THE REMOVAL OF TRACE ORGANIC IMPURITIES FROM WATER USING ACTIVATED CHARCOAL CLOTH.

A Thesis submitted to the Board of the Faculty of
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DOCTOR OF PHILOSOPHY

by

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TO

MOM, DAD AND MARLENE

FOR ALL THEIR HELP AND ENCOURAGEMENT.

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SUMMARY

In order to study the removal of trace organic compounds from water using activated charcoal cloth, phenol and 2 chlorophenol were chosen as typical organics, due to their widespread dissemination in the environment as toxic pollutants and the availability of relevant detailed information about them.

The adsorption capacity of the cloth was found, using the Freundlich isotherm, to be between three and four times greater than for granular charcoal, under normal conditions. In order effectively to model a system using charcoal cloth, it was necessary to establish the kinetics of adsorption on the cloth. Film diffusion could be neglected in a sufficiently turbulent, well-stirred reactor. Electron micrographs of the cloth surface had indicated that most of the porous structure of the cloth consists of micropores. Hence, phenol could only adsorb onto the surface, or into longitudinal surface corrugations. Therefore, pore transport was assumed to be negligible and adsorption to be surface-reaction-controlled.

The experimental apparatus constructed for this study consisted of three well-stirred reactors, through which a continuous length of charcoal cloth was transported, counter-current to the flow of polluted water. The cloth was then passed through a regenerator containing two 1 KW heaters, where it was reactivated and then returned to the adsorption section. It was discovered that the regeneration process was more efficient with only one heater operating; this was thought to be due to the lack of formation of surface carbon and the presence of steam formed from water on the cloth surface. Experimental results indicated that it was possible, using the continuous apparatus, to remove 90% phenol and 98% 2-chlorophenol from water, at steady state.

The adsorption of phenol, at steady state, was successfully modelled using surface-reaction-controlled kinetics.

Keywords

Charcoal Cloth, Kinetics, Phenols, Regeneration, Surface Adsorption, Carbon.

Chapter 1

Introduction

1 Introduction

Currently available forms of activated carbon, such as the granular or powdered varieties, possess distinct handling disadvantages when used in a process. For instance, when the capacity of granular carbon in an adsorber bed, used in industry, has been exhausted, it either has to be removed from the filter and regenerated as a whole, or mechanically transported to a regenerator. Whichever way is used, there are considerable losses of adsorbent due to abrasion and entrainment. Charcoal cloth, however, is a continuous medium enabling transport and handling without such difficulties, within a process. This form of adsorbent, therefore, readily lends itself to continuous treatment processes.

Charcoal cloth is manufactured by the heat treatment and activation of loomstate viscose rayon and was first manufactured in the early 1960's to aid the development of lightweight respirators. The early forms of activated charcoal cloth, while being suitable for adsorption, were not strong enough to be used in a manufacturing process. As understanding of the cloth increased and technology improved, then stronger, more resilient forms of activated charcoal were manufactured. The present day varieties of activated charcoal cloth are as strong as normal lightweight materials and possess adsorptive properties at least as good as earlier varieties.

The brief for this project indicated that the chemical engineering applications of activated charcoal cloth should be studied. However it was obvious that these applications would be too numerous to enable a successful project to be undertaken at sufficient depth. Hence, with the overall aim of identifying prospective profitable areas of application, it was decided to study the applications of this material in environmental pollution control. Surveying the literature, revealed that due to current handling difficulties, a form of water pollution control involving the continuous use of activated charcoal would be of special interest. Hence, the aim of this project was to investigate the operation of equipment to continuously remove trace organic contaminants from water. This would involve a detailed investigation into the surface and adsorptive properties of the cloth itself, to enable the formulation of theories about the adsorption of water borne chemicals onto the cloth. Detailed information would be required about the adsorption capacity of the cloth under realistic process conditions. The design of a piece of equipment would be necessary, such that the cloth was continuously transported in order to remove water pollutants and to provide for continuous cloth recycling. The aim of the continuous loop would be to provide direct regeneration, without complex handling techniques. Finally, it would be necessary to develop a mathematical model of the system, to aid future workers in scale-up.

Chapter 2

Literature Survey

2 Literature Survey

A review of current literature was undertaken, to ascertain the present use of charcoal in the water pollution control industry and to a lesser extent, in other industries.

Abram (1) has reported that activated charcoal was first used in the production of potable water as early as 1862, now both the granular and powdered forms are used extensively in water pollution control.

2.1 Properties of Activated Charcoal and Charcoal Cloth

2.1.1 Manufacture and Physical Properties

Activated charcoal has been manufactured from many cellulosic materials (2), however the most popular present day starting materials are lignite, animal bones, coconut shells and wood. Bone char has been used in the purification of sugar, while coconut shells provide a charcoal for gas cleaning. Abram (1), has stated that the term, 'activated charcoal', cannot describe a single chemical entity and must only be used in a descriptive form. This is easily understood from the above if one considers that coconut shells produce a charcoal for gas adsorption while bone char produces one for decolorisation.

The manufacturing process of activated charcoal (1,2,3,4) can take one of two forms, carbonisation of the base material, followed by oxidation or chemical dehydration of the carbonised intermediate. In the first instance, the base material is carbonised, in the absence of air, at about 200 to 600^{o}C. The resultant char is then oxidised at between 800 and 950^{o}C using steam or carbon dioxide. Alternatively, the carbanoceous base material is chemically dehydrated and charred at 200 to 650^{o}C, using dehydrating agents such as zinc chloride, sulphuric acid and phosphoric acid. Both of these methods yield highly porous charcoal and are currently used extensively in industry. A current list of activated charcoals is presented by Hassler (3).

For charcoal cloth, Bailey and Maggs (5) have used a combination of both the oxidation and chemical dehydration methods, to produce a highly adsorptive charcoal from loomstate viscose rayon. The rayon cloth is first soaked with a mixture of Lewis acids and then allowed to dry. The dry cloth is then subjected to mechanical flexing, usually over the edge of a smooth surface, to restore any flexibility lost by contact with the Lewis Acids. Hence, after passing through a carbonising furnace at about 250^{o}C, in an inert atmosphere, the cloth is already reasonably active, due to the chemical dehydration caused by the Lewis Acids. Finally, oxidation, in an activation furnace at 900^{o}C, using steam or carbon dioxide, provides activated charcoal cloth. The porous structure of activated charcoal and activated charcoal cloth is referred to later.

Physically, the active charcoals have a crystal structure similar to that of graphite, composed of crystal planes (2).

The granules of granular charcoal vary in size from several millimetres to several centimetres, but they must always be durable, since this determines the amount of attrition losses during regeneration (1). Powdered charcoal is formed by the careful pulverisation of granular charcoal, since too much force ruins the filterability of the charcoal. The properties of charcoal cloth have been documented by Maggs (6) and its physical properties are as follows:

BREAKING STRENGTH	2500-3500 g cm^{-1}
SURFACE DENSITY	10-14 mg cm^{-2}
BULK DENSITY	0.25 - 0.3 g cm^{-3}
ELECTRICAL CONDUCTIVITY	10-25 ohm $(square)^{-1}$
FLEXURAL RIGIDITY	100-400 mg cm^{-1}
AIR FLOW RESISTANCE	12-18 x 10^{-3}cm water gauge per cms^{-1} air velocity per layer of cloth.

TABLE 2.1: PHYSICAL PROPERTIES OF ACTIVATED CHARCOAL CLOTH

The chemical properties of activated charcoal, in both air and water pollution control are referred to later.

2.1.2 Structure and Surface Chemistry

The adsorption processes occurring with active charcoal are vitally dependent on its porous structure and the nature of its surface, since these can have marked effects on the extent and types of adsorption taking place.

Wolff (7,8) first indicated that activated charcoal has a microcrystallite structure of stacked graphitic planes, each of about 50Å diameter and up to 100Å apart, also that the porous structure of the charcoal is made up of fissures, interstices and channels between the graphitic planes. Two classifications have been postulated for the porous structure of an active charcoal (9,10,11). Firstly, Weber (9) Figure 2.1, reported that there are two types of pore; macropores and micropores, (running along and down the graphitic planes), the former being between 30 and 100000 Å, while the latter are anything smaller. Dubinin (10,11) Figure 2.2, also proposed a model based on gaseous adsorption, for the porous structure of activated charcoal. He suggested three pore sizes, macropores of diameter larger than 1000Å, interpores of between 20 and 1000Å and micropores of up to 20Å. The macro and interpores being formed by the burnout of larger, more reactive substances on the carbon surface, while the micropores are formed by the burnout, during activation, of part of the actual graphitic planes. The macropores are involved very little in the adsorption process, along with the interpores they serve to transport the adsorbate molecules to the micropores where most of the adsorption takes place, since up to 90% of the internal surface area is contained there. In the case of liquid, Abram (1) has indicated that larger molecules could block the

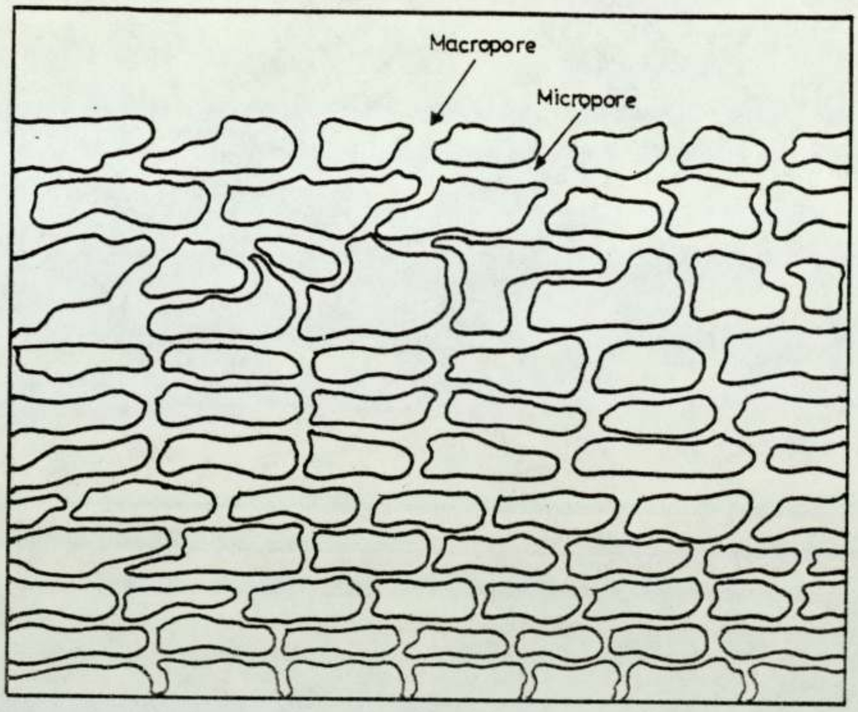


Figure 2.1 Two Pore Model for Charcoal Internal Structure (9)

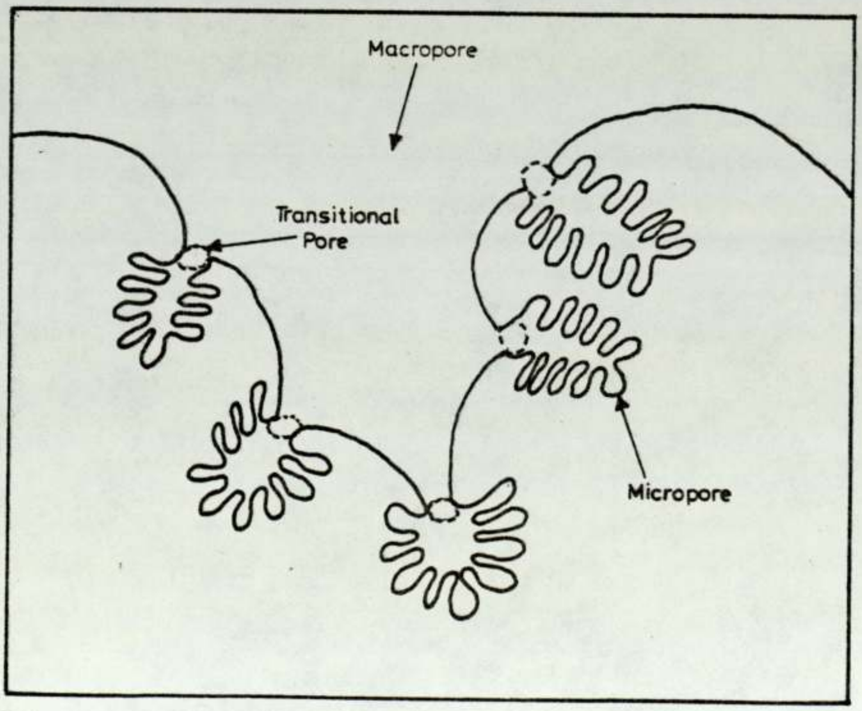


Figure 2.2 Three Pore Model (10,11)

micropores during adsorption, a fact acknowledged by Dubinin (12) who also reports that since some of the pores are of molecular dimensions, it is only possible for one molecule to occupy one micropore, in some cases. Bailey et al (13) have shown, from electron microscope studies and nitrogen, Brunauer, Emmett, Teller (B.E.T.) adsorption isotherms, that activated charcoal cloth consists of a completely microporous structure, with most pores less than 10Å and none greater than 20Å. It has, in fact, been favourably compared with a molecular sieve, making it conceivable that in the case of large molecules, all of the adsorption could occur on the surface.

The description of the surface chemistry of active charcoal will be confined to its affect on phenol adsorption, since this is very well documented and also, phenol studies constituted a major part of this research programme. Adsorption may occur in one of two ways, either physically or chemically. Physical adsorption (14) occurs mainly by Van der Waals forces attracting the non polar adsorbate and adsorbent. In the case of phenol, hydrogen bonding of the hydroxyl group can also occur (15), although this is not the major form of phenol adsorption (16). The main form of adsorption of phenol has been shown to be by the formation of donor/acceptor complexes (16,17,18). This happens in two ways, at lower concentrations, by the formation of these complexes with acidic surface oxides such as carboxyl, carbonyl, quinone, lactone groups, formed during activation, particularly with carbonyl groups and at higher concentrations by the formation of complexes with the actual graphitic structure. This is accomplished by the weak pi-bond electrons of the aromatic ring acting as acceptors for the pi-bond electrons of the donating surface oxide or charcoal. This type of adsorption occurs planar to the phenol molecule, as opposed to the 'end-on' approach of the hydrogen bonding mechanism and is hence stronger. Fairhurst et al (19) have indicated a similar method for the adsorption of ionised surfactants in water.

2.1.3 Factors Influencing Adsorption

The adsorption of impurities from water using activated charcoal is influenced by several factors, which may have an advantageous or detrimental effect on the adsorption process. Hassler (2) has listed some of these factors, including nature of the adsorbent, nature of the adsorbate, pH and temperature. The effect that the nature of the adsorbent has on the adsorption process was discussed, in the preceding section. The nature of the adsorbate can also influence adsorption; this includes its solubility, concentration, molecular size and the number of adsorbates present. Gauntlett and Packham (20) have shown that as the solubility of a component increases, then so, obviously, does its affinity for the solvent. However, a decrease in solubility initiates a driving force from the solvent to the charcoal and hence, adsorption increases. The concentration of adsorbate also has a marked effect on the adsorption process. This is described by the adsorption isotherm which is discussed in the next section. One of the most overriding factors in adsorption is that of molecular size and shape (4,20), as in general, when the size of a molecule increases then so does its adsorptive capacity. However, Bell (4), and Gauntlett and Packham (20) have indicated that the process is a little more complicated than this. Up to a certain molecular size the above holds, but above this size the sheer magnitude of the molecule prevents entry to the charcoal pores and adsorption decreases. The molecular shape has a direct bearing on both the capacity and the rate of adsorption, as shown by Weber and Morris (21), who conducted several experiments on phenol and alkylbenzenesulphonate, finding that as the branching and the size of the branches increased, the rate of adsorption decreased. Bell (4) has indicated that linear molecules show much better adsorptive properties. Under ideal conditions and for a single adsorbate in a pure solvent, it is possible to calculate the adsorption capacity of a given adsorbent. However, if the number of adsorbates is increased or the solvent character is changed, then so is the capacity (2,4,14,20). Gauntlett and Packham (20) have shown large reductions in the adsorption capacity of 2-chlorophenol, when compounds such as fumic and humic acids are introduced to the solution. Bell (4) has indicated that capacity for adsorption from wastewaters is greatly reduced from that using pure water only, a view echoed by Gauntlett and Packham (20), who found reductions in capacity of up to 30% for phenol and 2-chlorophenol adsorbed from Thames river water compared with distilled water.

The pH of a solution to be treated, alters the adsorption properties of the system by changing the charge on the surface of the charcoal, which is predominantly negative (4). Gauntlett and Packham (20) have shown that an increase in the pH of a solution containing phenol or chlorophenols, can result in up to a 50% decrease in adsorption.

It has been known for a considerable time that temperature has an effect on the adsorption rate of adsorbates, since this is controlled by mass transport rates which are temperature sensitive (22). Weber and Morris (21) have illustrated this by showing increased adsorption rates as the temperature of a solution is increased.

2.1.4 Adsorption Equilibria

When an equilibrium adsorption condition occurs, there is a defined distribution between the solid and liquid phases, usually expressed by plotting the amount of solute adsorbed per unit weight of adsorbent against the concentration of solute in the solution, in equilibrium with the adsorbent (14). The resulting graph is familiarly known as the "adsorption isotherm", since all of the measurements are made at constant temperature.

Weber (14,23) has listed three of the main types of adsorption isotherm as the Langmuir (24) Figure 2.3, Brunauer, Emmett and Teller (25) Figure 2.4, and the Freundlich (26) Figure 2.5 isotherms. Neretnieks (27) has added to these, the Temkin isotherm.

The Langmuir isotherm describes a situation where single layer adsorption occurs and makes the assumptions:

a) Maximum adsorption occurs when there is a saturated monolayer of adsorbate molecules on the adsorbent surface.

b) The heat of adsorption is constant.

c) There is no migration of adsorbate molecules in the plane of the monolayer.

The equation for Langmuir adsorption takes the form,

$$\frac{X}{M} = \frac{Q^{o}\ b\ C}{(1 + b\ C)} \qquad 2.1$$

where X = amount of solute adsorbed

M = amount of adsorbent used.

b = constant (related to the heat of adsorption)

C = concentration of solute in the solution in equilibrium.

Figures 2.3,2.4,2.5 from Weber (14)   Co - Initial Concentration

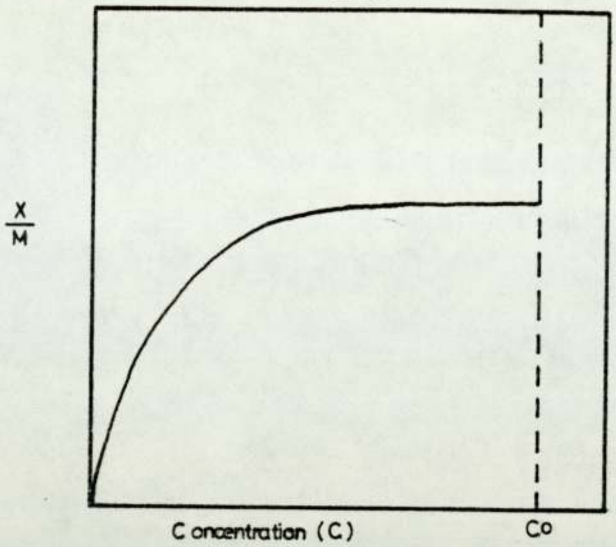


Figure 2.3 Langmuir Adsorption Isotherm

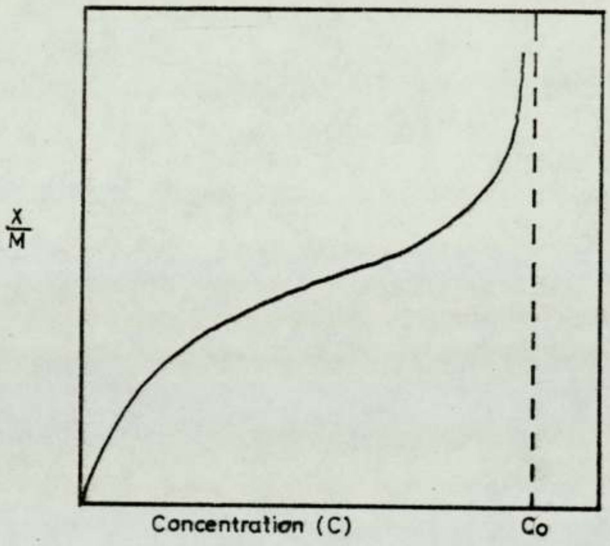


Figure 2.4 B.E.T. Adsorption Isotherm

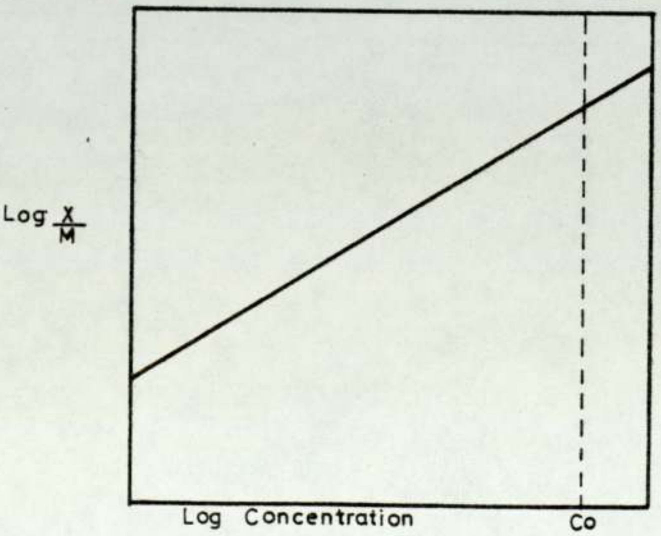


Figure 2.5 Freundlich Adsorption Isotherm

Q^o = number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer.

This reduces, at the extremes of adsorption, to two linear equations

Low Adsorption: $bC << 1 \quad , \quad \frac{X}{M} = Q^o bC$ 2.2

High Adsorption: $bC >> 1 \quad , \quad \frac{X}{M} \simeq Q^o$ 2.3

Weber (14) reports that, although the assumption of Langmuir are rarely met by liquid systems, some good results have been obtained in the past enabling the characterisation of various adsorbents. Jain and Snoeyink (28) have successfully used a modified version of the Langmuir equation to model bisolute systems. Maggs and Smith (29) have found that charcoal cloth exhibits Langmuir adsorption properties.

The Brunauer, Emmett and Teller (B.E.T.) isotherm describes a situation where adsorption occurs in multilayers, each layer described by a Langmuir equation. Also, that a given layer need not have completely formed prior to the start of another. The B.E.T. equation is as follows:

$$\frac{X}{M} = \frac{BCQ^o}{(Cs-C) \quad 1 + (B+1)(^C/Cs)} \qquad 2.4$$

where B = constant

Cs = saturation concentration of solute in solution.

This type of isotherm, is not as widely used in the liquid adsorption field, as the Langmuir and Freundlich equations.

The Freundlich isotherm has its origins in empiricism, although the relationship was later proved correct by kinetic theory. It is one of the more widely used isotherms in the water pollution control industry (2), due to the ease of its application and of correlating results. The equation takes the form:

$$\frac{X}{M} = K_F\, C^{1/n} \qquad 2.5$$

where n = constant

K_F = constant.

This may be fitted to a straight line logarithmic plot of,

$$\log_e\left(\frac{X}{M}\right) = \log_e K_F + \frac{1}{n}\log_e C \qquad 2.6$$

from this, the intercept gives the approximate value of the adsorption capacity, while the slope indicates the adsorption intensity.

The Langmuir and Freundlich isotherms agree very well over moderate concentrations, however at the extremes of concentration this agreement is not as marked. Bernardin and Froelich (3) have achieved a reasonable level of agreement with the Freundlich isotherm, at very low pesticide concentrations, while Weber and Morris (31) have found success with the Langmuir isotherm.

Neretnieks (27) has found that the Temkin isotherm may be applied in a modified form over the complete spectrum of concentrations with successful results. The normal Temkin isotherm is as follows,

$$X = 1 - \frac{1}{K} \ln Y \qquad 2.7$$

where $X = S/Sm$

$Y = C/Cm$

S = actual concentration of adsorbate in the particles of adsorbent

Sm = concentration in the particles in equilibrium with Cm

C = concentration of adsorbate in solution

Cm = maximum concentration of adsorbate in solution

K = constant.

