-400*
<table>
<thead>
<tr>
<th>Bed Volumes Passed (mg/l)</th>
<th>Benazolin Concentration (mg/l)</th>
<th>Bentazon Concentration (mg/I)</th>
<th>Imazapyr Concentration (mg/I)</th>
<th>Triclopyr Concentration (mg/I)</th>
<th>Total Mass (mg/I)</th>
</tr>
</thead>
<tbody>
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<td>0.00</td>
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<td>4.505</td>
<td>51.354</td>
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</tbody>
</table>

Table 5-5  Concentration of herbicides in regenerant solution for MN-200
The regeneration of MN-200 was virtually complete within 10 bed volumes, since 99.2% of the total mass of herbicide recovered was removed in this time. The
regeneration efficiencies were 100% except for imazapyr, for which only 79.5% was recovered. A lot more regenerant was required for F-400, in all 200 bed volumes were passed. The recoveries of bentazone and imazapyr were approximately 50%, which is similar to the recoveries observed in the trial regeneration. Benazolin and imazapyr exhibited dual elution maxima, which is attributed to the bed equilibration time at the start of the experiment. The HPLC chromatograms showed a large number of peaks in the early stages of elution which are probably due to impurities in the herbicides and the organic content of the ultrapure water. The total organic content of the ultrapure water was continually monitored and measured around 2 g/l, which corresponds to 428 µg for the 214 litres of water processed. Some peaks may have also been due to degradation products of the herbicides, but the absence of a mass spectrometer prevented further analysis of the compounds.

The adsorption cycle was repeated for the F-400 column to assess the regeneration recovery efficiency. Fig. 5-10 presents the breakthrough curve.

![Fig. 5-10](image)

**Fig. 5-10** *Mini-column breakthrough curves for regenerated F-400 column (EBCT ≈ 2.3 seconds)*
The herbicides breakthrough the column between 30,000 and 60,000 bed volumes, which is lower than for the virgin carbon. However, the regeneration cycle only removes approximately 50% of bentazone and imazapyr, so it is to be expected that the capacity is reduced. Regeneration of the column after the second adsorption cycle was performed by passing 200 bed volumes of the regenerant solution through the bed at 50 °C. Subsequently, 1 ml of the effluent was evaporated and reconstituted in 1ml of 15% acetonitrile, 85% 10mmol KH$_2$PO$_4$ buffer at pH 3.0 for HPLC analysis. The recovery efficiencies for the second adsorption cycle are presented in Table 5-6. The figures presented for bentazone and imazapyr represent the recovery efficiencies based on the total amount adsorbed after the two cycles. The figures in brackets show the recovery efficiencies based on the amount adsorbed in the second adsorption cycle only. It can be seen that almost all of the bentazone and imazapyr adsorbed in the second cycle is recovered in the second regeneration cycle and so the bed life will settle with repeated cycles. The loss of capacity could be supplemented by using larger beds such that the reduction in capacity will be offset by the larger amount of adsorbent used.

<table>
<thead>
<tr>
<th>Regeneration Efficiency (%)</th>
<th>Benazolin</th>
<th>Bentazone</th>
<th>Imazapyr</th>
<th>Triclopyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400</td>
<td>100.7</td>
<td>47.4 (89.3)</td>
<td>41.6 (94.1)</td>
<td>104.2</td>
</tr>
</tbody>
</table>

*Table 5-6 Regeneration efficiencies for second regeneration of F-400 adsorption column*
Section 5.5 Conclusions

A number of trials were performed using mini-columns with low loadings of each herbicide (20 μg/g). Ethanol adjusted to pH 12 and at 50°C was found to be the most effective regenerant, although at the low loadings benazolin and triclopyr were not recovered from F-400. Regeneration of the F-400 mini-column required 200 bed volumes and recovered 103%, 53%, 50% and 104% of benazolin, bentazone, imazapyr and triclopyr respectively. The MN-200 mini-column was effectively regenerated within 10 bed volumes with recoveries of 99%, 100%, 80% and 101% for benazolin, bentazone, imazapyr and triclopyr respectively. The chromatograms of the regenerant solutions suggested that the TOC present in the ultrapure water was also eluted. A second adsorption and regeneration cycle on the F-400 mini-column showed that the breakthrough times for the herbicides were reduced. However, recovery efficiencies of 101%, 89%, 94%, 104% were observed based on the amount adsorbed during the second cycle. This suggests that the bed life will reach a steady value with repeated cycles.
Section 5.6 References


Martin, R.J., Ng, W.J. “Chemical Regeneration of Exhausted Activated Carbon - II”, Water Research, 19, 12, pp. 1527-1535, 1985


CHAPTER 6

GENERAL CONCLUSIONS

Section 6.1 Conclusions

The objectives of this research were to investigate selected activated carbons and polymeric resins for the removal of 'key' organic pollutants, particularly herbicides, at various source concentrations from potable water. The regeneration of the adsorbents was also investigated using solvent stripping techniques.

Characterisation of the adsorbents was achieved using a number of physical and chemical methods. Pore size distributions of the adsorbents were investigated using nitrogen adsorption. A number of models were then applied to the data in order to model the micro- and meso-pore structures. Quantitative estimates of the pore sizes could not be made due to the dependency of the models on pore shape and interaction parameters. However, the models allowed reasonable comparisons to be made between the adsorbents. F-400, LF-1 and MN-200 possess similar microporous structure. The carbons also contain a reasonable degree of mesoporosity, which may enhance the diffusion of organic species into the micropores. The pore size distribution for XAD-4 shows an almost exclusive meso/macroporosity with very little microporous structure.