2.1.5 Kinetics of Adsorption

The kinetics of adsorption involves the prediction of the rate-limiting step, that is the step which most prevents the passage of an adsorbate molecule to the active sites of the adsorbent. The rate-limiting step is hence, the most significant step, since it describes the step which controls the speed at which the reaction proceeds, so that the reaction may then be described in terms of rate equations.

The adsorption process takes place in a number of stages and each one could represent the limiting stage. Weber (14) and Keinath and Weber (32) represent this as a three-stage system. Firstly, transport of the adsorbate through the surface film to the boundary of the particle or film diffusion. This is followed by diffusion of the adsorbate within the pores of the adsorbent particle, or pore transport and finally, adsorption on the interior surfaces of the pore walls. Any one of these stages could be rate-limiting. However Weber (14) suggests that the surface reaction stage is too rapid and hence that the limiting stage is either film diffusion or pore transport controlled, or possibly a mixture of both. Bell and Molof (33) expand on the ideas of Weber and suggèst a five-part adsorption process:

a) Diffusion through the external particle film layer.

b) Adsorption on the external surface and simultaneous filling of macropore volume.

c) Exhaustion of the external capacity, continued filling of the macropores and transport to the inter-pores.

d) Filling of the inter-pores with transport to the micropores.

e) Filling of the micropore volume with final adsorption.

This representation is similar to that of Weber and as before, any of the above processes could be rate-limiting.

The rate-limiting step has a direct bearing on the mathematical solution chosen for the system and hence, inherently the eventual characteristics of the system. Using the Weber situation of film diffusion, pore transport and adsorption, it is now possible to examine the effect of each one of these being the rate controlling mechanism.

Film diffusion is the diffusion of an adsorbate molecule through a stagnant layer of solvent surrounding the charcoal particle, to the surface of this particle. It is not usually rate limiting by itself, more often it is combined with pore transport to control the reaction rate. However, it may, according to Weber (14) and Brauch and Schlünder (34) be rate limiting in such a case as a continuous down-flow column, but as turbulence increases and the stagnant external film breaks down, then pore transport dominates. Weber and Morris (21) have suggested as, an approximation, that when film diffusion is controlling then,

$$\text{rate} \propto \frac{1}{\text{mean diam. of particle}}$$

Weber (14) has represented the situation for film diffusion using the classical type of driving force equation:

$$\frac{dy}{d\tau} = k_f \, \alpha \quad \left(\frac{\bar{\varepsilon}}{\rho e}\right) \; (C-Ce) \qquad 2.8$$

Using a concentration driving force and an area for mass transfer, with a constant coefficient of mass transfer. The situation may be expressed in terms of an overall transfer coefficient for film diffusion, K_f which in terms of a complete concentration profile, may be expressed as:

$$K_f = \frac{2k_f \alpha}{r^o+1} \qquad 2.9$$

This overall coefficient may be calculated from finite bath experiments (35).

The movement of the adsorbate within the pores of the charcoal particle is more often the rate limiting step, especially in situations where film diffusion may be expected to be negligible. Weber (14) has suggested that this is the case in turbulent flow through adsorption columns, or in continuously stirred batch reactors. Bruin and Luyben (36) have indicated that pore transport may take one of four forms;

1. Homogeneous diffusion in the pores of the solid

2. Diffusion through liquid-filled pores with adsorption at the pore walls that is, pore diffusion

3. Surface diffusion where the adsorbate molecules migrate along the walls of the pores.

4. A combination of both pore and surface diffusion.

They found that the homogeneous situation was usually too crude to describe experimental results, that pore diffusion predicted results which were too low and that surface diffusion was concentration dependent. However, a model using both pore and surface diffusion gave results which matched experimentally predicted values reasonably well. Neretnieks (27,37) tested a number of chemicals, including phenol and concluded that the pore diffusion contribution was small compared to that of surface diffusion in pore transport. This was illustrated when trying to predict experimental results, obtained from the phenol system, by using the pore diffusion model only. The resulting predictions were some fifteen times less than the experimental results. Indicating the presence of another form of resistance, which Neretnieks found to be surface diffusion. Weber (14) also suggests a mathematical formula based on the surface diffusion mechanism, since this is the more rapid of the pore diffusion mechanisms,

$$\left(\frac{dy}{d\tau}\right) = k_S\,\alpha\zeta \quad (y^{*}-y) \qquad 2.10$$

where there is now a driving force and mass transfer coefficient, both on the surface (adsorbent) side. The equation may also be expressed, for a complete concentration profile, in terms of the overall surface diffusion rate coefficient,

$$K_S = \frac{2k_S\alpha\zeta\, D_G}{(r^{o}+1)} \qquad 2.11$$

There are also increasing numbers of cases where it is thought that both film and pore transport control the adsorption process. In a study of the kinetics involved in adsorption systems, Westermark (38) found that in many cases, the effect of film diffusion could add up to 20% to the bed length. Weber and Digiano (39,40), using both finite and infinite bath systems found it advantageous to include the film diffusion and pore transport coefficients, usually as a ratio, in the mathematical model of the situation. Hence, as the ratio changes, a greater or lesser part is played by film diffusion or pore transport.

Finally, the rate controlling step could be at the surface of the adsorbent, that is, direct adsorption. Weber (14) and Weber and Morris (21) indicate that under normal circumstances, this reaction is so rapid that it could not constitute a rate limiting step. However, from work by Thomas (41), an equation relating to this has been postulated by Hiester and Vermuelen (42) using the following reaction scheme for second order kinetics,

$$\text{Sorbate} + \text{sorbent} \longrightarrow \text{sorbate . sorbent}$$

we have,

$$\frac{d(\text{sorbate.sorbent})}{d\tau} = k \left[(\text{sorbate})(\text{sorbent}) - (\tfrac{1}{b})(\text{sorbate.sorbent}) \right] \qquad 2.12$$

for a Langmuir type adsorption isotherm. It is hence, conceivable that if such a step were rate limiting that a mathematical model could be evolved from the Thomas equation.

This section has served to indicate the differing forms of mechanism which can constitute an adsorption step and the effect that each step may have on controlling the rate of this adsorption process.

2.2 General Applications of Activated Charcoal and Charcoal Cloth

Apart from being used widely as a catalyst support material, most of the applications of activated charcoal are in the separations field. It is used in such areas as air purification, water purification, solvent recovery, fractionation and in analytical separations. Due to its nature, it is more useful for removing trace quantities of compounds from process streams, whence they may be destroyed, as in purification, or recovered and reused in solvent recovery. Barneby (43) has indicated the growing use of charcoal in the petrochemical industry in every area from synthesis gas and liquefied petroleum gas purification to phosgene manufacture. Abram (1) has also shown that activated charcoal is being widely used, in industries as unrelated as sugar refining and electroplating for decolourising and electrode material respectively. He has also listed the wide range of granular charcoals now available.

The intention of this section is to deal with uses of activated charcoal other than in water pollution control, which is dealt with in section 2.4.3 and to show that as a specialist separating agent, it is increasingly used in a growing chemical industry.

2.2.1 Granular and Powdered Activated Charcoal

The primary uses of granular activated charcoal are in the removal and recovery of trace impurities from air and the recovery of valuable organics from solvent laden streams.

An important potential use of activated charcoal, in the air pollution control industry, is in the removal of sulphur dioxide from flue gases, since it has now been realised that its dispersal from tall chimney stacks over wide areas is not very efficient. Most current processes operate on what is known on the dry system, that is, the charcoal is in a dry state, producing either sulphuric acid or elemental sulphur as an end product. Braun et al. (44,45) report that charcoal catalyses the reaction:

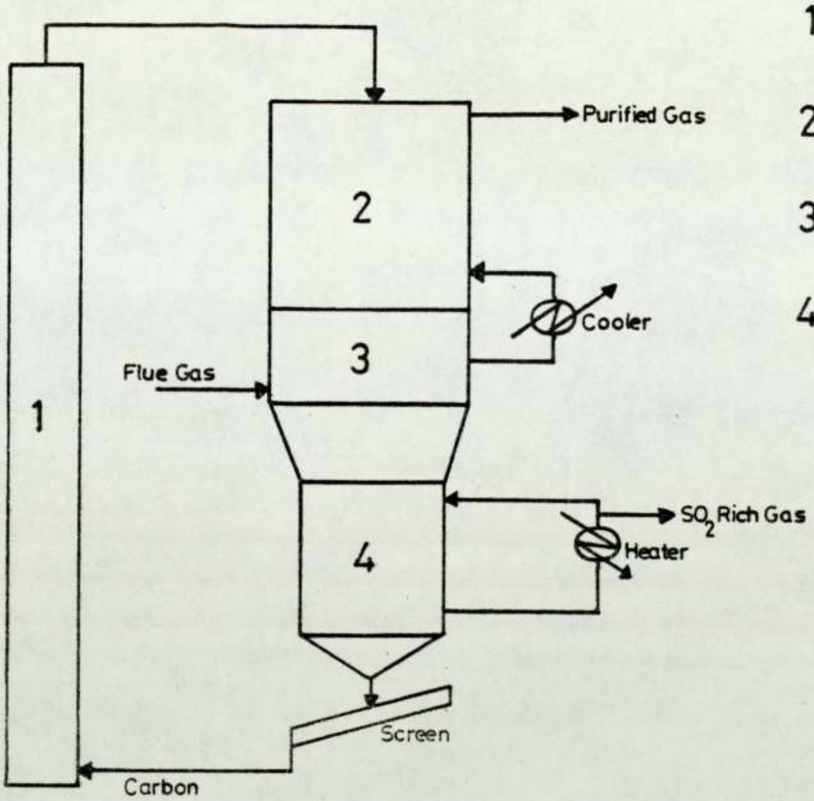
$$SO_2 + \underset{\text{(air)}}{{}^1/_2\,O_2} \longrightarrow SO_3$$

$$\underset{\text{(vapour)}}{H_2O} + SO_3 \longrightarrow \underset{\text{(sorbed)}}{H_2SO_4}$$

(Over carbon at about 100^{o}C)

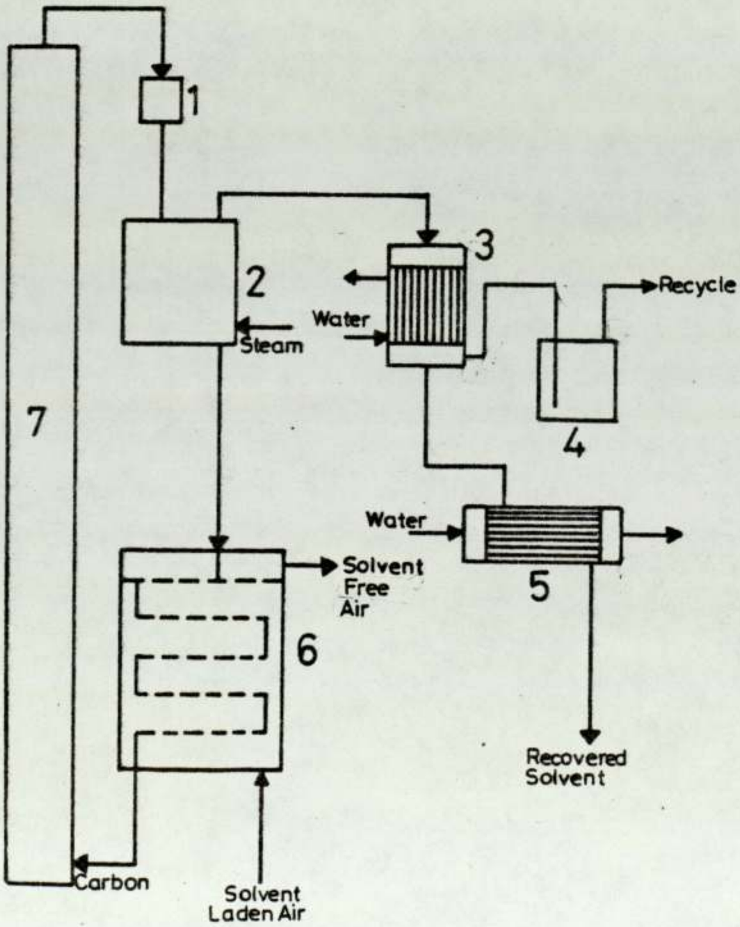
The sulphuric acid is adsorbed in the pores of the charcoal, which is then passed to a regenerator, where the temperature (300^{o}C) causes the acid to dissociate, leaving a sulphur dioxide-rich exhaust stream. The sulphur dioxide may then be reduced to elemental sulphur

(44,45,46,47) or reacted with water to form high-purity sulphuric acid as with the Reinluft process (48,49) Figure 2.6, although the latter is an expensive manufacturing process. Cariaso and Walker (50) have reported that hydrogen sulphide may be used to form elemental sulphur over activated charcoal, a fact which is employed in the Westvaco process (44,45) which also uses fluidised carbon beds as the reaction media, giving a high purity sulphur product. The Bergbau-Forschung process (46,47) employs a reaction media of charcoal moving slowly down a column counter-current to the gas stream. The sulphur product is made by reducing the sulphur dioxide-rich exhaust stream from the reactor in a 'RESOX' process. All of the above processes form sulphuric acid in the pores of the charcoal at some stage of the reaction. Polek (51) has shown that the effect of the pore blockage by the reaction product can cause a large drop in activity. Slack (52) has reviewed currently available charcoal adsorption methods for sulphur dioxide removal and found that while these processes are an alternative, they are extremely expensive to operate. The prime area of concern is in the removal of sulphuric acid from the charcoal pores which is always followed by a large net loss of carbon by oxidation. It is significant that in 1974 the American Industrial Gas Cleaning Institute (53) did not offer charcoal treatment as a commercial



1. Carbon Elevator
2. Adsorber Stage 1
3. Adsorber Stage 2
4. Desorber

Figure 2.6 Reinluft Process (48,49)



1. Capacity Vessel
2. Stripper
3. Condenser
4. Water Seal
5. Cooler
6. Adsorber
7. Carbon Elevator

Figure 2.7 Carbon Disulphide Recovery (55) alternative, although it mentioned that development in these processes is continuing. It is therefore obvious, that if charcoal cloth could provide an economical alternative to the above processes, a potential market exists.

Perhaps the most profitable use of charcoal is in the recovery of solvents from effluent gases. With the ever-rising cost of all chemicals, the cost of organic solvents has increased enormously. Hence, any process which can recover such solvents economically is of increasing value to large industrial concerns. Charcoal was used for solvent recovery as early as 1934 (54) in the recovery of benzole from the exhaust gases of a coal gasification plant and Barneby (43) has indicated its rising importance for solvent recovery in the petrochemical industry. Rowson (55) Figure 2.7, has reported an economical plant for the recovery of carbon disulphide, from the outlet of a rayon manufacturing process, using a continuous fluidised bed of activated charcoal; this and other processes were reviewed by Avery and Boiston (56) where is was found that in general, a moving bed is preferable to a fixed bed since more charcoal surface is available for mass transfer. Industrial manufacturers of charcoal offer 'packaged' solvent recovery processes (57) which are popular with smaller companies.

Moving beds of charcoal have also been used successfully in the fractionation of azeotropic mixtures of solvents (58). A commercial fractionation unit, known as a hypersorber, was suggested by Berg (59) Figure 2.8, although this saw little success.

It is clear that a moving bed of charcoal is preferable to a fixed one, especially where continuous reactivation is necessary. However, with granular charcoal, difficulties arise due to transport and attrition losses. It is possible that with the advent of charcoal cloth, some of these problems could be overcome by using the continuous nature of the cloth in some of the above mentioned processes. Maggs (60) has suggested processes along these lines, which are discussed in the following section.

2.2.2 Charcoal Cloth

All applications of charcoal cloth to date have dealt with the purification of air, possibly due to the special interest of the Ministry of Defence. Very few items of commercial interest have emerged, although many speculative suggestions for larger commercial ventures have been mentioned.

The earliest uses of charcoal cloth were in lightweight gas masks and portable air purification units (61), due to its lightweight nature and its massive

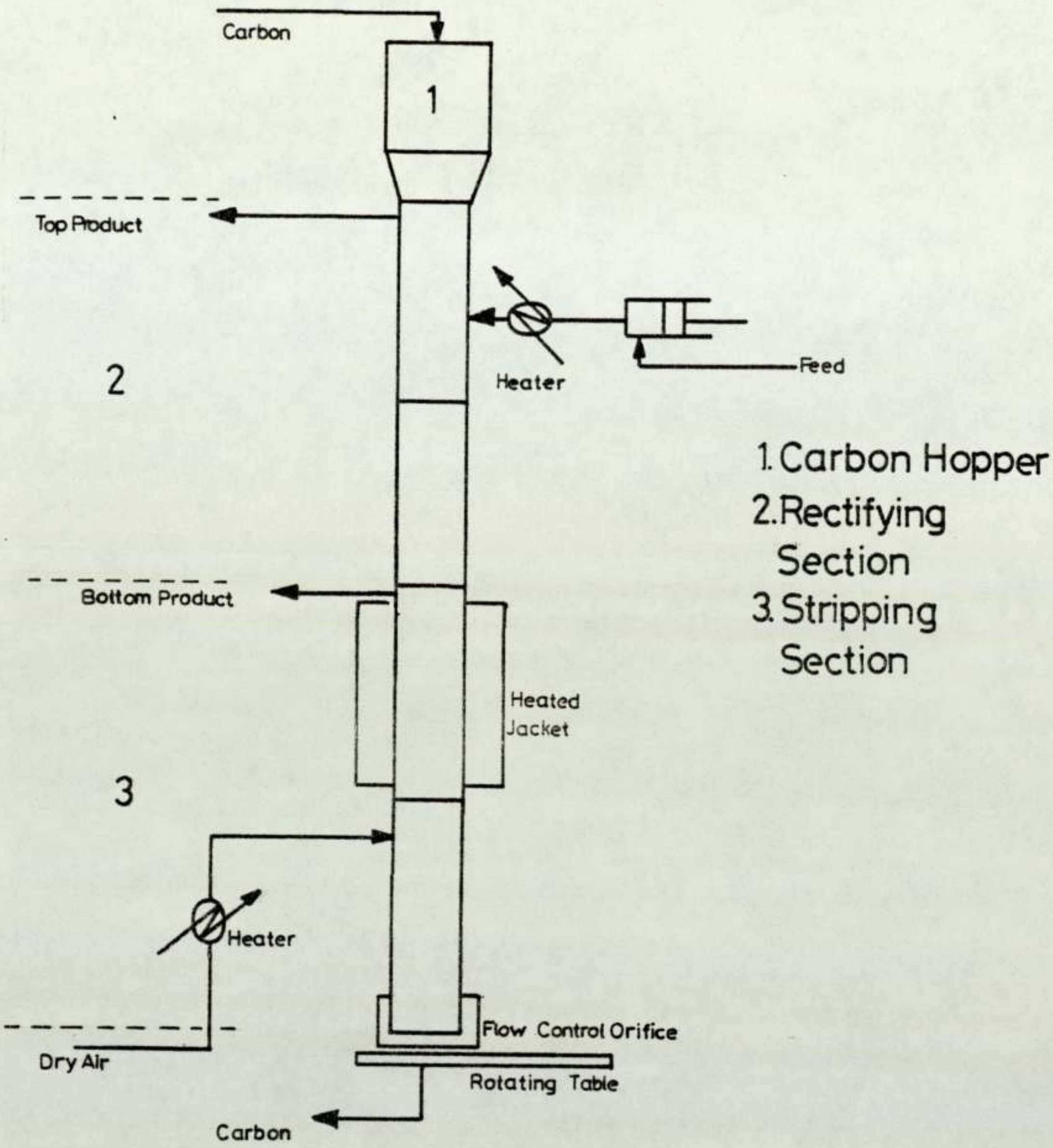


Figure 2.8 Hypersorption Process (59)

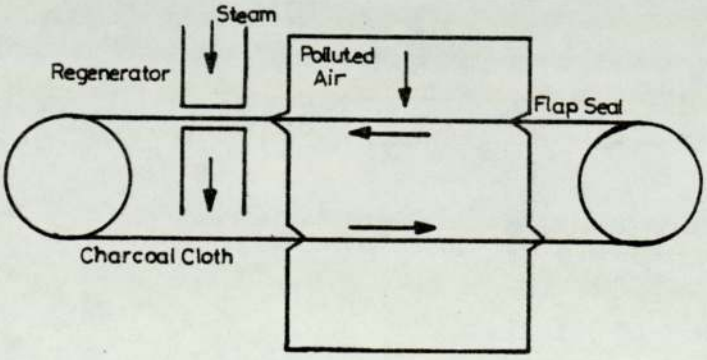


Figure 2.9 Air Pollution Control Device using Activated Charcoal Cloth (60)

adsorptive capacity. It has been suggested that charcoal cloth could be used in various forms (62), for example as a packing for a modern design of air purifier, using a long length of cloth folded and packed into the main filter body, also by cutting out discs of the cloth and using them in a compact face mask (63). Possibly the most commercially viable suggestion, is the use of charcoal cloth for the 'in situ' removal of sulphur dioxide from stack gases. Maggs (60) proposed a device, Figure 2.9, whereby a continuous roll of charcoal cloth passes in and out of an industrial chimney stack, being continuously regenerated on the external cycle. Work by Pooranathen (64) in this area has established that charcoal cloth does, in fact, adsorb sulphur dioxide very well. However, problems would occur with the transport of the cloth across the stack and the sealing of the stack at the points where the cloth exits.

Little work has been carried out in the field of solvent recovery using charcoal cloth, although Bailey and Hollingdale-Smith (65) have developed a device for monitoring the amount of solvent encountered by people working in solvent laden atmospheres. It is possible, therefore, for solvents to be removed from the atmosphere and a device along the lines of Maggs' sulphur dioxide apparatus could be installed at the outlet of a solvent process and modified for solvent recovery.

Within the overall objective of identifying profitable chemical engineering applications of charcoal cloth, the present research programme has been devoted to the study of continuous water pollution control, using activated charcoal cloth.

2.3 Water Pollution

To enable water pollution control with activated charcoal to be fully understood it is first necessary to classify some of the more common pollutants. Dictionaries define water pollution as "that which makes the water physically, impure, foul or dirty", derived from the Latin word 'pollutus' which means to soil or defile. A modern definition of the word (66) would be "the addition to the water of anything which changes its natural quality, such that the user does not receive the natural water of the stream". This definition encompasses the whole range of water pollution, including raising its temperature which can also be a major hazard. The Californian Water authority (67) prefers to define pollution as above but adds "that which does not constitute a health hazard" and contamination as "that which constitutes a major health hazard".

2.3.1 General

As already stated above, anything which enters a waterway could be described as a water pollutant. However, in general water pollution may be classified into various groups (67):

a. Biochemical Oxygen Demand (BOD), that is the measure of biodegradable organic content of the waste.

b. Chemical Oxygen Demand (COD), a measure of the total organic content of an effluent source both degradable and non-degradable.

c. Suspended, Settlable and Volatile Solids.

d. Total Solids.

e. pH, alkalinity and acidity.

f. Nitrogen and phosphorus.

g. Heavy metals and Inorganic salts.

Carbon is used mainly in a tertiary clean up rôle, that is, in advanced treatment of waste waters and the removal of non-biodegradable, or biorefractory compounds after the biological treatment stage. Hence, the main group with which this section deals, is that of COD and in particular, non biodegradable organics. The usual aim of carbon treatment is to remove the toxic substances, that is those which are poisonous to living organisms, from water. The most persistent groups of organic chemicals, phenolics, pesticides, detergents and dyes are dealt with in subsequent sections, there are however still many toxic chemicals remaining. Love et al. (68) and Miller (69) have indicated that chemicals such as isocyanic acid, methylbiphenyl and trichloroethane, have been found in drinking water supplies.

Probably one of the most toxic groups of chemicals, although not contained in the above group, since they were not included in the current research programme, are the polychlorinated biphenyls (70) of which many different types exist. Of the one million tons manufactured since 1945 about half has finally reached the environment. They are mostly a carcinogenic group of compounds, which are relatively insoluble in water and hence lend themselves to easy adsorption. Another particularly toxic group of compounds are the mercaptans, a group of sulphurous organic compounds, which impart a very unpleasant taste and smell to water supplies. Klein (71) has reported odours from water containing methyl mercaptan at 0.0011 mg/l. Ishizaki and Cookson (72) have enjoyed reasonable success in removing them from water using active carbon.

2.3.2 Phenols and Derivatives

The term 'phenols' encompasses a wide range of compounds, from phenol itself (C_6H_5OH) to such compounds as cresols and xylenols. While these groups of compounds are toxic in themselves, the substitution of chlorine into the molecule forms compounds which are in some cases carcinogenic and very persistent, in fact several were found in a New Orleans drinking water supply in 1975 causing widespread concern (73).

Phenols are toxic to fish at levels below 2 mg/l (74) and cause considerable taste and odour to water at 7 mg/l for phenol and around 0.002 mg/l for chlorophenols (66,71).

In general they are not removed by biological treatment and according to Klein (71) can actually inhibit bacterial action. The oxygen demand of phenolic compounds can be as high as 2.4 mg O_2/mg phenol (74) or two hundred times greater than domestic sewage (71), hence phenols have an extremely large COD.

Phenols are used in the manufacture of herbicides (75) and phenolic casting resins (71). They are also formed as byproducts in the coke oven effluent of steel works and coal liquefaction plants (71,74) and as part of the process of forming gasoline in the catalytic cracking of crude oil, where levels of 150/200 kg phenol per 1000 tons throughput of crude are passed into waste water (75). In the United States, the Environmental Protection Agency has published a list of 65 chemicals discharged from 21 chemical industries (77), some of which appear in Table 2.2 below, on which restrictions will be made. Generally the permitted level for phenols in water in the U.S.A. is 0.1 mg/l by 1977 decreasing to 0.02 mg/l by 1983, as the full force of legislation takes effect. Klein (71) has reported that European drinking water standards limited the amount of phenol in drinking water to 0.001 mg/l as early as 1961.

As can be seen from Table 2.2, the number of harmful chemicals containing chlorine is very high. However they are also relatively insoluble in water, hence lending themselves very well to removal by active charcoal.

Gauntlett and Packham (20) have shown that the decrease in solubility of phenols and the increase in substituted chlorine increases their adsorption on charcoal. As stated before, phenols are used in the manufacture of herbicides, such as 2.4 dichlorophenoxy-acetic acid (75). Henshaw (78) has reported a method for treating to acceptable levels, 10 mg/l of phenols and 100 mg/l of chlorophenols from the waste water of such a herbicide manufacturing plant.

Benzene
Chlorinated Benzenes
Chlorinated Ethanes
Chloroalkyl Ethers
Chlorinated Phenols
Dichloro ethylenes
Ethylbenzene
Haloethers
Halomethanes
Hexachlorobutadiene
Hexachlorocyclohexane
Hexachlorocyclo pentadiene
Isophorone
Nitrophenols
Nitrosamines
Phenol
Phenolate Esters
Polychlorinated Biphenyls
Polynuclear Aromatics
Tetrachloroethylene
Toluene
Trichloroethylene
Vinyl compounds

Table 2.2. ENVIRONMENTAL PROTECTION AGENCY RESTRICTED CHEMICALS (77)

2.3.3 Pesticides

These are by far the most catalogued group of pollutant compounds known to man. Ignorance in the early use of pesticides has led to many present day problems in the environment especially with birds of prey and fish. A typical food chain concentration for DDT is shown below:

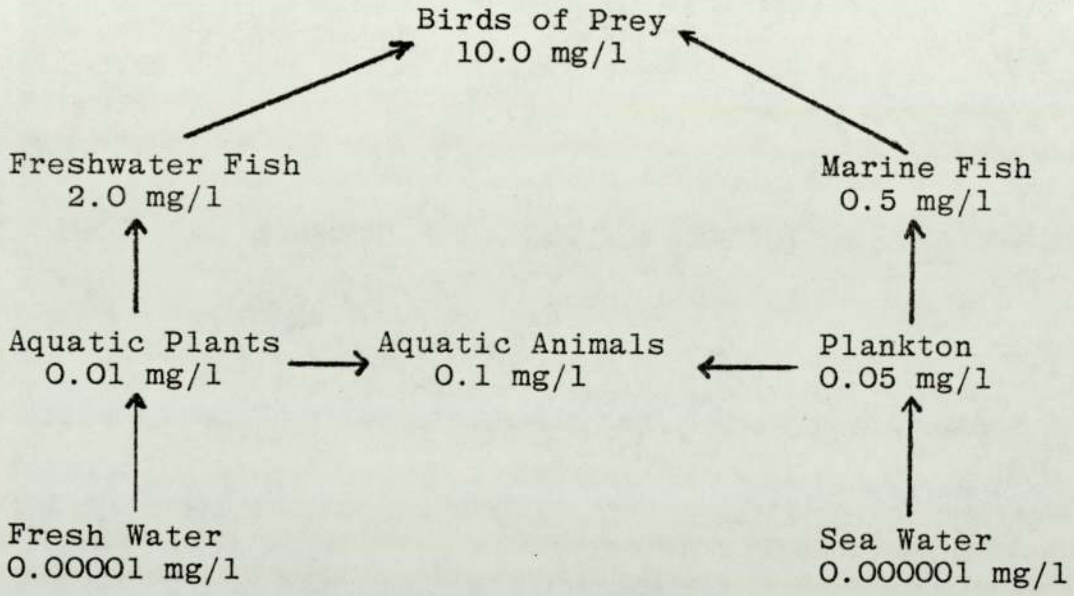


Table 2.3. Typical Food Chain Concentration of DDT

An illustration of the quantity of pesticides in the environment is given in a report by the American Chemical Society (79) where they quote levels of 10 to 20 mg/l of chlorinated hydrocarbon pesticides in most humans today. Many works have been published on the subject, including those by Hodges (80), Mitchell (75), Durham (81) and the American Chemical Society (79). The change in feeling about pesticides has been remarkable in the past ten to fifteen years, it is notable that Mitchell (75) referred, in 1965, to the fact that the worries about pesticides were unfounded, while in 1977 Hodges (80) refers to some pesticides as being among the most toxic chemicals in existence. The U.S. Environmental Pesticide Control Act of 1972 reflects the fears about some pesticides and their effect on human health.

2.3.3.1 Organo - Phosphorus Compounds

This group of compounds including parathion, malathion, TEPP, was found during research into nerve agents in World War II by the Germans, many of them are extremely toxic to man. Hodges (80) lists parathion and its metabolite paraoxon among the most toxic human poisons of which a dose of less than 5 mg/kg is fatal to humans. They act by inhibiting the enzyme cholinesterase and ultimately attacking the central nervous system. However, Mitchell (75) reports that in general they are easily broken down in nature, although still being toxic to fish. Klein (71) reports that as little as 0.2 ppm of parathion is lethal to bluegills. Walker (82) has stated that organophosphorus compounds are relatively soluble in water, but Mitchell (75) adds that some lose their toxicity (TEPP has a half life in water of eight hours). It is of note that some of the compounds break down in water to form even more toxic metabolites, for example parathion reacts to form paraoxan (83). They are however, a very useful group of insecticides, effective against a broad spectrum of insects and in general are broken down naturally. Eichelberger and Lichtenberg (84) have had reasonable success in removing bidrin from water using activated charcoal. They report however, a lower success rate with parathion and with malathion they experienced little success at all.

2.3.3.2 Chlorinated Hydrocarbons

Although chlorinated hydrocarbons are mainly a group of insecticides, chlorinated phenols and chlorinated phenoxy compounds are also herbicides, which will be dealt with at the end of this section. Chlorinated hydrocarbons are among the most persistent chemicals known to man; DDE has a half life in pigeons of about 250 days, while dieldrin and DDT have half lives in soil of up to five years (82). Fries (85) has indicated that this is due to the non polar nature of the compounds imparted by the substitution of the chlorine atoms. Hodges (80) has listed many of the more toxic chlorinated hydrocarbons, including DDT and its metabolites, dieldrin, endrin, methoxychlor and toxaphene. They act by adsorption through the skin into the fatty tissues and from there they attack the central nervous system. It is this accumulation in the tissues which can lead to food chain concentration, as mentioned earlier. Robeck et al. (85) have indicated that 1-70 μg/l of most chlorinated hydrocarbons can be fatal to fish, a figure agreed with by Klein (71) who reported fatalities of goldfish in less than 100 μg/l of DDT. The food chain concentration in fish eating birds has been demonstrated, alarmingly, by Benson et al. (87) in a study of dead pelicans, they found one with seven different chlorinated hydrocarbons in its system, with 1498 ppm of DDT in its liver alone. While these chemicals are highly useful in dealing with a large range of insects, especially mosquitoes, in the case of DDT, the overall effect on the environment was considered too harmful and hence in 1972 the U.S. Environmental Protection Agency introduced its Environmental Pesticide Control Act. This act saw the banning, in all but the most essential cases and then with consent, of DDT in 1972, aldrin and dieldrin in 1974, with heptachlor and chlordane following in 1975. Levels of methoxychlor have been limited to 0.01 mg/l and toxaphene to 0.005 mg/l. It must however, be noted that as mentioned above, the persistence of these chemicals in the environment will make them a hazard for many years to come.

The other group of chlorinated hydrocarbons, the herbicides and fungicides such as 2,4 dichlorophenoxyacetic acid (2,4D), do not constitute a major pollution hazard (88), since they are broken down easily and excreted by animals, but taste and odour thresholds for 2,4D, the most widely used herbicide, are still 2 and 8 μg/l respectively.

The successful removal of these groups of compounds using activated charcoal has been reported by Weber and Gould (83), Robeck et al. (86), Eichelberger and Lichtenberg (84) and Mulligan and Fox (77); these will be referred to again later.

2.3.3 Carbamates

This is a relatively new group of compounds used both as herbicides and more recently, as insecticides. Hodges (80) reports the most popular one as Sevin (carbaryl) and indicates that they have a very low toxicity to mammals. They are relatively easily broken down by ultra-violet light and high pH conditions (75,89). Again they are cholinesterase inhibitors, attacking the central nervous system. El-Dib et al. (90) have reported the successful removal of Sevin and Baygon from water using activated charcoal, as process which is necessary, since although carbonates are easily broken down they can remain stable in acid conditions and large quantities have been known to be carcinogenic.

2.3.4 Dyes and Detergents

According to Klein (71) and Hodges (80), detergents occur in three main groups:

i) Anionic:

This group contains about 90% of the total production of all detergents, examples are,

Linear Alkyl Sulphate (LAS), $ROSO_3^-$ .... Na^+
sodium alkyl sulphate
e.g. "Teepol"

Alkyl Benzene Sulphonates (ABS), $RC_6H_4SO_3^-$ .... Na^+
sodium alkyl benzene
sulphate
e.g. "Tide"

The former group are easily biodegradable, however, the Alkyl Benzene Sulphonates are almost completely non-biodegradable and up to 50% of the input to a conventional waterworks appears in the effluent. As little as 1 ppm can cause unsightly foaming and Degens (91) has reported that due to rapid oxygen removal in foaming, 5 ppm can cause fish fatalities. Most detergent manufacturers now use linear alkyl sulphates (LAS) since these are more readily biodegradable. In fact, in Europe, legislation was introduced to enforce this, since massive foaming problems were occurring in the industrialised rivers. Berry and Horton (92) have quoted figures of up to 9 mg/l of detergent in Illinois river up to the introduction of LAS in 1965 and figures of 0.2 mg/l afterwards. According to Hodges (79) the problem now appears to be with the 'builder' part of the detergent, which imparts the detergent properties to the compound. Most of these builders are phosphates and when the main surfactant is biodegraded, the phosphate molecule causes massive cutrophication that is, algal and weed growth. This problem had been solved by using caustic salts instead of phosphates, however, this can burn and irritate if swallowed by young children. These compounds have been removed from water using activated charcoal by Weber and Morris (23) and Gauntlett and Packham (20).

ii) <u>Non-ionic</u>

These are typically polyglycol ethers of alkylated phenol, for example:

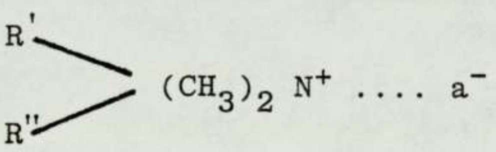
$$RC_6H_4\ (C_2H_4O)_nOH$$

e.g. 'Stergene'

They are usually broken down quite easily, but persistent types are easily moved by activated charcoal (93).

iii) <u>Cationic</u>

These are usually quaternary ammonium or pyridium salts, for example:



$$\begin{matrix} R' \\ R'' \end{matrix} \Big> (CH_3)_2\ N^+ \ldots\ a^-$$

due to their strong bactericidal properties, they are commonly used in hotels and hospitals for cleaning utensils. Fairhurst et al. (19) have used DTAB ammonium salt to characterise the extent of formation of surface oxides on charcoal.

Dyes, while not being necessarily toxic are classical pollutants due to their persistent colour. Klein (71) has reported that low concentrations can cause massive colour pollution usually from compounds such as azo group which are relatively insoluble in water. Salts of some inorganic chemicals such as chromium, can also cause persistent colours.

2.4 Water Pollution Control

2.4.1 Types of Charcoal Adsorption System

There are two types of charcoal adsorption system in current use, the continuous system and the fixed system (2,77,94,95).

The continuous system, Figure 2.10, consists of a vessel into the top of which charcoal granules are continuously placed. These are then periodically removed from the base of the vessel, usually as a slurry and then passed on for regeneration and returned to the beginning. The liquid enters the vessel through a ring header at the bottom of the vessel, passes upwards, countercurrent to the charcoal flow, and leaves through another ring header at the top of the vessel, protected by a wire mesh to prevent charcoal from fouling it. This system has the advantage that capital investment is lower than for the fixed bed type, but it needs a pretreatment system, since it will not handle suspended solids at concentrations greater than 60 mg/l. A disadvantage is that the movement of the carbon around the system causes large losses due to attrition and hence charcoal costs can be excessive. The structure of the system is similar to that of the hypersorber (59) mentioned in section 2.2. Lederman (95) has reported the construction for American Cyanamid, of a moving bed treatment system to test 20 million gal/day of effluent.

Figures 2.10, 2.11, 2.12 from Hager (94)

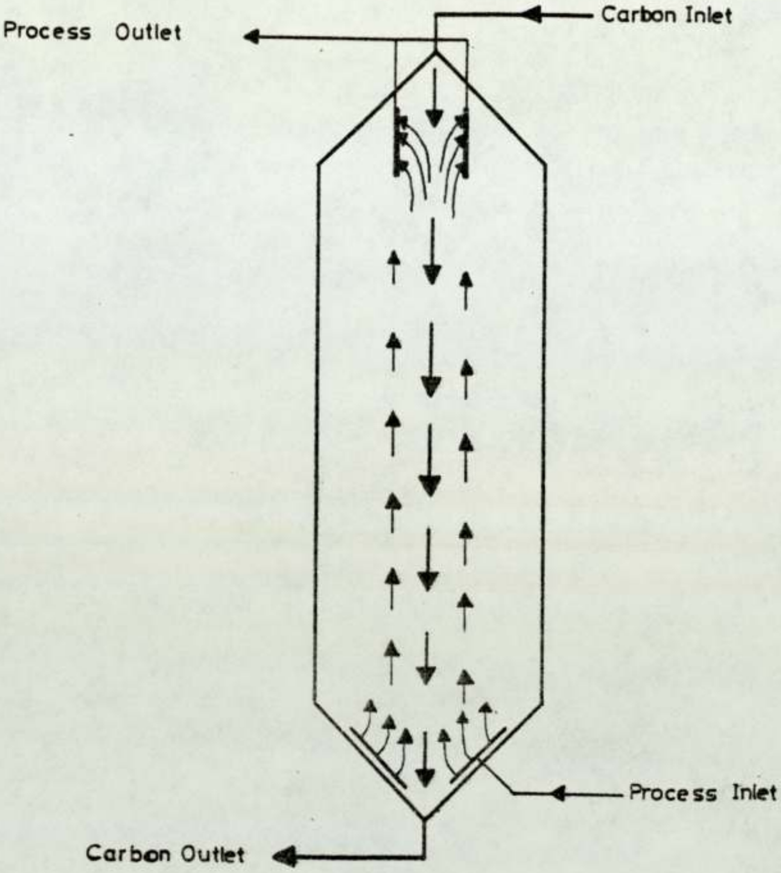


Figure 2.10 Moving Bed System

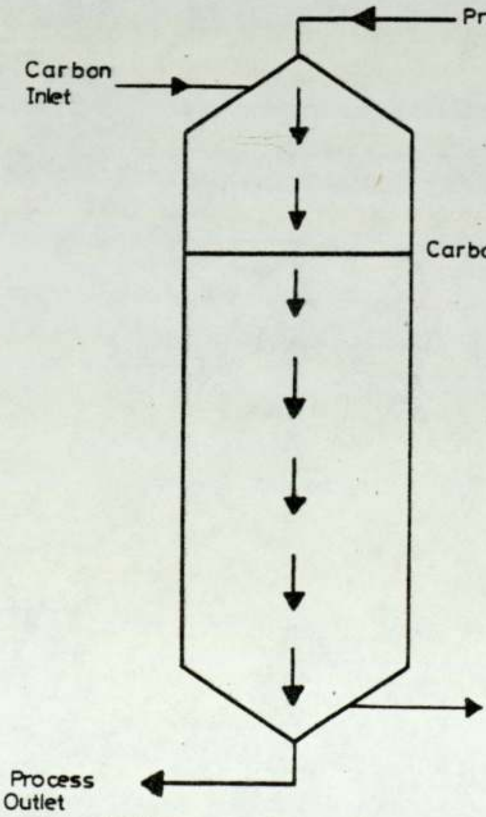


Figure 2.11 Downflow System

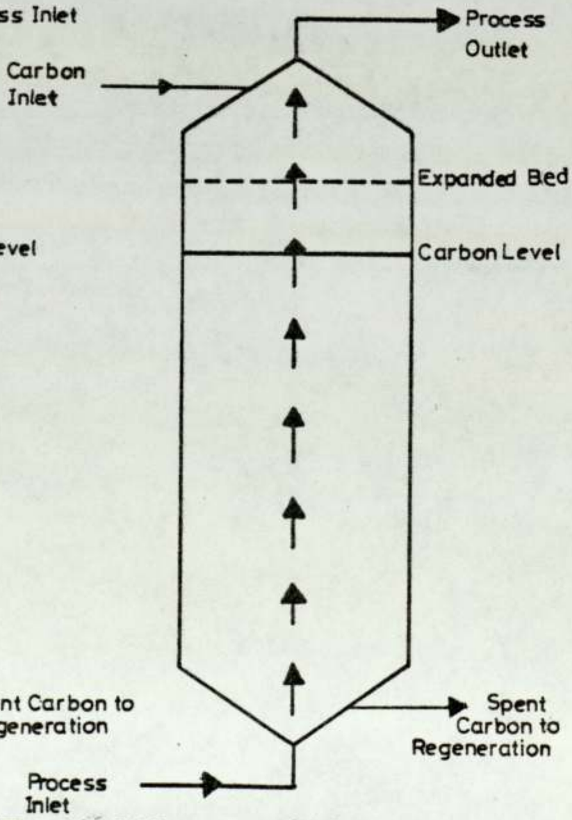


Figure 2.12 Upflow System

The more popular control system is the fixed one, which may operate under gravity or pressure and upflow or downflow conditions. Each type of system consists of a vessel containing an amount of charcoal, calculated from adsorption isotherm and kinetic tests. In the downflow configurations, Figure 2.11, the liquid passes downwards through the bed of charcoal, which remains in the vessel until breakthrough of pollutants occurs in the effluent stream, when it is removed and regenerated. This type of application can also act as a solids filter, removing suspended solids. In this case, the vessel needs an extra 50% capacity to cope with bed expansion during backwashing, which removes the collected solids. The upflow (or expanded bed) configuration, Figure 2.12, consists of the same type of vessel as for the fixed system with 10% excess to allow for bed expansion. The liquid is then fed into the bottom of the vessel, causing the bed to expand, enabling more of the adsorbate to come into contact with more of the adsorbent. Pretreatment is necessary with this system, however, since suspended solids are able to pass through and are not filtered out. Each of the above systems can operate as a single stage, in parallel or as a multistage system, in series. The series operation is often favoured since the beds downstream act as polishing stages, allowing isolation for regeneration when the capacity of the primary bed is exhausted. Weber et al. (97) have compared the operation of upflow and downflow columns under pilot plant conditions for a four month period, finding that for the same quality effluent, the expanded bed needed no maintenance and cleaning, while operating at a constant flow rate and head loss. However, the downflow system required constant cleaning due to fluctuation in flow rates and large build-ups of pressure. They also found that if biological activity was allowed to take place on the charcoal surface, the effluent quality was greatly improved. Bishop et al. (98) have found that the removal of suspended solids prior to a downflow system improves its performance significantly allowing removal of soluble organics to below 1 mg/l. Smaller undertakings with little water pollution problem are finding it advantageous to rent adsorption systems in order to comply with the strict U.S.A. pollution laws. Among the chief operators of this type of system are Calgon (99,100) and Illinois Water Treatment (101) in the U.S.A. and Chemviron and Sutcliffe Speakmann (57) in the U.K.

Powdered carbon is usually introduced into a process by mixing it into the process fluid as a slurry. Adams (102, 103) has indicated that it is possible to mix it with the sludge of a biological treatment unit and hence eliminate the need for a tertary treatment system.

The American Environmental Protection Agency have recently produced some useful guides to the design and use of granular activated charcoal systems, notably, the Process Design Manual for Carbon Adsorption (104).

2.4.2 Regeneration of Activated Charcoal

When the adsorption capacity of charcoal in an adsorber has been exhausted, the charcoal needs to be regenerated. Loven (105) has indicated three main methods of regeneration:

1. Thermal
   a. Multiple Hearth Furnace
   b. Rotary Kiln Furnace
   c. Fluidised Bed Furnace
2. Chemical
   a. Acid-Base Extraction
   b. Wet Oxidation
   c. Chemical Oxidation
   d. Solvent Extraction
3. Biological

Thermal regeneration, which is the most popular form of regeneration involves the reactivation of the charcoal in a similar way to its formation, as described in section 2.1, i.e., carbonisation and activation at high temperature. This type of regeneration involves the destruction of the pollutant but in some cases, pollutants may be driven off without destruction. In which case, Schuliger and MacCrum (106) have indicated that an afterburner is usually necessary to prevent air pollution from the furnace. The most popular furnace used in thermal regeneration is the multiple hearth furnace (105,107) Figure 2.13, due to its ease of design and efficiency of operation. As shown in the diagram, the charcoal is moved down the furnace, to successively higher temperature shelves by rabble arms, countercurrent to the flow of hot regeneration gases. The reactivated charcoal is then collected at the base of the regenerator, from where it may again be used. The newest furnace in the U.K. is a fully automatic one recently installed at Coleshill Sewage Works (108).