Spectroscopic analysis and titration of the adsorbents has indicated a number of different oxygen functional groups. The concentration of oxygen functional groups was greater on the surface of the carbons than those present on the surface of the polymers. FT-IR analysis of the polymers revealed a complicated mixture of oxygen containing functional groups, such as, ketones, ethers, alcohols and carboxylic acids. Higher oxygen concentrations than those obtained using direct titration were experienced using XPS and elemental analysis, which is probably due to bound oxygen within the structures of the adsorbents, which is not accessible to adsorbates.
The adsorption capacity of phenol was also assessed. The capacity of the carbons was much greater than the polymeric adsorbents. The capacity of MN-200 was shown to be greater than XAD-4.

The adsorption of benazolin, bentazone, imazapyr and triclopyr in the parts per billion range was investigated in batch and mini-column modes. An analytical technique was developed for these herbicides comprising solid phase extraction followed by HPLC analysis of the extracts. The adsorption capacity of the carbonaceous materials were far superior to that of the polymeric materials. Of the two classes of adsorbents, F-400 and MN-200 had the highest uptake of the herbicides. The activation energies of the polymers were higher than those of the carbons, suggesting a difference in the mechanism of adsorption. Analysis of the Biot number suggested that film diffusion was the rate-limiting diffusional process.

Adsorption of the herbicides on F-400 is thought to be by a donor-acceptor complex mechanism, involving carbonyl oxygen on the carbon surface acting as the electron donor and the aromatic rings of the solutes acting as the acceptors. The selectivity of adsorption on MN-200 was affected by pH and it is thought that electrostatic interactions such as dipole-dipole or hydrogen bonding play a significant role in the adsorption of benazolin, bentazone, imazapyr and triclopyr.

F-400 has a significantly higher adsorption capacity for the herbicides in ultrapure water than MN-200. Breakthrough above the EU legal limit occurs between 50,000 and 160,000 bed volumes with an EBCT of 2.3 seconds. MN-200 showed instant breakthrough even with a longer empty bed contact time. In the presence of fulvic acid, F-400 also showed instant breakthrough.

The adsorption capacity of fulvic acid was very low due to size exclusion from the micropores and electrostatic repulsion of the negatively charged adsorbates with the
negatively charged adsorbent surface. F-400 showed a larger uptake than MN-200, due to the mesoporous nature of the carbon.

Trial regeneration of F-400 and MN-200 was performed on mini-columns loaded with low quantities of each herbicide. Ethanol and acetonitrile were selected as regenerants and the effect of pH and temperature was investigated. Ethanol adjusted to pH 12 and at 50°C was found to be the most effective regenerant, although at the low loadings benazolin and triclopyr were not recovered from F-400. Complete recovery of benazolin and triclopyr from the F-400 mini-column was achieved using 200 bed volumes of regenerant. Approximately 50% of bentazone and imazapyr was recovered, the rest being irreversibly adsorbed. The MN-200 mini-column was effectively regenerated within 10 bed volumes with complete recovery of benazolin, bentazone and triclopyr, and 80% recovery of imazapyr.

A second adsorption and regeneration cycle on the F-400 mini-column showed that the breakthrough times for the herbicides were reduced. However, recovery efficiencies of 101%, 89%, 94%, 104% for benazolin, bentazone, imazapyr and triclopyr were observed, suggesting that the bed life will reach a steady value with repeated cycles.

Section 6.2 Future Work

The present study has provided an insight into the problems facing water companies with the advent of new highly functionalised and hydrophilic herbicides. Although activated carbon shows high adsorption uptakes in spiked ultrapure water samples, the capacity was drastically reduced in the presence of commercial fulvic acid. However, the fulvic acid may not be representative of the background organic matter present at the adsorption stage of a water treatment process, and therefore further trials are required using actual water from a treatment works prior to GAC adsorption.
Although the polymeric materials used in this study showed very low uptake compared to F-400, Purolite and other companies manufacture functionalised polymers which should also be investigated for their potential to remove such organic species.

Very little work has been focussed on the kinetic limitations of the herbicide uptake. This was partly due to the requirement to work at small-scale in order to generate results. Pilot scale column experiments are required to assess the effect of whole particles and the microbiological fouling of columns to model their true breakthrough behaviour.

A brief study of the potential of solvent stripping has been performed. Further investigation of solvent flow rate, temperature and pH is required. For example, pH adjustment using an amine may provide enhanced recovery.

In conclusion, for the herbicides used in this study, MN-200 does not provide a viable alternative to activated carbon. However, the polymers possess the advantages of enhanced mechanical strength and much easier regeneration over F-400. Further investigation of functionalised polymeric adsorbents is required for application to the removal of highly functional hydrophilic herbicides from potable water supplies.
APPENDIX ONE

BATCH TEMPERATURE KINETIC DATA

Fig. A-1  Batch Concentration Decay Curves for Bentazone Adsorption on F-400 at 25, 50 and 80°C
Fig. A-2  Arrenhius Data for batch adsorption of Bentazone on F-400