Chemical regeneration has been proved possible by Himmelstein, Fox and Winter (109) who have recovered phenol from a phenolic brine solution by using sodium hydroxide, Figure 2.14, When the adsorption capacity of the adsorber is exhausted, a 4% sodium hydroxide solution is passed through the charcoal, forming sodium phenate, which passes on with the regenerant stream. The column is then washed through with hydrochloric acid and water. Phenol may be recovered from the sodium phenate solution by springing it with acid, the sodium hydroxide being used again. Himmelstein et al. (108) report that this method has also been successfully used for 2,4D and chlorophenol, also

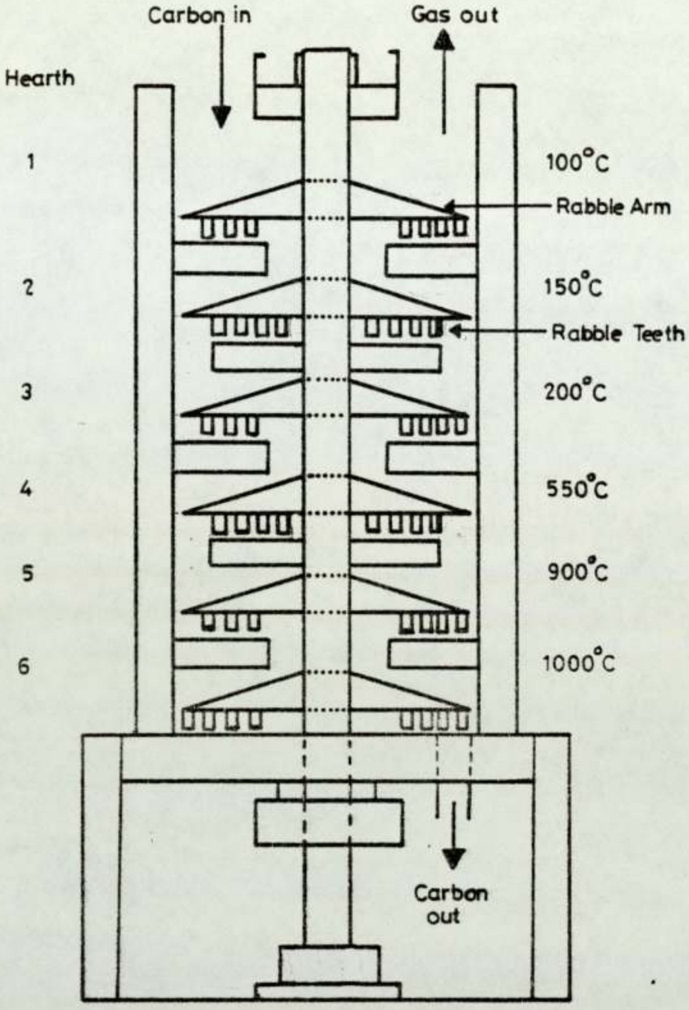


Figure 2.13 Multiple Hearth Furnace (104)

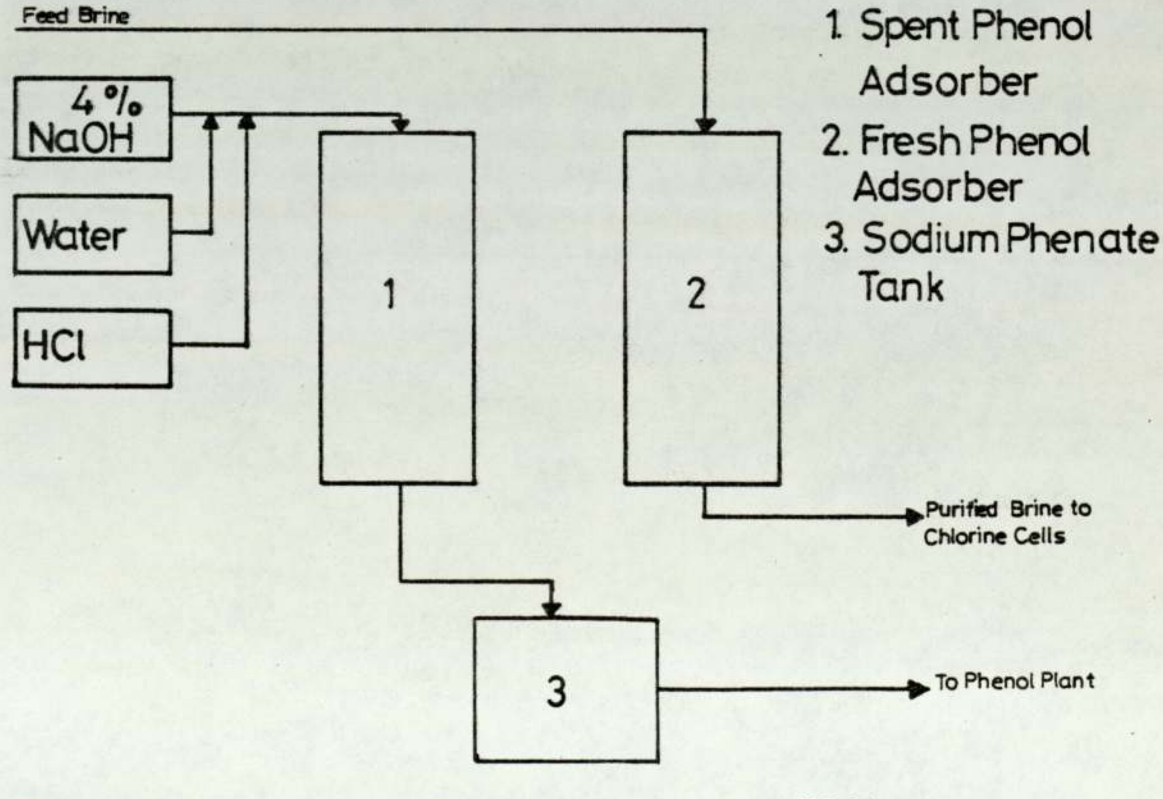


Figure 2.14 Caustic Soda Regeneration (108)

Loven (104) has indicated its use on recovery of cresols.

Solvent extraction is a popular form of adsorbent regeneration in the solvent recovery field, while biological regeneration involves the use of activated charcoal mixed with activated sludge in biological treatment processes. This type of application is reported by Perotti and Rodman (110), Adams (102,103) and Weber et al. (97), where great increases in total organic carbon removal have been reported on the addition of activated charcoal.

2.4.3 The Control of Organic Water Pollution

Activated charcoal adsorption is used mainly as an advanced removal stage in a wastewater purification plant, taking out only those chemicals which biological treatment will not, that is bio-refractory compounds. Weber et al. (97), however, suggest that a non-biological treatment plant, using activated charcoal, could provide effluents of similar quality in a somewhat smaller plant.

2.4.3.1 General Organic Compounds

Several papers concerning the successful treatment of industrial wastewaters in France, West Germany, United Kingdom and U.S.A. using granular activated charcoal beds, were presented at a 1975 conference at the University of Reading in England. Hager (95,111) has given a list of the plants in the U.S.A. using the various forms of activated charcoal adsorption system, on effluents ranging from oil refinery effluent to insecticide and detergent effluents. An indication is given of the type of system used in each case and of the special features, including throughput and contact time. Levels of effluent quality are given for many types of industrial effluent, prior to and after treatment. Indications of the percentage organic reduction and charcoal exhaustion rates are also included. Weber et al. (97) and Bishop et al. (98) have used physics-chemical treatment systems, as described in the previous section, as have Maqsood and Benedek (112) who come to the conclusion that a high quality effluent may be obtained from an adsorption system continuously, over the range 5 - 25°C. Maqsood and Benedek also agreed with Weber et al. that the influence of biological activity on the granules, has a great effect on the adsorption, even of bio-refractory chemicals.

Pilot plant systems, in general, deal with effluents containing many differing chemicals, which as mentioned before, can have a marked effect on adsorption. Many workers have, however, worked on effluents containing known amounts of given pollutants, in experimental situations. Most experimental work is conducted on one of three groups of compounds, that is taste and odour compounds such as phenol (discussed in the next section) and mercaptans, pesticides and to a lesser extent general groups of toxic compounds such as detergents. Cookson and Ishizaki (72) have removed taste and odour containing compounds from water under laboratory conditions, using granular charcoal, finding that the removal of both n-butyl mercaptan and quinones does not follow a simple pattern, since the surface of the charcoal oxidises them to n-butyl disulphide and hydroquinone, a factor which needs to be considered at the design stage. The removal from water of pesticides, due to their extremely toxic nature, is a subject which is always being investigated and Weber and Gould (83) and Robeck et al. (86) have conducted experiments on effluents containing a broad spectrum of pesticides, including DDT, parathion, dieldrin and endrin. Robeck used both powdered charcoal in slurries and granular charcoal in a series of downflow beds, concluding that most pesticides were almost 100% removed by the granular charcoal beds and that around 90% were removed by a 20 mg/l slurry of powdered charcoal. El-Dib et al. (90) have removed both mono and di-methyl carbamates, such as Sevin and Baygon, from water, using charcoal in fixed beds, although as indicated before, these chemicals break down quite rapidly in nature, under the action of ultra-violet light. Bernardin and Froelich (31), while undertaking a range of adsorption isotherm tests for the Calgon Corporation of the U.S.A., have achieved final effluents of 1 μg/l or less for many pesticides including DDT, DDE, DDD, aldrin, endrin and toxaphene, finding that endrin and DDD had by far the largest adsorption capacities. Eichelberger and Lichtenberg (84) have used charcoal for the recovery of various pesticides, by their adsorption from grab samples, taken from polluted waters and then subsequently recovering them using solvents. Endrin and dieldrin along with several other chlorinated hydrocarbons were successfully recovered, while the recovery of DDT was more difficult. However, Heptachlor and aldrin could not be recovered using this method and the recovery of organo-phosphate pesticides was found to be exceptionally difficult.

2.4.3.2 Phenolic Compounds

Phenols and phenolic compounds are notably toxic and persistent, especially the chlorinated varieties, as mentioned in section 2.3. Phenolic compounds lend themselves readily to charcoal adsorption and hence, their adsorption characteristics are very well documented. In fact, due to their ease of adsorption and the extent of documentation on them, many workers use this group of compounds for characterisation of adsorption kinetcs and surface properties (17,28,93,113). Hoak (114) has used activated charcoal, on phenolic effluent streams, as part of a recovery and identification programme, however, he found that phenol oxidises on the charcoal surface and hence appears after recovery as a different compound, which may mislead the analysis. An adsorption-filtration wastewater treatment plant has been constructed for Rhodia Incorporated, in the U.S.A. (78), operating on their 2,4D manufacturing plant. The effluent levels contain 10 mg/l of phenol and 100 mg/l of chlorophenols, which have both been reduced to less than 1 mg/l to comply with American legislation. Bernardin (94) mentions the use of a two fixed bed series system in the treatment of waste waters from a phenolic casting resin plant. However, Lanouette (74) points out that carbon adsorption, while being a reliable form of controlling phenolic pollution, may be most successfully used on small concentrations, as a polishing stage, providing effluent concentrations at 1 mg/l or lower.

2.4.4 Mathematical Modelling of Water Pollution Control Systems

Most of the theory relating to the design and mathematical modelling of charcoal adsorption systems is based on adsorption equilibria and kinetics, which are discussed in sections 2.1.4 and 2.1.5 respectively.

However, several workers have presented complete mathematical models, which describe the system as a whole. It was decided for completeness to include these in a separate section.

Keinath (115) and Keinath and Weber (32) have developed a predictive model for the design of fluidised bed adsorption units (similar to the expanded upflow design). Numerical analysis models have also been developed by Weber and Crittenden (116) for multicomponent systems using a fixed bed adsorber and by Svedberg (117) for multicomponent, countercurrent adsorption, however, these types of approach very often need computer facilities making the overall aim of adsorber design very complicated. It must also be remembered that carbon adsorption kinetics can be difficult to predict accurately.

2.4.5 Legislation Relating to Water Pollution Control

The increase in water pollution, has seen drastic increases in legislation on both sides of the Atlantic, in the past six years or so.

The Americans first put forward an anti-pollution plan as early as 1969-70 (76,118) and the acts which made control measures compulsory, came in 1972 with the Federal Water Pollution Control Act (118,119,120,121).

Zarytkiewicz (118) has indicated that this act takes the following form:

1. National Pollutant Discharge Elimination System.
2. Effluent Guidelines and Standards.
3. Pretreatment Standards.
4. Oil and Hazardous Substances Rules.
5. Ocean Dumping Rules.
6. Toxic Pollutant Standards.

The second of these rules is the one causing most concern in the U.S.A., since under the effluent guidelines and standards there is a call for Best Practicable Technology (BPT) by 1977 and Best Available Technology (BAT) by 1983, with swimmable, fishable waterways by 1985. The National Commission on Water Quality (NCWQ), a body formed by the 1972 act, is very sceptical about the standards required by BPT and BAT (122), suggesting that installations could meet the long term technology and effluent standards, but probably not the daily effluent limits set by the Environmental Protection Agency (EPA). They indicate that the technology for BAT will be available by 1983, but wonder whether the small increase in water quality which will be obtained, is worth the massive costs required to install the necessary equipment. In fact, NCWQ have suggested that since the water quality has improved so dramatically under BPT, the need for BAT is not so great as first thought (121). By July 1st 1977, the deadline for BPT, 90% of all industrial pollutors and 30-40% of municipal pollutors had complied with the EPA regulations (121). A list of violators has already been published (120) and penalties for non-compliance are strict; the Gary, Indiana plant of the U.S. Steel Company was fined four million dollars for non-compliance. However, there have been cases of non-compliance due to bureaucratic inefficiency or technical difficulties involved with the installation of new equipment. Some firms, such as Weyerhauser have indicated that the cost of installing BPT is so great that they would rather go ahead and install the BAT equipment now and as such, save money.

The main requirement of legislation after the 1977 target is now to limit specific effluents singularly, instead of in groups. The EPA have made a list of 129 substances under these limitations. Phenol levels, for instance, have been set at 0.1 mg/l for BPT and 0.02 mg/l for BAT (74). The 1972 act also provided for the limitation of insecticides and pesticides under the Environmental Pesticide Control Act (80), which has seen the banning of DDT in 1972, dieldrin in 1974, heptachlor and chlordone in 1975 and the limitation of endrin to 0.002 mg/l and lindane to 0.004 mg/l. Further limitation of toxic substances will come with the passing of the Toxic Substances Control Act in 1976.

In the United Kingdom, increased legislation came in the 1974 Control of Pollution Act (123) of which part I deals with water pollution control. Under this act, each of ten water authorities, set up under the 1973 Water Act, is responsible for dealing with water pollution control in its own area. Restrictions on discharge to sewers are much stricter than before, with limitations of zero discharge set on insecticides and of less than 30 mg/l on synthetic detergents.

The high levels of water quality required ~~by the~~ legislations described above can only be obtained by an efficient tertiary treatment process, such as charcoal adsorption, reverse osmosis, electro-dialysis and so on. Dallaire (122) favours the use of the more easy to handle charcoal adsorption. It is also notable that this part of the process can prove to be the most costly and hence, careful planning must be undertaken before a final decision is made.

Also, after widespread public concern, involving the finding of carcinogenic chlorinated hydrocarbons in drinking water supplies to New Orleans, the Safe Drinking Water Act was introduced in late 1974 (73).

It is clear from the preceding pages that activated charcoal is effective as a water pollution control device, especially in controlling pollutants from low concentrations. It is also clear however, that activated charcoal is expensive and difficult to handle, due to transportation problems. There are large losses involved when the charcoal is transported either through a process or a regenerator, due to attrition.

Charcoal cloth is able to remove significantly more pollutants from water than an equivalent amount of granular charcoal. Due to its continuous nature, it is possible to transport the cloth through both processes and regenerators with relative ease. It was decided, on this basis, to investigate the properties of charcoal cloth in a continuous water pollution control device. The following pages contain details of the design and experimental details of a research programme to investigate such a control device.

Chapter 3

Analytical Apparatus

3 Analytical Apparatus

3.1 Introduction

The analysis of streams of water containing pollutants requires very sensitive techniques, which may be carried out on a generalised basis or on specific chemical groups. Generally, the types of analytical apparatus which analyse groups of organic chemicals, either detect the total organic content (TOC) of those chemicals, in a given sample, or the amount of oxygen these chemicals use (COD). However, since this experimental programme required information about the removal of specific chemicals from water and not merely the general pollutant effect, these methods were rejected in favour of either gas or liquid phase chromatography. The chemicals chosen for the experimental programme were phenolics which are of relatively high molecular weight and in general not readily analysed using gas-liquid chromatography. Analyses of phenolic compounds in water have been reported, but these involved the extraction and concentration of the chemical in a volatile substance prior to analysis. It was envisaged that large amounts of samples, containing very small quantities of phenol, would be taken during an experiment. Hence, it would be essential to analyse these samples directly without extracting the phenol. Liquid chromatography provided the facility whereby this could be achieved and so it was decided after initial studies to use this equipment.

3.2 High Performance Liquid Chromatography

3.2.1 Selection of the Method of Operation

High performance liquid chromatographs operate by passing a liquid mobile phase over a stationary phase, which may be a solid packing or liquid coated onto the surface of a packing. The sample is then injected into the mobile phase and separates out, as with gas-liquid chromatography. The packing required in normal circumstances may be either normal or reverse-phase, in the case of liquid-liquid chromatography. In normal phase chromatography, the mobile phase is non polar, while the stationary phase, coated onto the packing surface is polar. Since the polluted water containing phenol is polar, then to allow a sample to be injected into the mobile phase directly, a polar mobile phase would be required. It was found that this could be achieved by using reverse phase chromatography, with a water based polar mobile phase. A methanol-water system was used as the mobile phase, with a packing coated with octadecylsilane.

There are also two types of detector which may be used with a liquid chromatographic system, namely a refractive index detector or a U.V. detector. In many cases a liquid has a specific ultra-violet absorbance with a given concentration of chemical in solution. As the concentration of the chemical changes, then so does its ultra-violet absorbance, which may be used for detection and estimation of that concentration. For many liquids, a similar analysis may be made using refractive index. Preliminary investigations, using a spectrophotometer indicated that phenol, due to the double bonds in the benzene ring, absorbed ultra-violet light strongly. It was thus possible to quantify phenol in water solutions using a spectrophotometer, down to concentrations substantially lower than 0.001 kg m^{-3} (1ppm). It was hence decided to use an ultra violet detector in the high performance liquid chromatograph operated for the experimental programme.

3.2.2 Description of the Apparatus

A high performance liquid chromatograph consists of several basic major items; shown in figure 3.1.

The liquid chromatograph used in the experimental programme was an Anachem HPLC 153. The mobile phase used was a 50:50 mixture of methanol and 1% sulphuric acid, which passed from the solvent reservoir, through a six port injection valve and into the column. The six port valve allowed by-passing of the injection system to enable a sample to be introduced to the system. Two ways of introducing samples to the system were used, either through a microlitre syringe directly into the sample loop or through a Luer adaptor and a larger syringe into a fixed volume sample loop. The method of injection is

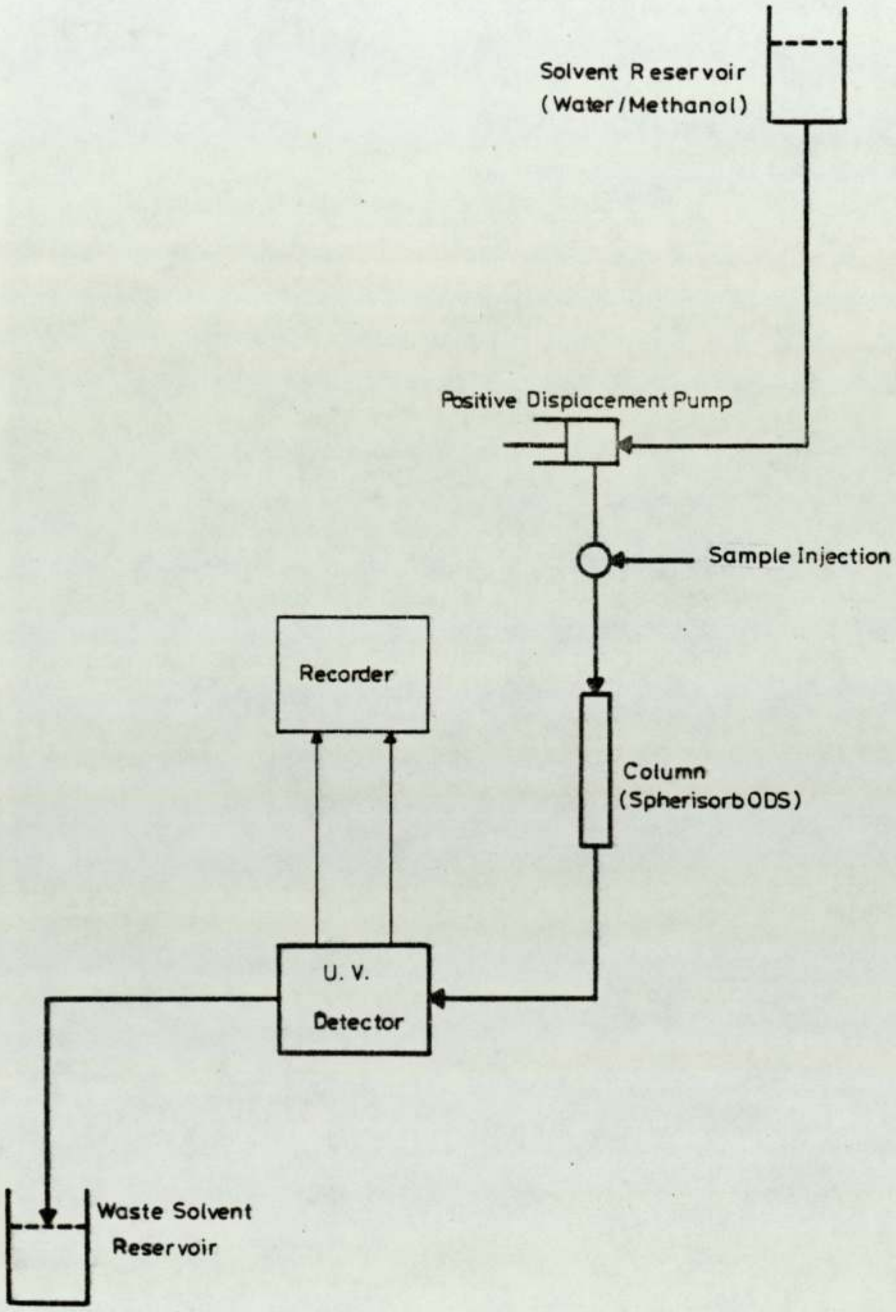


Figure 3.1 A Schematic Representation of the High Performance Liquid Chromatograph

discussed in the next section. As indicated above the system used was reverse phase, the column packing was Spherisorb ODS, with octadecylsilane as the stationary phase. A Milton Roy 'minipump' was used capable of delivering up to 2 x 10^7 Nm^{-2} and with micrometer adjustment, for accurate flow setting of between 0.3 x 10^{-8} m^3s^{-1} and 4.5 x 10^{-8} m^3s^{-1}. The pump was a positive displacement pump giving a pulsed output and a pulse damping mechanism was therefore also employed, incorporating a direct pressure readout onto the column. The mobile phase passed through the detector and out into a waste reservoir. The detector used was an Altex model 153 ultra violet absorber incorporating a 254 nm wavelength ultra violet filter, with a sensitivity of up to 0.005 absorbance units full scale. A flow cell of 8 μl was used, having a 10 mm path length, enabling the detection of such trace organics. The detector output was recorded on a single pen recorder. The method employed to measure the concentration of phenol in a given sample was to compare the peak from an unknown sample with that from a sample containing a known amount of phenol. Peak height measurements were used to calculate the concentrations in each sample.

3.2.3 Commissioning the Analytical Apparatus

The first essential was to ensure separate identification of phenol from the normal constituents of town water. However, this was relatively easy, since the town water employed was free from other ultra violet absorbing substances, making the phenol peak very easy to identify. The only problem was the fact that a twin peak started to emerge, due to the formation of the phenate ion in water. This was prevented by using 1% sulphuric acid solution instead of water, as the mobile phase. In this way, a well defined phenol peak was obtained by using a 50:50 mixture of methanol and 1% sulphuric acid at 6.7×10^{6} Nm^{-2} and 1.3×10^{-8} $m^{3}s^{-1}$.

The range of the detector was 2.56 - 0.005 a.u.f.s. linear absorbance. It was necessary at the commissioning stage to test the linearity of the detector. A graph of absorbance against concentration should yield a straight line, in accordance with Beers Law. It was found however, that this was not so at first. Further investigation indicated that the fault lay in the injection mechanism. It was discovered that on average, a sample size of between 15 and 20µl could be obtained from a 20µl syringe, causing variation in peak sizes. A fixed loop injection system was hence installed and the linearity of the detector rechecked. Using a 75µl loop, as for the whole experimental programme, it was discovered that the detector was in fact linear over its whole range.
Methanol was used in the mobile phase to decrease the retention time of phenol on the packing.

Chapter 4

Adsorption Equilibria

4 Adsorption Equilibria

As explained in section 2.1.4, the adsorption isotherm gives an indication of the adsorption capacity of a given sample of charcoal, under constant temperature conditions and in an equilibrium adsorption situation. The isotherm is obtained by plotting the amount of solute adsorbed per unit weight of adsorbent against the residual concentration of solute in equilibrium with the adsorbent.

There were three reasons for including isotherm testing within the overall experimental programme of this research project. Firstly, to establish that certain common pollutants could be adsorbed and to what extent. Secondly, it was clear from preliminary investigation into mathematical modelling of the continuous adsorption apparatus, that information was required, relating to the total adsorption capacity of a given specimen of cloth, under saturation conditions. Finally, it was thought necessary to conduct tests to compare with results from other workers (at Porton Down) C.D.E., where 0.9 kg phenol/kg cloth had been removed from water. Also, it was decided that several isotherm tests using granular charcoal must be conducted, since the obvious comparison with charcoal cloth is sure to be made.

4.1 Chemical Pollutants Employed in the Experimental Programme

Initially several qualitative experiments were conducted using organic dyes, such as fluorescein and ultramarine and inorganic chemicals such as potassium permanganate. These experiments proved that, while not removing any inorganics, the charcoal cloth removed the organics rapidly and to quite a large extent. It was hence decided, that to conduct a successful experimental programme, characteristic organic water pollutants would be required.

Most of the major pollutant chemicals are too toxic to handle under normal laboratory conditions, on any scale larger than bench size. Furthermore, many of the more hazardous and persistent insecticide chemicals are almost insoluble in water (2,4D:solubility 900 mg/l (83), DDT: solubility 0.016 mg/l and parathion:solubility 18 mg/l (86)), while still constituting a major health hazard. As indicated in chapter 2, the overall aim of this experimental programme was to investigate the continuous removal of pollutants from water using charcoal cloth. Hence, it was necessary to have pollutants in solution at such a concentration that any significant amount of adsorption could easily be measured. However, as indicated in chapter 3, the detector of the high performance liquid chromatograph is not able to detect concentration substantially lower than 0.001 kgm^{-3} (1 mg/l) and since between 50-60 samples per run are needed during the experiments on the continuous equipment, then concentration of the samples prior to analysis is not feasible. Hence, it would not be possible to detect many of the pesticides.

Gauntlett and Packham (20) have indicated that phenol and 2-chlorophenol have solubilities in water of 67 kgm^{-3} (67000 mg/l) and 29 kgm^{-3} (29000 mg/l) respectively, which allow reasonable concentrations in water to be investigated and modelled. Since these compounds are typical water pollutants in their own right (71,73,74), then their use as pollutants in an experimental water pollution control programme would be invaluable. Preliminary investigation using phenol and 2-chlorophenol with charcoal cloth, indicated that they were adsorbed quite strongly as indicated in section 4.4, and hence were used as model pollutants for this experimental programme. It is also true that a great deal of information is known about the surface characteristics of phenol adsorption and adsorption kinetics data.

4.2 Isotherm Testing Procedure

The experimental procedure adopted was similar to those presented by Hassler (2) and Weber and Morris (31). It is as follows:

a) The charcoal cloth was cut into square sections, enough to cover the range of equilibrium solute concentrations of interest, or in the case of granular charcoal, differing amounts of charcoal were placed into sample bottles.

b) The charcoal samples were then weighed to four places of decimals.

c) A solution of the chemical or chemicals to be examined was prepared. Due to the toxic nature of phenols, strict safety measures were employed, as presented in appendix VII. The solution was then poured, in 200 cm^3 amounts, into 250 cm^3 flasks, which were then sealed.

d) The prepared samples of charcoal were added, one to each of the flasks containing the solution. For each study, flasks of solution not containing charcoal were prepared as blanks.

e) The flasks were then agitated intermittently, at a constant temperature of 19°C, over a period of about eight days, to allow equilibrium to be attained. Weber and Morris (31) indicate that the requisite period could be as short as one week or as long as four weeks.

f) At the end of the contact period, the charcoal was then filtered from the solution, in each flask. The filtrate was then placed into a sealed flask prior to analysis.

g) The filtrate was then analysed on the Anachem HPLC-4153, high performance liquid chromatograph and the results recorded. The capacity of a given sample of charcoal could then be calculated.

4.3 Results and Applications

The results from this section are presented in detail in appendix V.

To investigate the adsorption properties of charcoal cloth under practical 'process type' conditions, it was decided to use the cloth as supplied, without any pre-treatment and at a process temperature of 19°C. Two systems for charcoal cloth adsorption were investigated and compared with two granular charcoal adsorption systems.

Charcoal Cloth Tests (Initial Liquid Concentration)

1. 0.1 kgm^{-3} (100 mg/l) Phenol.

2. 0.1 kgm^{-3} (100 mg/l) 2-chlorophenol.

Granular Charcoal Tests (Initial Liquid Concentration)

1. 0.1 kgm^{-3} Phenol

2. 0.1 kgm^{-3} 2-chlorophenol.

The charcoal cloth used came from differing production run numbers and had varying activities; although all types were categorised as highly active. The granular charcoal was of an experimental grade supplied by C.D.E., Porton. (Details of properties of the charcoals used may be found in appendix VI).

To determine the most favourable initial concentration to use in the adsorption isotherm tests and eventually in the runs on the continuous equipment, some initial experiments were conducted with the cloth. Firstly, a solution of phenol of concentration 1 kg m^{-3} (1000 mg/l) was used, which quickly saturated even large amounts of cloth. Lower concentrations took too long to equilibrate and presented detection difficulties at the analysis stage.

Henshaw (78), had however, indicated that a typical effluent stream from a 2,4 dichloro-phenoxyacetic acid manufacturing plant can contain 0.1 kg m^{-3} (100 mg/l) of phenols and chlorophenols. Hence, experiments using an initial concentration of around 0.1 kg m^{-3} (100 mg/l) proved that while not quickly saturating the cloth, this concentration gives a good characterisation of a given sample of cloth. In accordance with Weber (14) and using preliminary results for the adsorption of phenol on charcoal cloth, a graph was plotted of the amount of solute adsorbed (X/M) against the residual solute concentration, in equilibrium with a given amount of adsorbent (C). That is, the adsorption isotherm, from which the adsorption capacity may be calculated. Figure 4.1 shows typical adsorption isotherms for both earlier and later phenol experiments; it will be noted that different charcoal cloth samples were used for each one. In general, the adsorption isotherm was of type I which Weber (14) indicates as being favourable to adsorption. Hence, from the data obtained from the initial phenol experiments, indicating that adsorption was favourable, it was decided to continue with more phenol experiments and experiments using 2-chlorophenol. Hassler (2) and Weber (14) have indicated that it is possible to obtain a straight line plot of the Freundlich isotherm, equation 2.5, by plotting on log-log axes, equation 2.6. This type of plot was used for the analysis of most of the

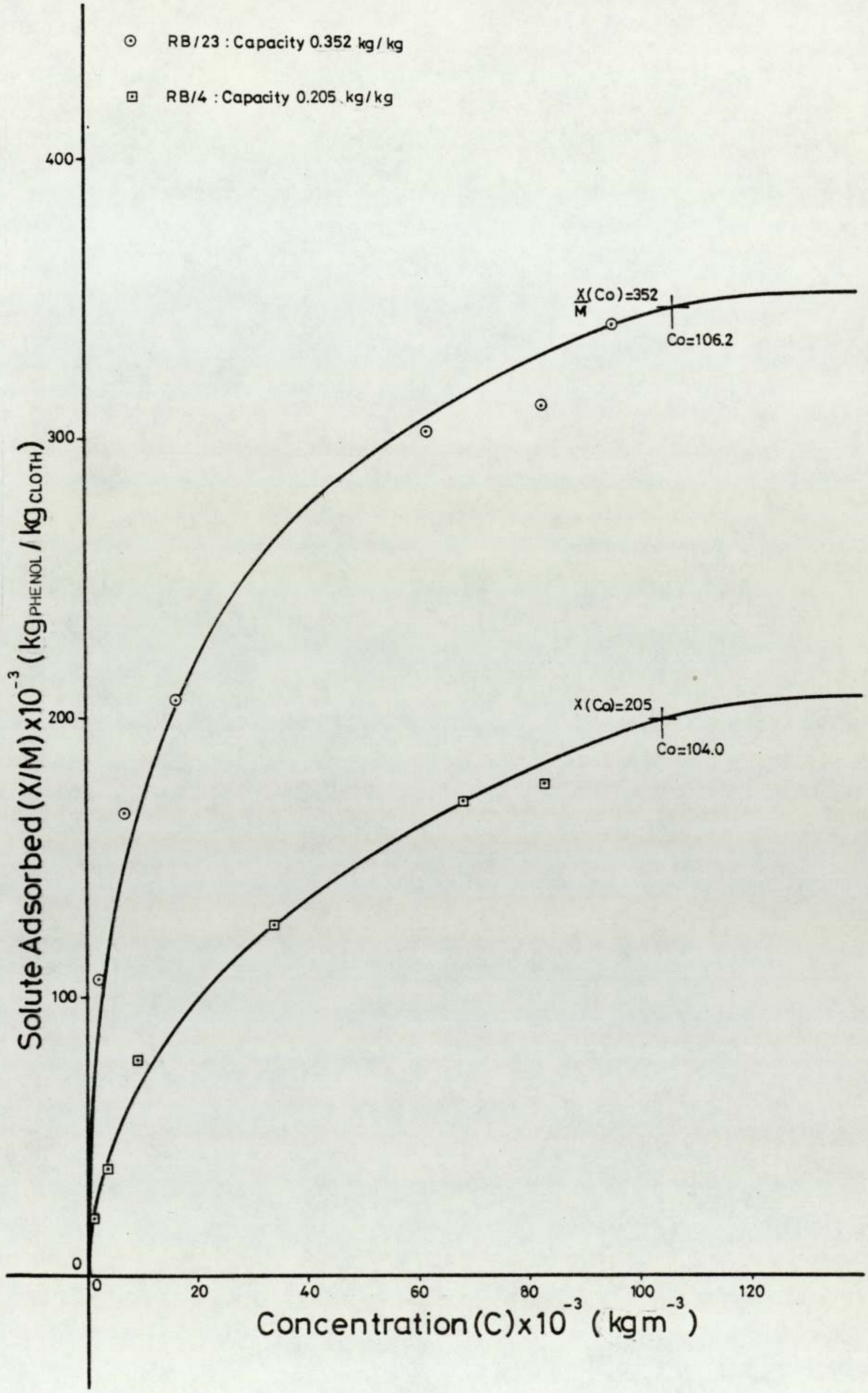


Figure 4.1 Adsorption Isotherms for Phenol Adsorption on Charcoal Cloth

experimental results of this section as indicated in Figures 4.2, 4.3, and 4.4, since Hassler (2) has indicated that in liquid adsorption, the results provided by this isotherm are reasonably reliable. Figure 4.2 shows a Freundlich isotherm plot for an earlier phenol experiment compared with a later one. The adsorption capacity of the cloth, from which the samples were taken, is given by the intersection of the solution initial concentration (Co) with the isotherm. The values for the activity of the various charcoal cloth samples are different, as are most of the adsorption capacity values obtained from these isotherm experiments. However, it must be remembered that the Freundlich isotherm is mainly an empirical formula, as is the study of charcoal adsorption itself. As indicated in Figure 4.2, the phenol isotherms both correspond to the Freundlich isotherm, as shown by the straight line plots. The adsorption capacity values for the phenol experiments varied around an average figure of 0.299 kg phenol/kg cloth, the figure eventually chosen for the phenol capacity in mathematical modelling of the continuous adsorption system, assuming that the capacity was attributable to phenol adsorption only and not to the adsorption of water. Figure 4.3 shows Freundlich isotherm plots for the adsorption of 2-chlorophenol an activated charcoal cloth, indicating that the cloth has a much larger capacity for this than for phenol. By averaging the individual experimental adsorption capacities obtained

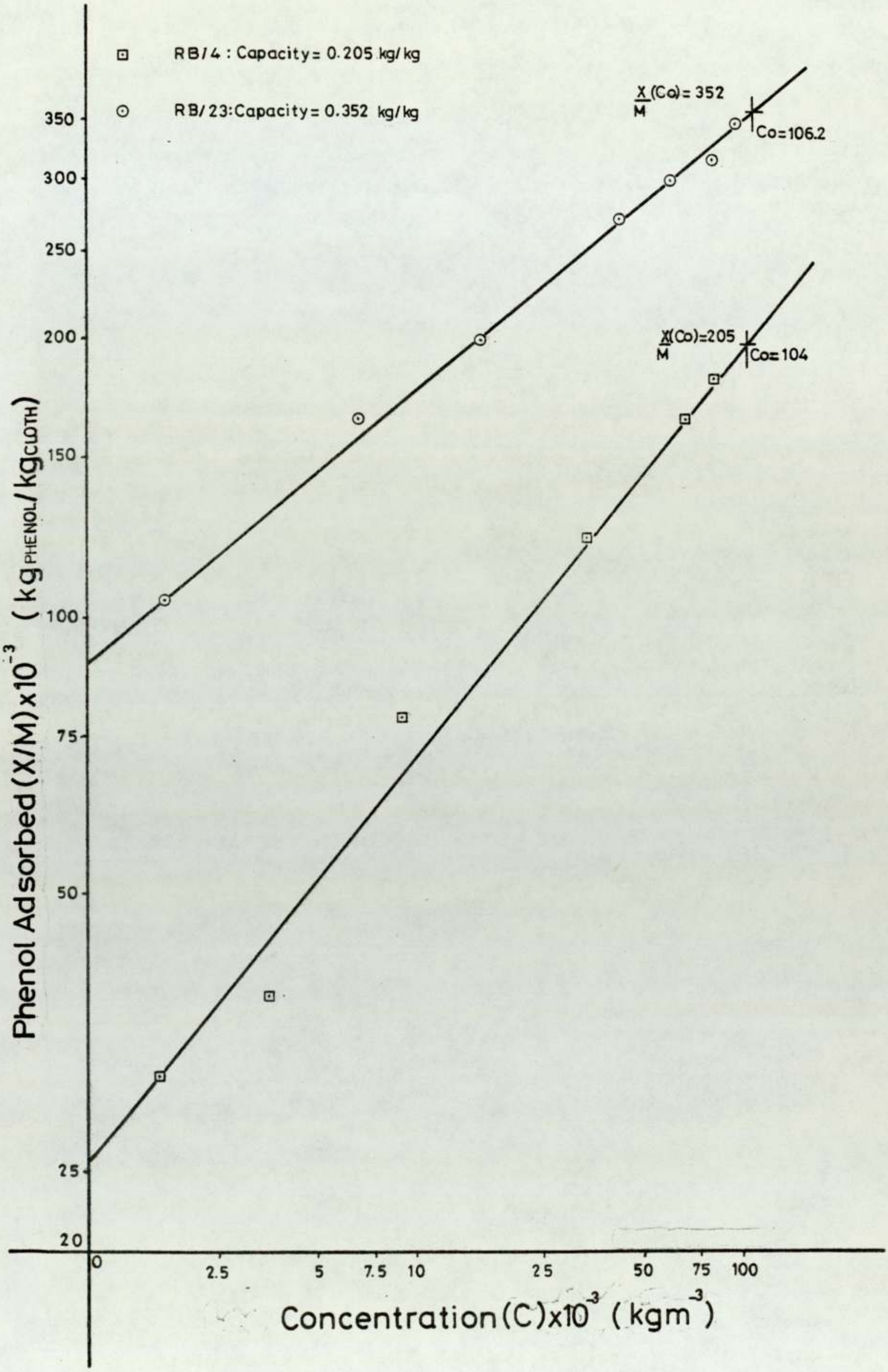


Figure 4.2 Freundlich Isotherms for Phenol Adsorption on Charcoal Cloth

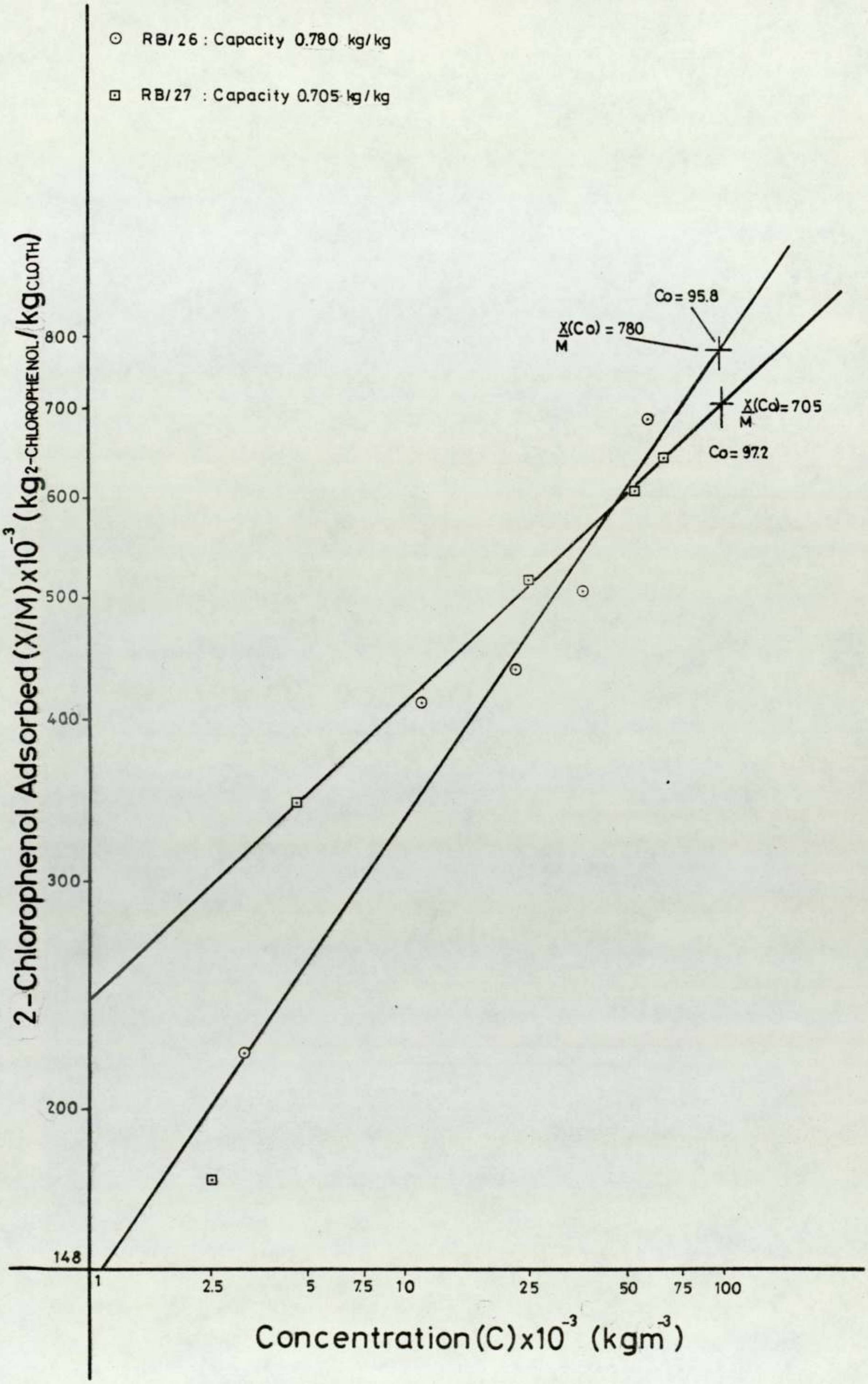


Figure 4.3 Freundlich Isotherm for 2-Chlorophenol Adsorption on Charcoal Cloth

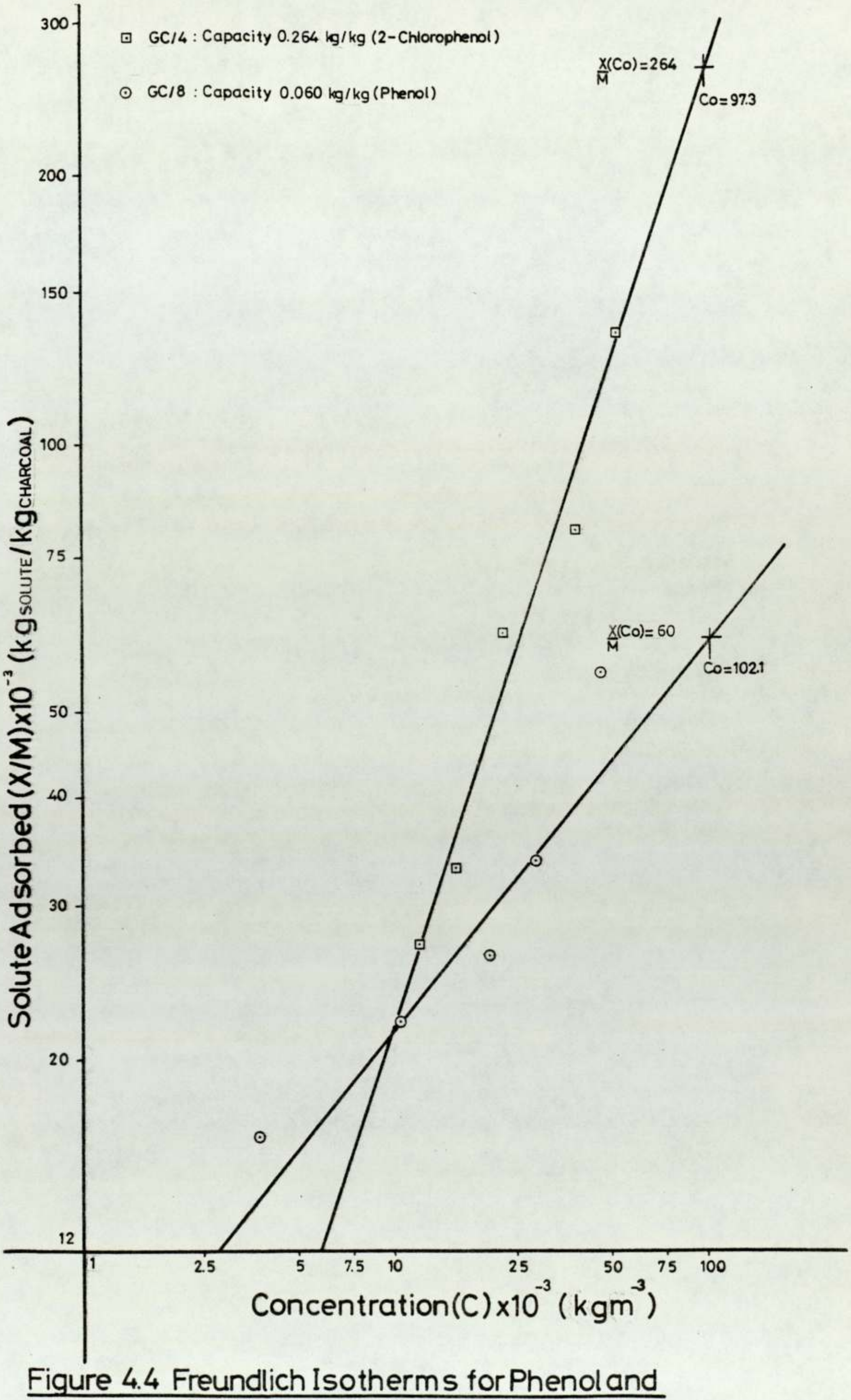


Figure 4.4 Freundlich Isotherms for Phenol and 2-Chlorophenol Adsorption on Granular Charcoal

for 2-chlorophenol, the overall capacity used for modelling, from experiments, was found to be 0.698 kg/kg, a figure more than double that of the phenol capacity. This value was used for the 2-chlorophenol capacity in mathematical modelling of the continuous system.

A similar set of experiments for granular charcoal (Details of the charcoal can be found in appendix VI) were carried out under the same conditions and using the same chemical systems as those for charcoal cloth. Typical Freundlich isotherms for phenol and 2-chlorophenol are shown in Figure 4.4. Average values for phenol and 2-chlorophenol adsorption capacity on granular charcoal, were 0.077 kg/kg and 0.25 kg/kg respectively, obtained from similar isotherm plots. The figure for phenol adsorption agrees very well with one presented by Lanouette (74) of 0.073 kg/kg, for adsorption in neutral solution. Considering that the granular charcoal had a similar activity to the cloth samples used, the difference in capacity was 74% and 64% respectively per unit weight of charcoal.

4.4 Discussion

4.4.1 Adsorption on Charcoal Cloth

By plotting adsorption isotherms, similar to those in Figure 4.1, for each of the phenol runs, it was clear that adsorption was favourable and that a type I adsorption isotherm could be obtained, of the type indicated by Langmuir (24), as shown in Figure 2.3. This could mean that adsorption is of the traditional monolayer type or since the cloth is microporous, multilayer adsorption as explained in chapter 5. The Brunauer, Emmett and Teller isotherm which usually indicates the formation of gaseous multilayers, does not hold, in this case, even for dilute solutions. The Freundlich isotherm, although its origins are in empiricism, has for many years been used as a direct method of predicting the adsorption capacity of charcoal. Using the Freundlich isotherm a logarithmic plot of the solute adsorbed against the concentration of solute in the solution in equilibrium with the adsorbent, gives a straight line, over a wide concentration range. The type of Freundlich isotherms obtained for the adsorption of phenol and 2-chlorophenol from pure solutions are indicated in figures 4.2 and 4.3. These plots generally follow reasonable straight lines, from which the adsorption capacities may be calculated by extrapolation to the intersection with the feed concentration, as shown. It has already been mentioned that different cloths were used for the tests, to find out the spread in capacities from cloth to cloth. Also, the samples were taken at random places across the cloth widths, since on the continuous equipment, half of one cloth width is used as the adsorption media and it was hence, necessary to find if there were significant variations in capacity across the cloth. As can be seen in appendix V, there are variations in the values obtained for both phenol and 2-chlorophenol adsorption capacities. These capacities have mean values of 0.299 kg/kg and 0.698 kg/kg respectively, with deviations from the mean value of plus or minus 30% and 8% respectively. Since it is considered that the properties of charcoal cloth vary from one production run to another and also across the cloth widths as shown in appendix VI, a deviation in values of this magnitude was not unexpected. In fact, the same sort of variation can be found in one batch of industrial granular charcoal (74). These mean figures were hence used in the mathematical modelling, as the respective adsorption capacities on charcoal cloth of the two chemicals. It may be noted that the capacity for adsorption of 2-chlorophenol is more than double that for phenol, a fact which is agreed with by Gauntlett and Packham (20), for adsorption in neutral solution, since the reduced solubility of the 2-chlorophenol increases the driving force from solution to adsorbent. The results were not radically effected by the use of town water in place of distilled water. It is possible however, that river water with a greater chemical content than town water, could cause a drop in the adsorption capacity of a sample of charcoal for a given chemical, due to competitive adsorption, Gauntlett and Packham (20) have shown that this can be true for adsorption from Thames water.

The figures obtained for phenol and 2-chlorophenol adsorption capacities are lower than those reported by Smith and Maggs (29) and Fairhurst (124). This is believed to be due to the fact that the above workers carried out pretreatment of the cloth prior to experimentation, which involved extensive cleaning. For instance, Fairhurst has indicated that for complete wetting of the cloth, it is necessary to wash and boil the cloth in both solvents and acids, for several weeks prior to experimentation. At Aston, it was decided that the isotherm tests needed to be conducted on a cloth closely related to that which would eventually be used on the continuous equipment; a large pretreatment system would not be possible, on the grounds of both time, expense and safety. Furthermore, any such elaborate pretreatment in large scale applications would be quite unrealistic. Therefore, in the experimental programme, isotherm tests were carried out on cloth as directly supplied by C.D.E., without pretreatment and thus would explain the difference between the figures obtained in this research programme and those obtained at C.D.E., Porton Down. It is possible that the two values for cloth adsorption capacity, represent the ideal value, in the case of C.D.E. and operational value, in the case of Aston. It may be possible with a small amount of pretreatment, in an industrial process, to increase the adsorption capacity marginally.

4.4.2 Comparison of Adsorption on Charcoal Cloth with Granular Charcoal

Experiments into the adsorption capacity of granular charcoal for phenol and 2-chlorophenol were carried out on a granular charcoal of similar activity to the charcoal cloth samples, as explained in appendix VI. Maggs and Smith (29) have indicated that results for phenol adsorption capacity on granular charcoal have been obtained, which are comparable to those for charcoal cloth, using pretreated samples. However, Lanouette (74) has reported that under process conditions, the capacity of granular charcoal for phenol can vary between 0.09 - 0.4 kg phenol/kg charcoal. In our experimental programme, the average values obtained for phenol and 2-chlorophenol adsorption capacities on granular charcoal were 0.077 kg/kg and 0.25 kg/kg respectively, which are lower than values for cloth adsorption, under similar conditions. It is possible that Maggs and Smith used a granular charcoal of relatively high activity which could have been pretreated. However, from the results of this experimental programme, compared to Lanouette, it appears that charcoal cloth has a higher capacity for adsorption of phenol than granular charcoal, under process conditions. Weber and Morris (31) found that adsorption capacity increases as particle size decreases. Since, the charcoal cloth fibres are, in most cases about 10μm in diameter, this could explain the large adsorption capacity of the cloth.

Chapter 5

Scanning Electron Microscopy

5 Scanning Electron Microscopy

5.1 Introduction

As explained in chapter 2, the kinetics of adsorption may be determined by one, or a combination of three factors, which are:

a. Film diffusion.

b. Pore transport.

c. Surface adsorption.

Of which b. requires an inlet to the internal pore structure, large enough to accommodate the adsorbing molecules. Granular charcoal, in general, contains many pores large enough to accommodate even the largest pollutant molecules. However, since it has been said that charcoal cloth contains a pore structure of almost entirely micropores, it might not be possible for internal transport to take place.

It was decided to conduct a short investigation into the surface properties of charcoal cloth using a scanning electron microscope to obtain high magnification micrographs of the cloth surface. Scanning electron micrographs of the cloth at magnifications of up to 10000 times should distinguish pores of 5 nm diameter. It was hoped that stereo-micrographs of the cloth before and after use would indicate, in some way, the possible mode of adsorption. Also, that these could be compared with similar pictures of granular and powdered charcoal and with electron-micrographs taken at Porton.

5.2 Operating Procedure for the Scanning Electron Microscope

The scanning electron microscope used for these studies was a Cambridge mk.2. Analysis of the cloth and particles was also carried out using a 'Kevex' x-ray microanalyser.

A piece of cloth about 0.5 cm^2 (or in the case of granules, about 6) was mounted onto an aluminium stud using 'silverdag', an electrically conducting adhesive. The stud and cloth were then placed into the microscope, which was then evacuated. Micrographs were then taken of both reacted and unreacted cloth, along the lengths of fibres, as well as of fibre ends at fractures. A full range of magnifications was used (50 times magnification to 20 000 times magnification) to obtain an overall picture of the cloth as well as specified topics at high magnification. The same procedure was then adopted for granular and powdered charcoal.

5.3 Stereo-Electron Micrographs

Plates 5.1 and 5.3 show a single strand of unreacted cloth at approximately 10 000 times magnification and 5000 times magnification respectively; of note are the corrugations running along the length of the strand, also shown by plate 5.7. There is a remarkable lack of macroporous structure even at 10 000 times magnification. Strands of cloth which have been reacted with phenol are shown in plates 5.2 and 5.4 at approximately the same

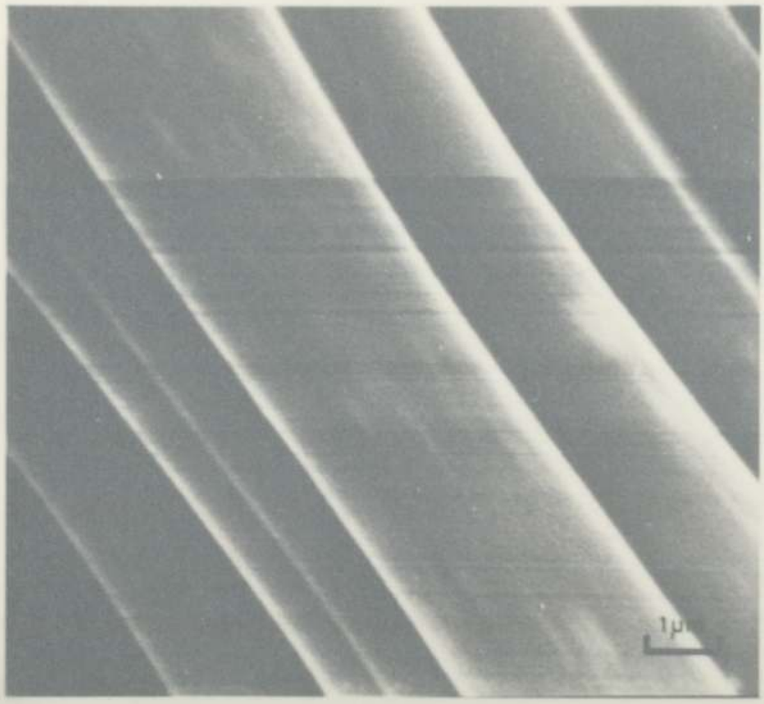


Plate 5.1 A Charcoal Fibre (x 9900)

Plate 5.2 A Charcoal Fibre after Reaction with Phenol (x 9750)

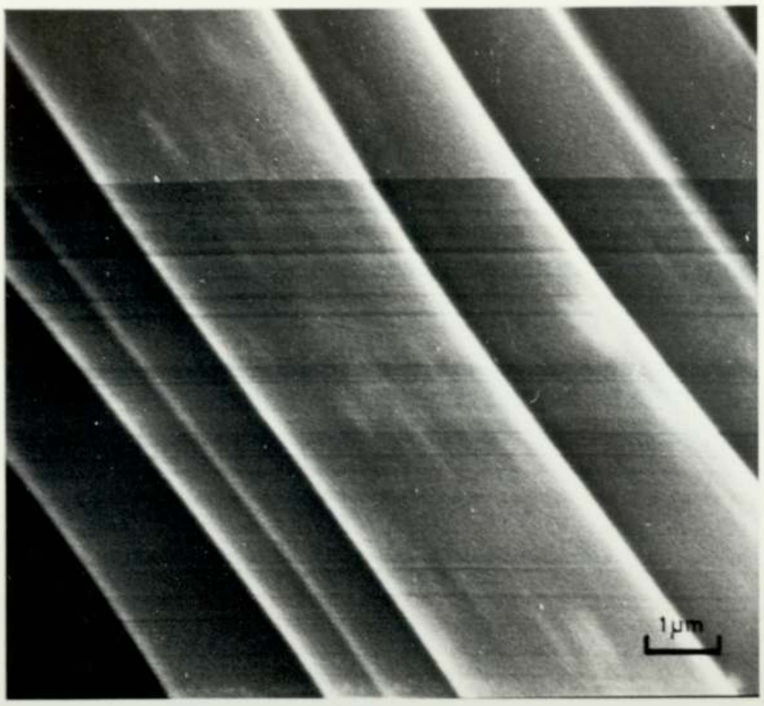


Plate 5.1 A Charcoal Fibre (x 9900)

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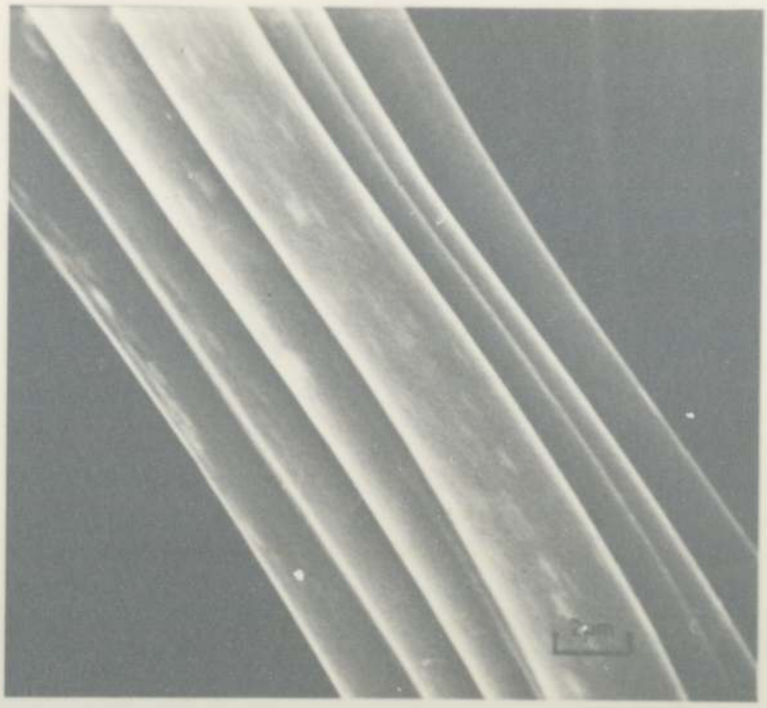

Plate 5.3 A Charcoal Fibre (x4950)

Plate 5.4 A Charcoal Fibre after Reaction with Phenol (x4875)

Plate 5.3 A Charcoal Fibre (x4950)

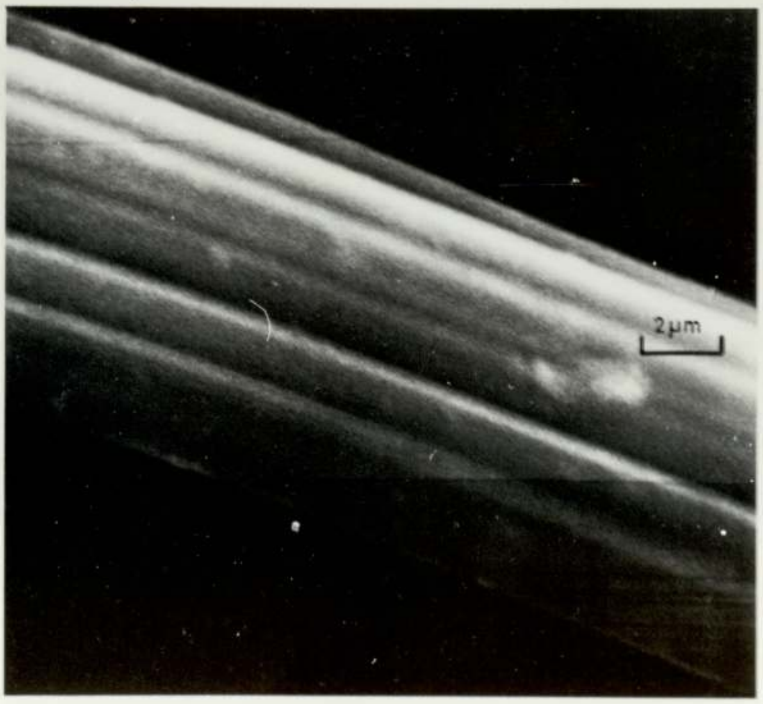

Plate 5.4 A Charcoal Fibre after Reaction with Phenol (x4875)

Plate 5.5 The End of a Charcoal Fibre (x 5600)

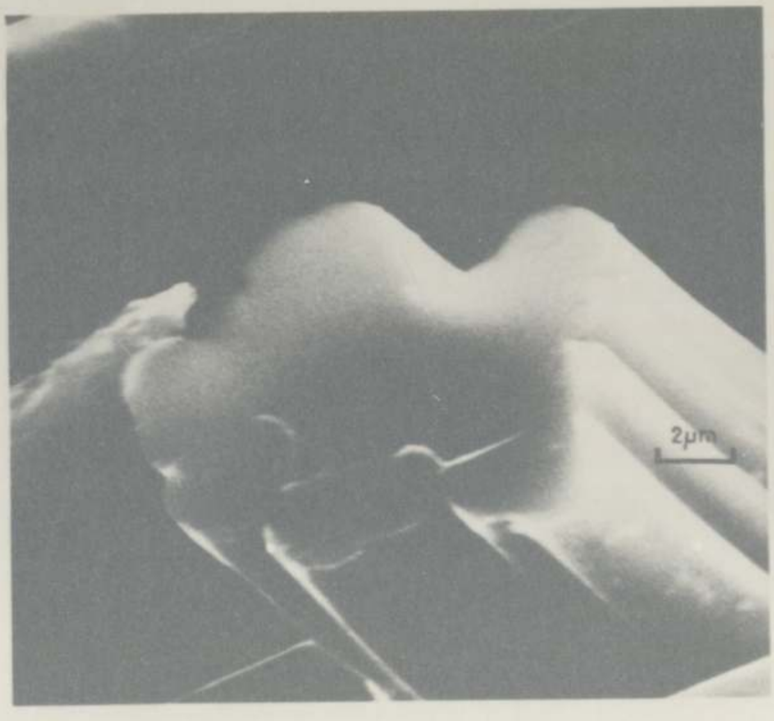

Plate 5.6 The End of a Charcoal Fibre after Reaction with Phenol (x 5400)

Plate 5.5 The End of a Charcoal Fibre (x 5600)

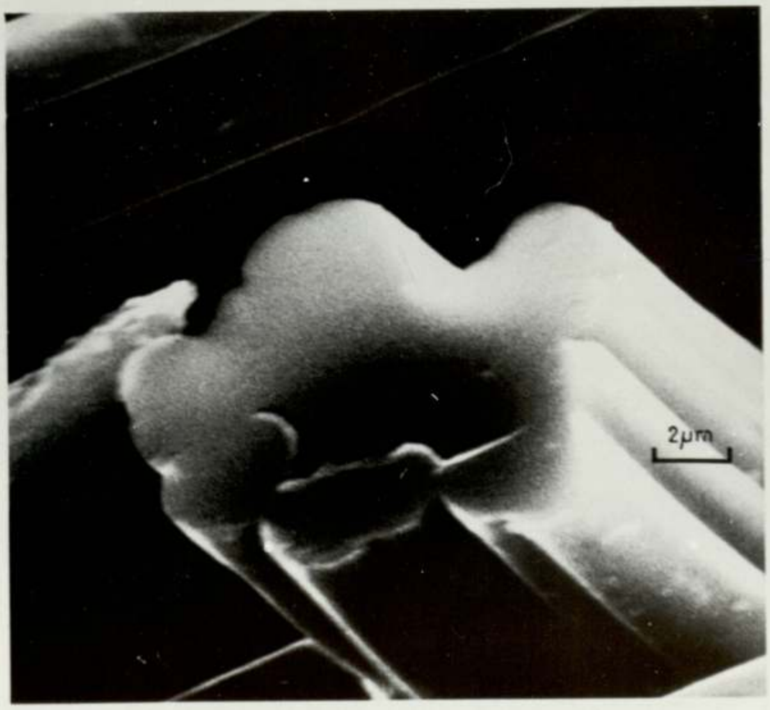

Plate 5.6 The End of a Charcoal Fibre after Reaction with Phenol (x 5400)

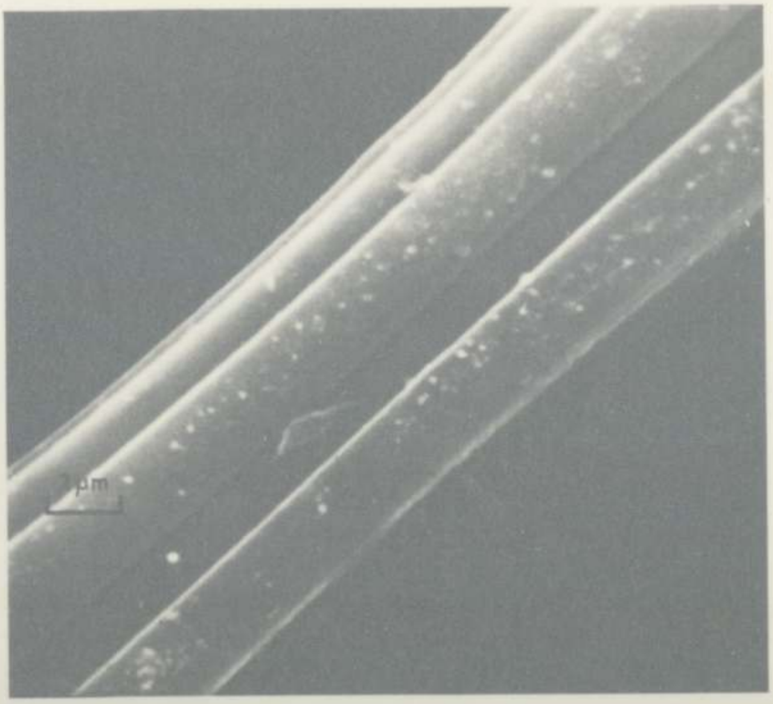

Plate 5.7 A Charcoal Fibre (x5800)

Plate 5.8 The End of a Charcoal Fibre (x5400)

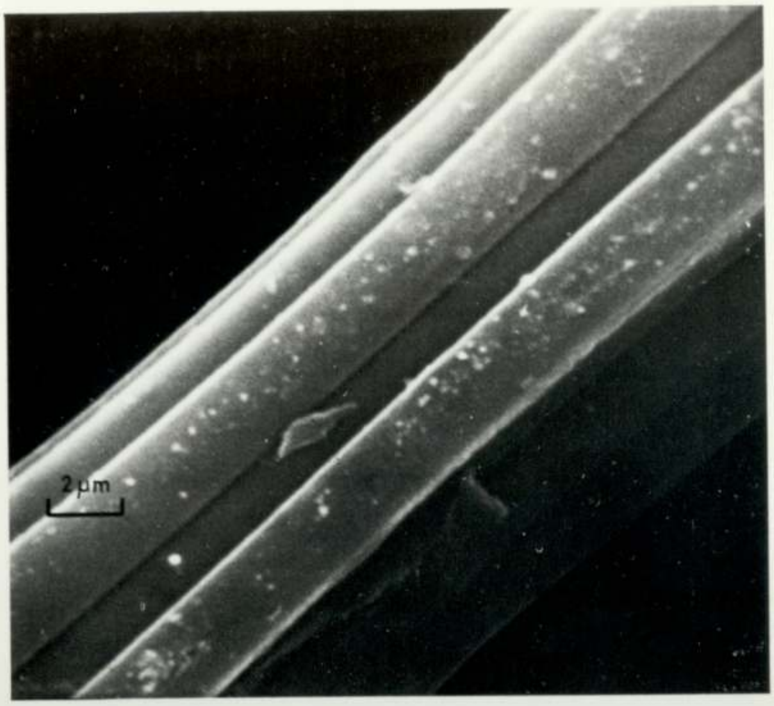

Plate 5.7 A Charcoal Fibre (x 5800)

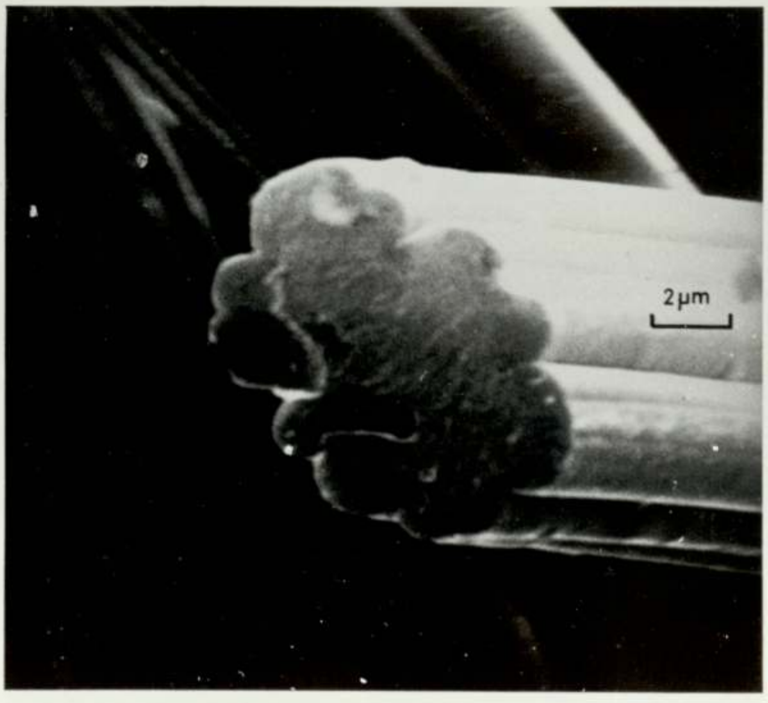

Plate 5.8 The End of a Charcoal Fibre (x 5400)

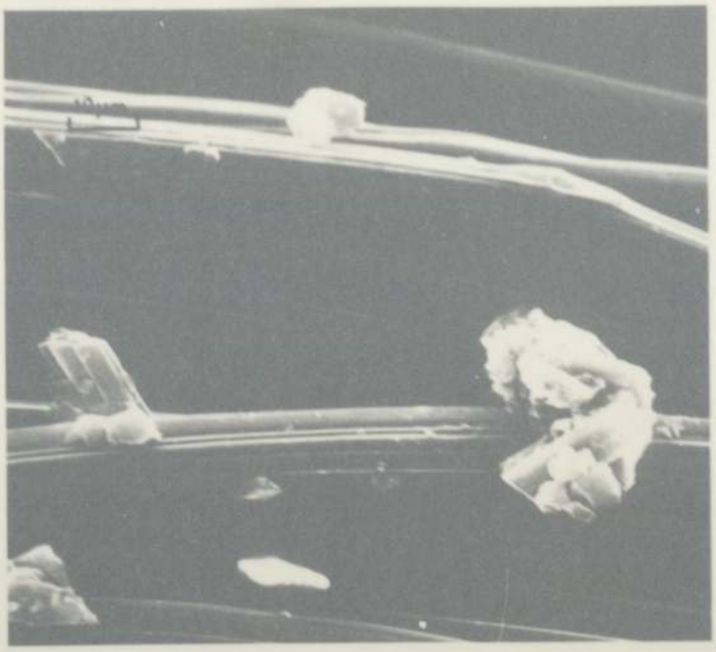

Plate 5.9 Phenol Crystals attached to Charcoal Fibres(x1060)

Plate 5.10 Fractured Ends of Charcoal Fibres (x1100)

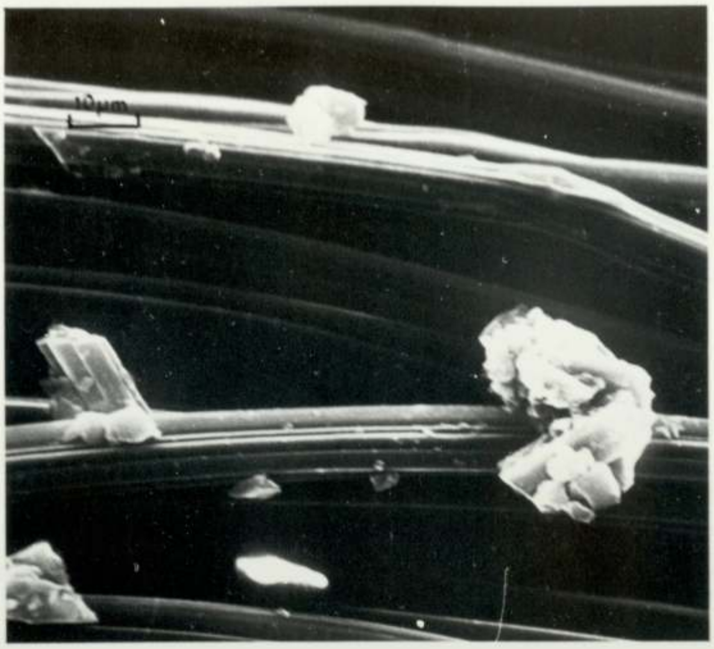

Plate 5.9 Phenol Crystals attached to Charcoal Fibres(x1060)

Plate 5.10 Fractured Ends of Charcoal Fibres (x1100)

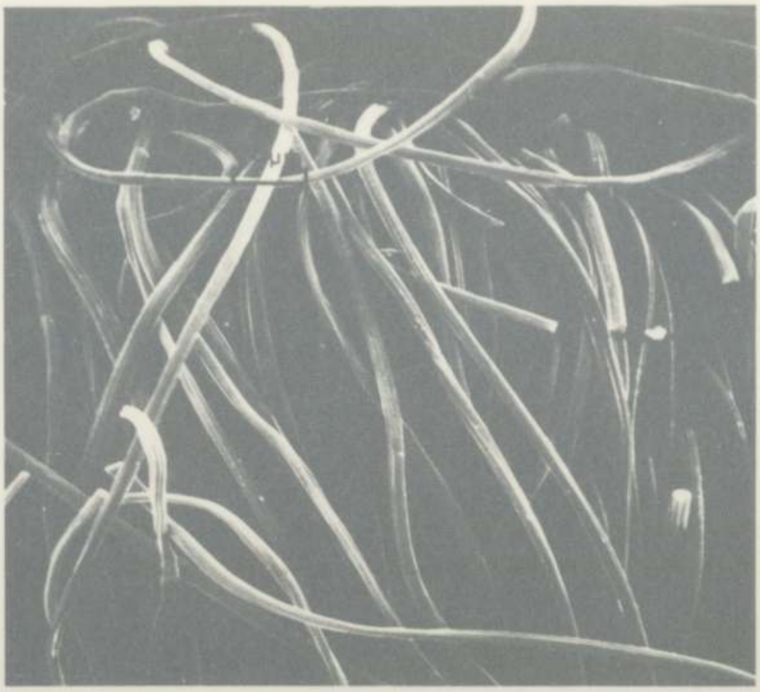

Plate 5.11 General View of Charcoal Fibres (x198)

Plate 5.12 Powdered Charcoal (x2240)

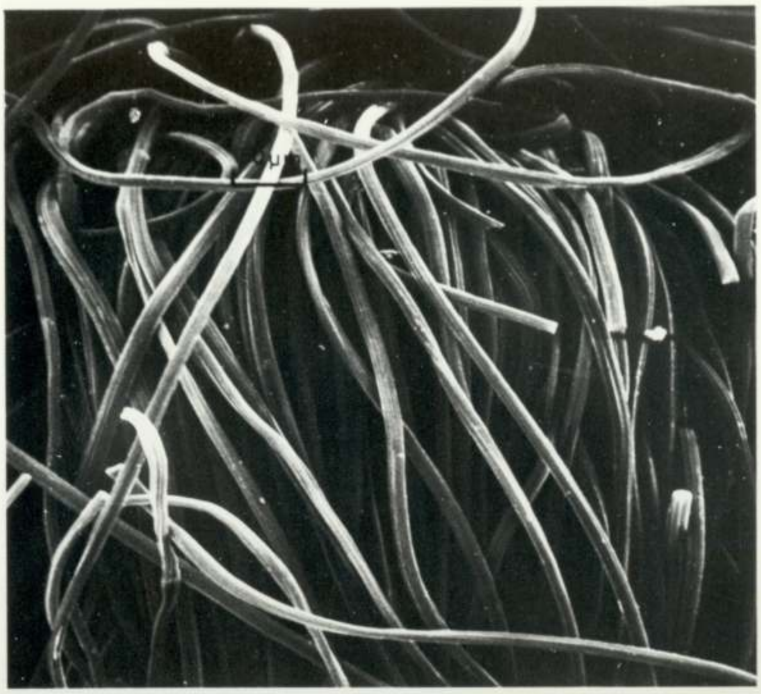

Plate 5.11 General View of Charcoal Fibres (x198)

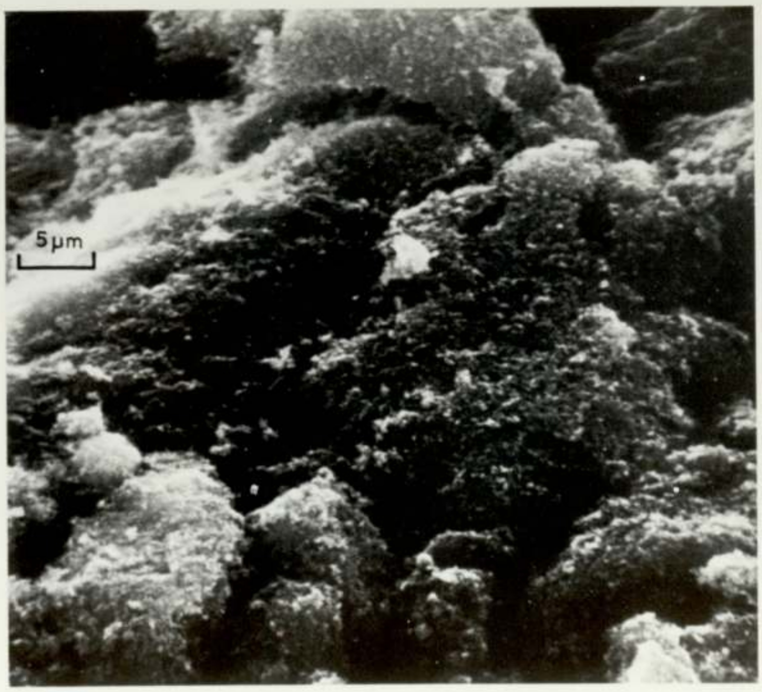

Plate 5.12 Powdered Charcoal (x2240)

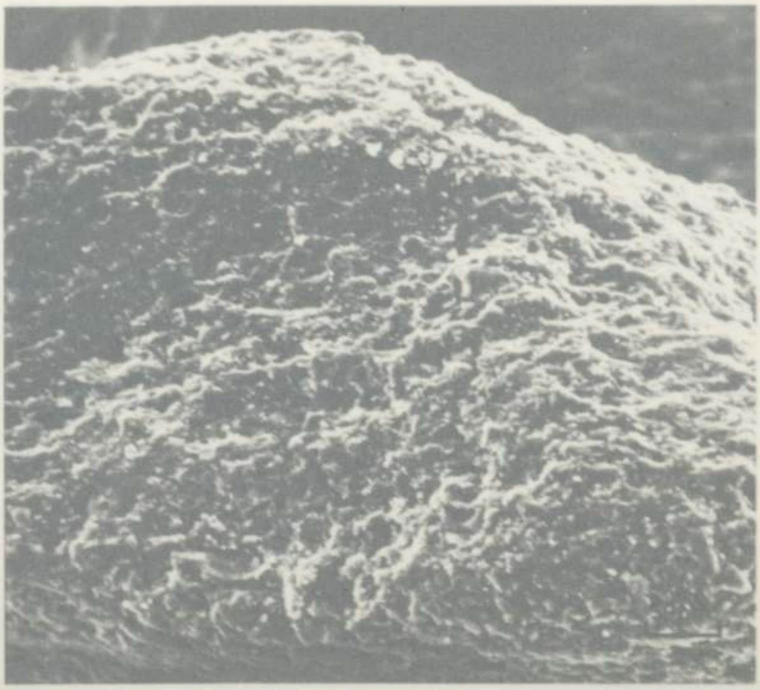

Plate 5.13 A Charcoal Granule (x 225)

Plate 5.14 Macropores on Granular Charcoal (x 2200)

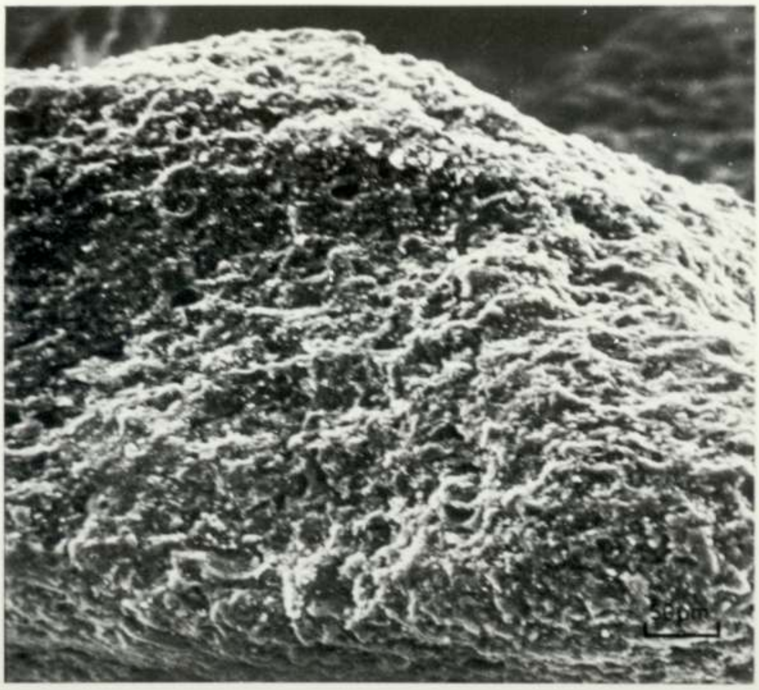

Plate 5.13 A Charcoal Granule (x 225)

Plate 5.14 Macropores on Granular Charcoal (x 2200)

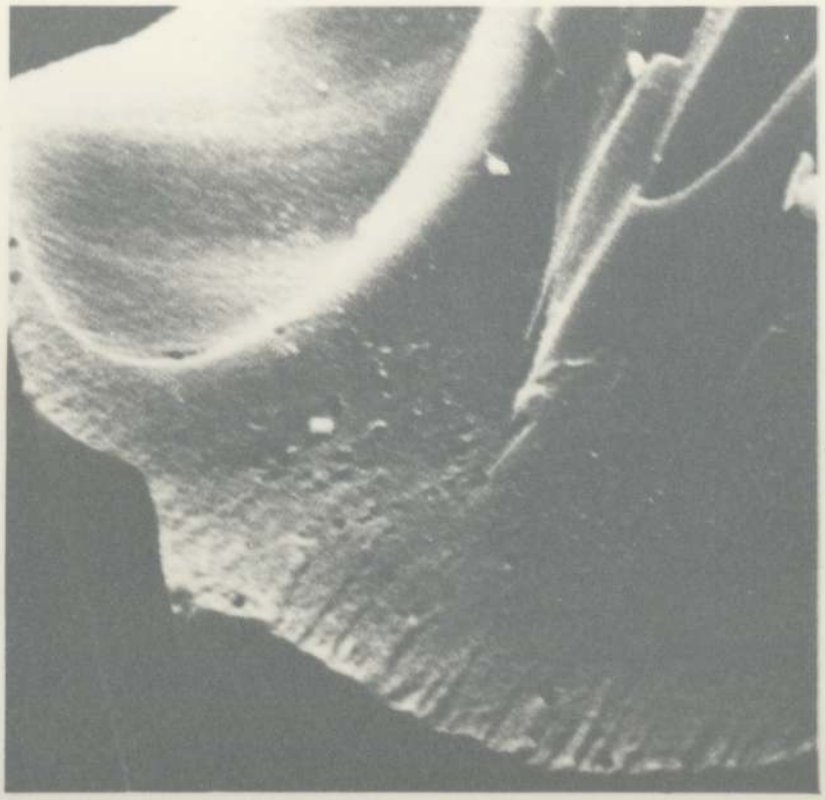

Plate 5.15 A Fractured End of a Charcoal Fibre (x10000)

(Taken at C.D.E., Porton Down)

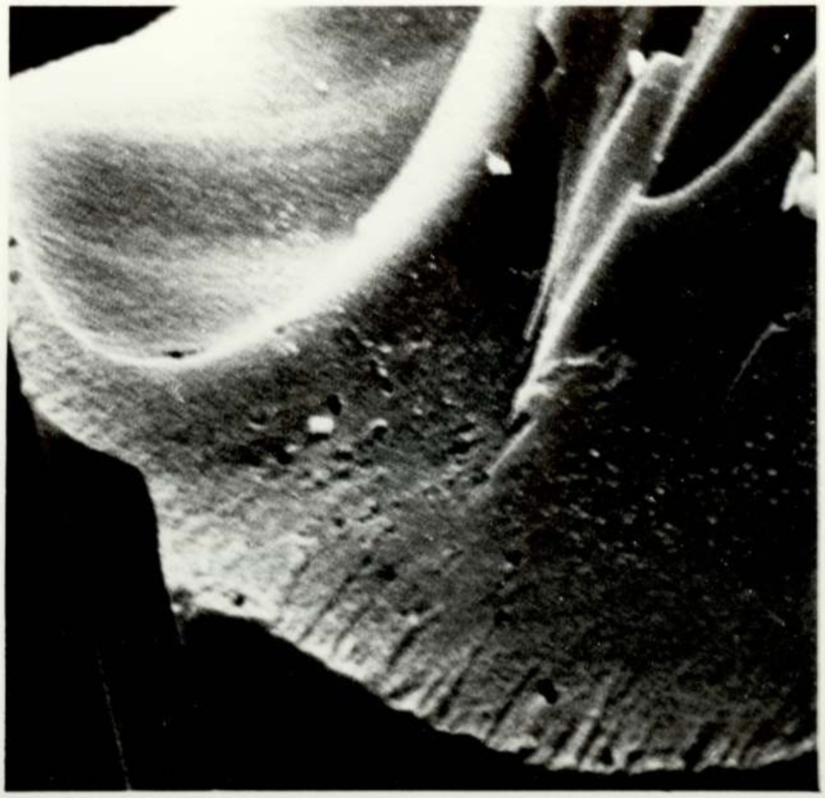

Plate 5.15 A Fractured End of a Charcoal Fibre (x10000)

(Taken at C.D.E., Porton Down)

magnification. It is notable that the corrugations do not appear so marked in these pictures. Plates 5.5, 5.6 and 5.8 show micrographs of ends of charcoal strands at approximately 5500 times magnification, for unreacted cloth, in the case of plates 5.5 and 5.8 and reacted cloth in plate 5.6. It is clear from the micrographs that all strands have longitudinal holes, which are more likely to be a consequence of manufacture than actual pores. Plates 5.9 and 5.10 show strands of the reacted cloth at about 1100 times magnification. Plate 5.9 clearly indicates the formation of crystals on the cloth surface, which were shown by analysis with the 'Kevex X-ray', analyser, not to be inorganic. From the crystal structure and the fact that the sample was taken from cloth which had reacted with a phenolic solution, the crystals were of phenol. It is also possible to see smaller crystals on the fractured end of charcoal cloth shown in plate 5.10. Plates 5.11, 5.12 and 5.13 are micrographs of charcoal cloth, powder and granules, at magnifications of about 200 times for the cloth and granules and 2000 times for the powder. The porous structure of the granular charcoal may be clearly seen at a magnification as low as 200 times. In comparison, the charcoal cloth at a similar magnification, shows no sign of its porous structure. The powdered charcoal porous nature may also be clearly seen at 2000 times magnification. Plate 5.14 is a micrograph of a charcoal granule at 2200 times magnification, on which it is possible to see pores of 200 nm relatively easily, compared with plate 5.1 on which it is very difficult to see any porous structure even at 10 000 times magnification. Plate 5.15 shows a micrograph taken at C.D.E. Porton of the end of a strand at 10 000 times magnification.

5.4 Discussion

5.4.1 Details of the Scanning Electron Micrographs

The classical ideas for the pore structure of activated charcoals are indicated by Weber (9) and Dubinin (10,11) and illustrated in Figures 2.1 and 2.2 respectively. Both theories postulate the idea of macropores in excess of 100 nm (1000 Å), leading to micropores of up to 2nm (20 Å). From plates 5.12, 5.13 and 5.14, it is clear that macropores exist in granular and powdered charcoal. The largely porous structure of granular charcoal is easily seen in plate 5.13, at 200 times magnification and pores in excess of 2 μm (20 000 Å) are easily seen at 2000 times magnification in plate 5.14. Micrographs of nutshell charcoal taken by Bailey et al. (13), also clearly show macropores of 1 μm (10 000 Å) and larger at 2000 times magnification. The ideas of porous structure as presented by Weber and Dubinin hence appear to hold for granular and powdered charcoals. A micrograph of charcoal cloth at 200 times magnification is shown in plate 5.11, showing many strands, on which no macroporous structure can be seen. Similar micrographs of graphite cloth taken by Yamiv and Ariel (126) at 3000 magnification, agree with this type of structure. In fact, micrographs of charcoal cloth at magnifications of up to 10 000 times, in plate 5.1, show no sign of macroporous structure when at this magnification, 5 nm pores should be clearly seen. It appears from the micrographs of unreacted cloth in plates 5.1, 5.3, 5.5 and 5.8 that the porous structure of charcoal cloth consists completely of pores less than 5 nm in diameter. In fact, the micropore openings to the surface of the cloth give the strands a 'hazy' appearance, noticeable if the end of the strand in plate 5.8 is closely studied. This type of porous structure is more clearly shown in plate 5.15, taken by C.D.E, Porton, since if this plate is studied closely a finely porous structure similar to sandstone, is noticeable. Transmission electron micrographs, at 2 x 10^6 times magnification, coupled with gas adsorption analysis undertaken by Bailey et al. (13), indicate that the porous structure of charcoal cloth consists almost entirely of pores less than 1 nm (10 Å) wide which are smaller than most micropores in granular charcoal. Furthermore, these and further studies have shown that the micropores become smaller towards the centre of a strand and that they are formed in between the graphite planes, of the charcoal. It is also clear from the plates, that most unreacted cloth and some reacted cloth strands possess quite deep longitudinal corrugations. These are probably due to both the structure of the base material and to the manufacturing process. Scanning electron micrographs of graphite cloth, taken by Yaniv and Ariel (126) fail to show any of these corrugations at 3000 times magnification.

5.4.2 Interpretation of the Scanning Electron Micrographs

The classical form of adsorption onto active charcoal is presented by Weber (14), Weber and Keinath (32) and Bell and Molof (33), which involves in general, three stages:

a. Diffusion through a stagnant external layer or film to the adsorbent surface.

b. Internal transport in the macropores and interpores.

c. Adsorption on the micropore surface.

Mathematical modelling shows that it is usually film diffusion, pore transport or a combination of both which provides the rate limiting step for adsorption kinetics. However, in the case of charcoal cloth, electron micrographs and adsorption studies have indicated that most of the pore volume occurs in pores of 1 nm or less, in fact Bailey et al. (13) have indicated that charcoal cloth can act as an effective molecular sieve (removing methanol from larger molecules, which in itself suggests that the micropore diameters are in the range 0.3 - 1 nm). The fact that no macropores exist, that the micropores, which open directly to the cloth surface are less than 1 nm in size and that the micropores are slit-shaped and relatively short in length, suggests that pore transport would play little part in the kinetics of phenolics adsorption on charcoal cloth. A molecule of phenol has such dimensions that the probability of it entering a micropore of size less than 1 nm is quite small, due to energy and electrostatic considerations. It has also been shown (16,17,18) that the phenol molecule usually approaches planar to the charcoal which would also hinder internal adsorption. If the liquid surrounding the charcoal is sufficiently turbulent that is, if the charcoal is in a fast flowing process or if the process fluid is agitated sufficiently, then according to Weber (14), film diffusion is negligible. It would hence appear that adsorption of phenol on activated charcoal cloth could take place mainly on the surface. There are indications in the micrographs of two possible procedures for surface adsorption on charcoal cloth, either nucleation of phenol crystals or the build up of layers of phenol on the surface. Examples of crystals on the surface of the cloth are shown in plates 5.9 and 5.10. It is however thought that the main form of surface adsorption on charcoal cloth is due to the build up of phenolic layers on the surface and in some pores very close to the surface, accounting for its large adsorption capacity.

Small amounts of adsorption actually within micropores is also suggested by Abram (1) and Dubinin (12). Abram suggests that as molecular size increases and pore size decreases, at some stage the shape and size of a molecule will prevent its entry into the micropores. Dubinin also states that since most micropores are of molecular dimensions, it is only possible for one molecule to pass into these pores. A possible example of surface adsorption on charcoal cloth is illustrated in plates 5.2 and 5.4, when compared with plates 5.1 and 5.3, it is noticeable that the logitudinal corrugations are not as deep after reaction with the phenolic solution as before. It is thought that layers of phenol forming in the troughs cause them to fill up during the adsorption process, although no positive evidence of this has been obtained.

Studies of adsorption equilibria have shown that the adsorption of phenols, from dilute solution, follows Langmuir-type adsorption, giving a linear plot which normally indicates monolayer adsorption. However, linearity is a necessary condition for the application of Langmuir theory, but does not in itself prove the validity of the Langmuir equation, since precise experimental values of the Langmuir constants, for a given system are required, which are very difficult to calculate accurately. Furthermore, the assumption of monolayer adsorption is unreasonable, except at very low solute concentrations, when the number of molecules available to form multilayers is small (125). It is also of note that a Langmuir-type plot is given by most microporous solids, which is only by coincidence, since these are the types of solid least expected to fit Langmuirian theory. Adsorption may hence, take place in multilayers on each fibre, each one following a Langmuir type equation.

This could explain the large adsorption capacity of charcoal cloth, due to the very large numbers of charcoal fibres.

The scanning electron micrographs of charcoal cloth coupled with the findings of Bailey et al (13), show that there is a remarkable lack of macropores or interpores and the porous structure of the cloth is made up almost entirely of micropores. This may be clearly seen when a comparison with micrographs of granular and powdered charcoal is made at a similar magnification. Since these micropores open directly to the surface of the cloth, pore transport may hence be neglected in a study of the kinetics of adsorption on charcoal cloth. It may be assumed therefore, in a suitably turbulent contactor, that the rate controlling step is adsorption onto the surface and into certain micropores near to the surface. The adsorption kinetics are based on multilayer adsorption, with some monolayer adsorption in the surface micropores, since each pore is about one molecule wide, the formation of each layer being described by a Langmuir type equation.

Chapter 6

Theoretical Development and Mathematical Modelling of the System

6 Theoretical Development and Mathematical Modelling of the System

6.1 Introduction

In the current research programme two mathematical models were required. Firstly, a model was required to predict the concentration of pollutant in the liquid phase, at any time, in the absence of charcoal cloth, thus enabling the true amount of adsorption in each continuous experiment containing charcoal cloth to be calculated. Secondly, it was necessary to provide a model which could predict parameters for the system for scale-up purposes.

6.2 Mixing Characteristics of the System

The adsorption section of the continuous system consists of a continuous band of charcoal cloth, which passes through three well stirred contactors, counter-current to the flow of polluted liquid. Prior to the start of an experiment, when the cloth is placed into the contactors, if the water contained any pollutants, they would be rapidly adsorbed, contaminating the cloth and making virtually impossible, the calculation of the amount of adsorption taking place in a contactor at a given time.

Hence, it is necessary at the start of an experiment, to place the cloth into the system with clean water in each stage and then introduce the polluted water to the first contactor. If the concentration 'build-up' in the system is then monitored and the concentration profile for each contactor in the absence of charcoal cloth is known, then the amount of adsorption at a given time, may be calculated. However, it may be noted, that the concentration profile for each contactor without cloth present must be calculated. This may be achieved by modelling the mixing characteristics of the system.

The system may be represented by a cascade of three well-stirred reactors as shown in Figure 6.1, of volume V_1, V_2 and V_3 respectively. Liquid passes through the system at a flowrate of u and the concentration in each tank is C_1, C_2 and C_3 respectively, with a feed concentration of C_o. The model is based on a step change to the feed concentration entering tank 1.

At $t = 0$, $C_o = C_1 = C_2 = C_3 = 0$

At $t > 0$, feed concentration = C_o

Mass balance on tank 1,

$$C_o - C_1 = \frac{1}{x_1} \frac{dC_1}{dt} \qquad 6.1$$

where $x_1 = \frac{u}{V_1}$

taking Laplace transforms and rearranging,

$$C_1 = \frac{C_o}{s(\frac{s}{x_1} + 1)} \qquad 6.2$$

inverting,

$$\underline{C_1 = C_o \, (1 - e^{-x_1 t})} \qquad 6.3$$

The value of C_1 thus obtained, now becomes the inlet concentration to tank 2,

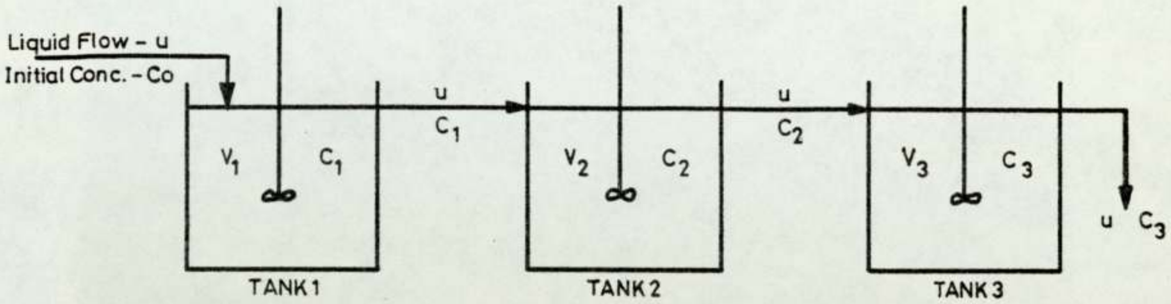

Figure 6.1 The Adsorption Contactors without Charcoal Cloth, for Modelling Mixing Characteristics

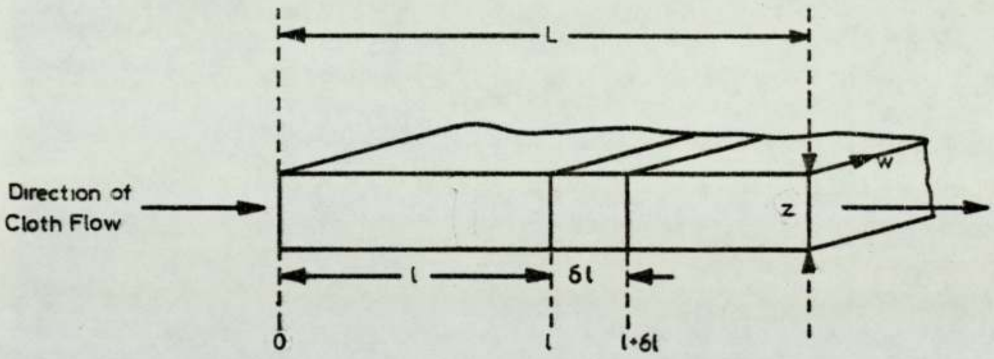

Figure 6.2 A Schematic Representation of the Charcoal Cloth from One Adsorption Contactor

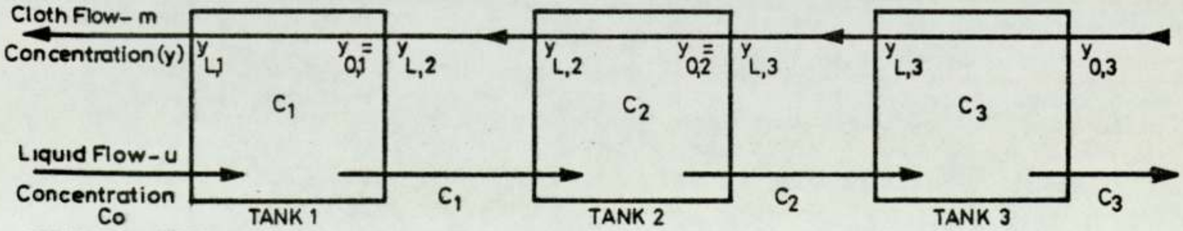

Figure 6.3 The Adsorption Contactors, containing Charcoal Cloth, for use in the Steady State Adsorption Model

Mass balance on tank 2,

$$C_1 - C_2 = \frac{1}{x_2} \frac{dC_2}{dt} \qquad 6.4$$

where $x_2 = \frac{u}{V_2}$

transforming this becomes,

$$C_2 = \frac{C_1}{(\frac{s}{x_2} + 1)} \qquad 6.5$$

substituting 6.2,

$$C_2 = \frac{C_o}{s(\frac{s}{x_1}+1)(\frac{s}{x_2}+1)} \qquad 6.6$$

solving 6.6 using partial fractions and inverting,

$$C_2 = C_o \quad 1 - \frac{1}{(x_2-x_1)} \left[x_2 e^{-x_1 t} - x_1 e^{-x_2 t} \right] \qquad 6.7$$

Again, this concentration becomes the inlet concentration to tank 3. If the same procedure is used of mass balancing over tank 3 and then taking Laplace transforms, this yields,

$$C_3 = \frac{C_o}{s(\frac{s}{x_1}+1)(\frac{s}{x_2}+1)(\frac{s}{x_3}+1)} \qquad 6.8$$

which may be solved using partial fractions and then inverted to give,

$$C_3 = C_o \left[1 - \frac{x_2 x_3}{(x_2-x_1)(x_3-x_1)} e^{-x_1 t} + \frac{x_1 x_3}{(x_2-x_1)(x_3-x_2)} e^{-x_2 t} - \frac{x_o x_1}{(x_3-x_1)(x_3-x_2)} e^{-x_3 t} \right] \qquad 6.9$$

Hence, knowing the feed concentration into tank 1, the liquid flow rate and volume of each tank, then using equations 6.3, 6.7 and 6.9, it is possible to estimate the concentration of pollutant in each tank, at a given time. Experiments were conducted to compare the model of the mixing characteristics of the continuous adsorption equipment with results obtained practically, which are discussed in Chapter 8. Figure 6.4 shows concentration profiles obtained for each tank, with the liquid flowrate and feed concentration most commonly used in experiments on the continuous adsorption equipment. These graphs agree well with similar profiles for reaction in three continuously stirred tank reactors.

When charcoal cloth was introduced to the system and adsorption occurred, it was now possible, using the predicted concentration profiles, to obtain some idea of the efficiency of the adsorption process, by plotting similar concentration profiles for each experimental run, as shown in Chapter 8.

6.3 The Steady State Adsorption Model

It is necessary, when designing an essentially new piece of equipment, to be able to predict the response of this equipment to a given set of circumstances. These could be changes in operation of a current system, or the scale-up of an existing system. The prediction is usually

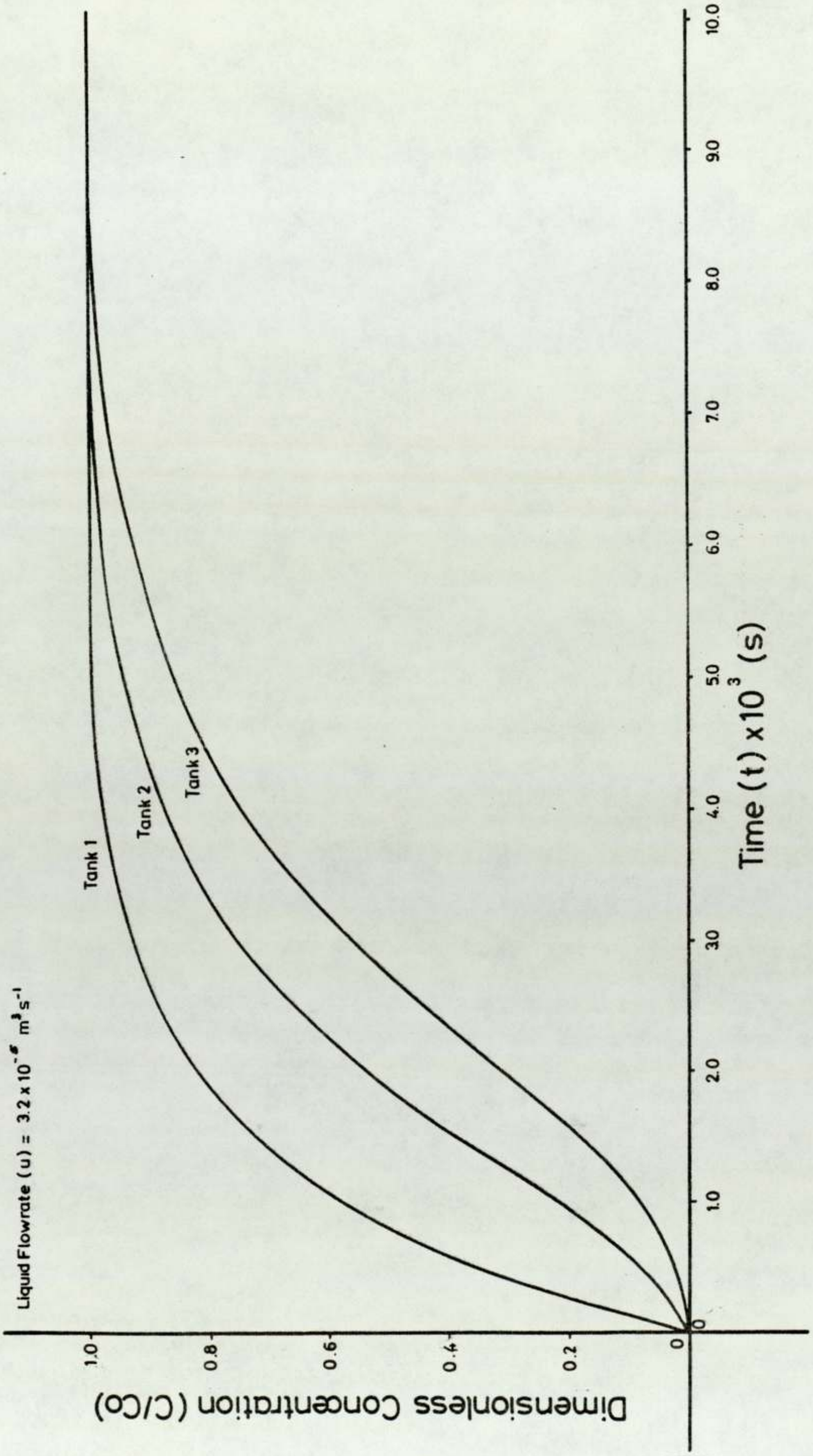

Figure 6.4 Concentration Profiles predicted by the Mixing Model as Response to a Step Change in Feed Concentration

accomplished mathematically by the use of a modelling technique. It was hence decided to postulate a mathematical model for the continuous adsorption system, which however, would be difficult to develop. The primary complication to the successful mathematical modelling of the adsorption system, was the concentration of pollutant in the liquid phase, which varies with time. Therefore, to model the adsorption system, a complex numerical analysis was required, unless the pollutant concentration could be maintained constant. It was hence decided to try to simplify the theoretical system in some way.

From plots of the mixing model it is clear that a pseudo-equilibrium position is reached after a certain time, as shown in Figure 6.4 (p106), when only small increases in concentration are taking place, which is to be expected from this type of exponential plot, as the feed concentration is approached. Initial experiments on the continuous adsorption equipment, using charcoal cloth, indicated that the concentration profiles for adsorption follow a similar pattern as for the mixing model. The profiles have a characteristic shape as in Figure 6.4, however, the values of C/C_o are much lower and it was apparent that after a short time during the adsorption process, a pseudo-equilibrium state occurred where the pollutant concentration in the liquid phase remained almost constant. It was hence decided that the modelling of adsorption on charcoal cloth in the continuous system would initially take the form of a steady state adsorption model.

6.3.1 Adsorption Kinetics on Charcoal Cloth

As mentioned previously, in classical adsorption theory, the rate limiting step, that is the step which controls the adsorption process, could be one of or a combination of three processes, which are:

a. Film diffusion

b. Pore transport

c. Surface adsorption.

Film diffusion involves the movement of pollutant molecules through the stagnant layer surrounding a charcoal particle. However, Weber (14) has indicated that if the liquid phase is agitated sufficiently, then the turbulence causes the breakdown of the external film, making film diffusion negligible. The effect of pore transport on the adsorption of phenols from water was discussed in Chapter 5. It was decided, due to the very small size of the micropores and the fact that these open directly to the surface, that pore transport is negligible in charcoal cloth. It was therefore assumed that most of the adsorption on charcoal cloth takes place on the external surfaces. Hence, assuming:

a. Since each adsorption contactor is vigorously stirred, film diffusion is neglible.

b. Pore transport is negligible.

Adsorption of pollutant on the cloth surface hence takes the form,

Pollutant + Unoccupied Active Site ⟶ Occupied Active Site

This may be re-written,

$$\text{Sorbate} + \text{Sorbent} \longrightarrow \text{Sorbate. Sorbent.}$$

A rate equation for this type of reaction has been presented by Thomas (41), for Langmuir type adsorption and second order Kinetics:

Using equation 2.12,

$$\text{Adsorption rate} = k\,.\left[(\text{sorbate})(\text{sorbent}) - \frac{1}{b}.(\text{sorbate.sorbent})\right] \qquad 6.10$$

where,

k is the forward rate constant for second order kinetics, and

b is the Langmuir equilibrium constant relating to the energy of adsorption.

If,

C_u is the concentration of unoccupied active sites on the 'wet cloth'

C_n is the pollutant concentration in stage n of the system

C_{os} is the concentration of occupied active sites on the 'wet cloth' and

k_d is the reverse rate constant for second order kinetics,

then,

$k_d = -\frac{k}{b}$ and equation 6.10 becomes

$$\text{Adsorption rate} = k\,C_u\,C_n - k_d\,C_{os} \qquad 6.11$$

From Chapter 4, it is clear that large amounts of adsorption occur on charcoal cloth. It was hence assumed that the forward rate constant was much greater than the reverse rate constant and that the latter was therefore negligible. (This is justified in section 6.3.5). Hence, the rate equation used for adsorption on charcoal cloth in the development of a steady state model was,

$$\text{Adsorption rate} = k\,\mathcal{C}_u\,C_n \qquad 6.12$$

assuming second order kinetics and since Langmuir type adsorption is taking place, as shown in Chapter 4.

6.3.2 Development of the Mathematical Model

Consider a single adsorption contactor; stage n

a. Mass balance over the liquid phase,

$$u\,C_{n-1} = u\,C_n + \text{Rate of removal} \qquad 6.13$$

b. Mass balance over the cloth (assuming wet cloth)

For a length of cloth L in stage n, consider an element of length δl, of distance l along the cloth, as shown in Figure 6.2.

$$m\,\mathcal{C}(os, l).p + \text{rate of adsorption} = m\,\mathcal{C}(os, l + \delta l).p \qquad 6.14$$

where,

m is the mass flowrate of the charcoal cloth

p is the mass of phenol per occupied active site.

from equation 6.12,

$$\text{Adsorption rate} = k\mathcal{C}_u\,C_n.$$

for the control volume, this becomes,

Rate of adsorption on charcoal cloth $= k.\mathcal{C}u,l.Cn.z.w.\rho c.\delta l$ 6.15

where,

ρc is the density of the wet cloth.

Substituting 6.15 into 6.14 and expanding gives,

$$m\,C_{os,l}\,.p + k.\mathcal{C}_{u,l}\,.Cn.z.w.\rho c.\,\delta l = m\mathcal{C}_{os,l}\,p + mp\,\frac{(d\mathcal{C}_{os,l}}{dl}\,.\,\delta l + \ldots \qquad 6.16$$

Rearranging 6.16,

$$(k.Cn.z.w.\rho c)\,\mathcal{C}u,l = mp\,\frac{d\,\mathcal{C}os,l}{dl} \qquad 6.17$$

If C_T represents the total number of active sites, then,

$$\mathcal{C}u = \mathcal{C}_T - \mathcal{C}os \qquad 6.18$$

Hence, for the total length of cloth in stage n,

$$\int_{l=0}^{L} \frac{d\mathcal{C}os,l}{\mathcal{C}_T-\mathcal{C}_{os,l}} = \frac{k.z.w\rho_c}{m\ p}\,.\,C_n.\,L \qquad 6.19$$

$$-\ln\,(\mathcal{C}_T - \mathcal{C}os,l)\,\Big|_{l=0}^{L} = \frac{k.z.w.\rho c.Cn.L}{mp} \qquad 6.20$$

which becomes, for stage n,

$$-\ln\,\left[\frac{\mathcal{C}_T-\mathcal{C}os,L}{\mathcal{C}_T-\mathcal{C}os,0}\right]\Bigg|_{stage\ n} = \frac{k\ z\ w\rho c}{mp}\,.\,Cn.L \qquad 6.21$$

Equation 6.21 may be rewritten

$$\ln \left[\frac{y^* - yo}{y^* - yL}\right] = \frac{KL}{V} . Cn \qquad 6.22$$

where,

K is the forward rate constant for surface adsorption on charcoal cloth in the steady state model (p k/p)

$y^* = \rho_{Tp} = \frac{\text{mass of phenol}}{\text{unit mass of wet cloth}}$ (under saturation conditions)

$y = \rho osp = \frac{\text{mass of phenol}}{\text{unit mass of wet cloth}}$

v is the velocity of wet cloth in each stage

$\frac{L}{V}$ is the residence time of cloth in each stage.

An overall balance on stage n gives,

$$u\, C_{n-1} + m\, yo \Big|_n = u\, Cn + m\, y_L \Big|_n \qquad 6.23$$

Using equation 6.22 and 6.23, it is possible to calculate concentration values for each tank, if the desired effluent concentration and the feed concentrations are known.

6.3.3 Calculation of the Forward Rate Constant

The value of the forward rate constant must be known for the successful operation of the steady state adsorption model. Rate constants for adsorption on granular charcoal are usually found empirically, which is also true for adsorption on charcoal cloth. Preliminary experiments had shown that the major pollutant load is removed in the first tank, while the second and third tanks act as polishing stages or safety overflow tanks, to cope with a surge in input flowrate. However, of more interest was the fact that in each tank, a pseudo-equilibrium occurred after a short time, at which stage the rate of adsorption and hence the rate constant do not vary.

Hence, knowing the value for the equilibrium pollutant concentration from empirical data, the rate constant could be calculated. It was decided to base the calculation of the rate constant on results from tank 1, since the greatest quantity of pollutant is removed in this tank.

The amount of pollutant on the cloth, on recycle to tank 1 was assumed to be negligible. The method used for calculating the forward rate constant is presented below:

Consider tank 1, Figure 6.3,

Equation 6.23,

$$u\ (C_o - C_1) = m\ (y_{L,1} - y_{o,1})$$

The ratio of liquid to cloth flow rate (u/m) is calculated, while the feed concentration (C_o) is known. The value for the equilibrium pollutant concentration (C_1) is found from empirical data. The pollutant concentration on the cloth entering tank 1 ($y_{o,1}$) is assumed to be negligible. The pollutant removed in tank 1 ($y_{c,1}$) may then be calculated, and then substituted into equation 6.22.

$$\ln \left[\frac{y^* - y_{o,1}}{y^* - y_{L,1}} \right] = \frac{K\ L}{V} \quad C_1$$

The adsorption capacity of the cloth at saturation (y*) is known from chapter 4 and the cloth residence time in tank 1 (L/V) is calculated. The forward rate constant (K) may now be calculated.

Initial experiments involving the forward rate constant were conducted with cloth passing through one tank alone, to make the pollutant concentration on the cloth entering tank 1 negligible. However, the calculation of the rate constant in the steady state model, uses the experimental values for equilibrium pollutant concentration obtained from each individual experiment. It may be argued that this cannot be justified, since most of the experiments are conducted using three stages, with the cloth polluted on entry to tank 1. However, it can be shown that the system may be operated for many hours, before the pollutant concentration on the cloth has a significant effect on the model.

Consider Figure 6.3,

At equilibrium, a typical experiment starting with a feed of 0.1 kgm^{-3} (100 mg/l) has pollutant concentrations in each tank as follows:

C_o - 0.1 Kg m^{-3}

C_1 - 0.05 Kg m^{-3}

C_2 - 0.02 Kg m^{-3}

C_3 - 0.01 Kg m^{-3}

If the liquid flow rate is 3.2 x 10^{-3} m^3s^{-1} and the cloth mass flowrate is 1.0×10^{-4} Kgs^{-1}. Then assuming that the pollutant concentration on the cloth entering tank 1 is negligible from equation 6.23,

$y_{L,1} = 0.016$ kg/kg and, if $y^* = 0.299$ kg/kg for phenol substituting into equation 6.22,

$$\ln \left[\frac{y^* - y_{o,1}}{y^* - y_{L,1}}\right] = \ln (1.057)$$

$$= 0.0554$$

However, if the above values for the pollutant concentration in the liquid are taken, then,

$y_{L,2} = y_{o,1} = 0.013$ kg/kg and, $y_{L,1} = 0.029$ kg/kg

$$\ln \left[\frac{y^* - y_{o,1}}{y^* - y_{L,1}}\right] = \ln (1.059)$$

$$= 0.0573$$

This is due to the logarithmic series,

$$\ln (1+x) = x - \frac{x^2}{2} \quad .....$$

where a change in value of 1.057 to 1.059 would make little difference.

Hence, the assumption of negligible pollutant concentration on the cloth entering tank 1, makes little difference to the forward rate constant, unless the cloth is continuously recycled for long periods without regeneration.

6.3.4 Operation of the Adsorption Model

The steady state adsorption model may be operated as follows:

Consider Figure 6.3,(p.103)

Tank 3, kinetic equation, from equation 6.22

$$\ln \left[\frac{y^* - yo,3}{y^* - yL,3}\right] = \frac{K\ L}{V} \cdot C_3 \qquad 6.24$$

It may be assumed, if the cloth is not recycled for long periods without regeneration, that the cloth is not polluted on entry to tank 3.

Hence,

$$yo,3 = 0$$

The equilibrium value for adsorption capacity of charcoal cloth, for a given chemical, (y^*) is known from chapter 4 and the cloth residence time in tank 3 may be calculated. The rate constant (K) may be calculated, from empirical values for the equilibrium pollutant concentration, as shown in section 6.3.3, and the value of C_3, that is, the final effluent concentration is set. Substituting these values into equation 6.24, the concentration of pollutant taken from tank 3 by the cloth ($yL,3$) may be calculated.

From equation 6.23,

$$u\ (C_2 - C_3) = m\ (yL,3 - yo,3) \qquad 6.25$$

The ratio of liquid flowrate to cloth mass flowrate is known. Substituting C_3 and yL,3 from equation 6.24, the liquid concentration in tank 2 (C_2) may hence be calculated. This process may be repeated for tank 2, to obtain a value for C_1 and for tank 1 to obtain a calculated value for the feed concentration, C_o. Having specified a feed concentration, a comparison may be made with the calculated value. If a given tolerance is not reached, a new value for C_3 may be guessed and the process restarted.

A computer program has been developed to carry out the iteration process, as presented in appendix II. The program also calculates the rate constant, from a given value of the equilibrium pollutant concentration in tank 1. Since the system could consist of two or more adsorption contactors, the program has also been adapted to cope with this.

6.3.5 Effects of the Reverse Rate Constant on the Rate Equation

During the development of the adsorption kinetics equation, it was stated that, due to the large amounts of adsorption on charcoal cloth, the forward rate constant is much larger than the reverse rate constant, making the latter negligible. However, it is necessary to justify such an assumption.

Recalling equation 6.11 (p.109)

$$\text{Adsorption rate} = k\mathcal{C}uCn \; - \; kd\ \mathcal{C}os$$

If equation 6.11 holds, equation 6.19 becomes,

$$\int_{l=0}^{L} \frac{d(\mathcal{C}os,l)}{((kCn)(C_T-\mathcal{C}os\ l)-kd\ \mathcal{C}os\ l)} = \frac{z\ w\ \rho c}{mp} \cdot L \qquad 6.26$$

Since $kCn\mathcal{C}_T$ is constant, equation 6.26 becomes, on integration,

$$\ln \left[\frac{(kC_n\mathcal{C}_T) - (kC_n + kd)\ \mathcal{C}os,L}{(kC_n\mathcal{C}_T) - (kC_n + kd)\ \mathcal{C}os,o}\right] = \frac{(kC_n + kd)\ zw\rho_c L}{mp} \qquad 6.27$$

If $y^* = \mathcal{C}_Tp$ and $y = \mathcal{C}osp$ (p.112), then substituting in equation 6.27.

$$\ln \left[\frac{(kC_ny^*) - (kC_n + kd)\ yL}{(kC_ny^*) - (kC_n + kd)\ yo}\right] = \frac{(kC_n + kd)\ zw\rho_c L}{mp} \qquad 6.28$$

For adsorption to take place, the value of k must always be greater than kd. However, from equation 6.28, if a reverse rate constant half as large as the forward constant is used, the difference in calculated feed concentration in the steady state model, compared to a situation not using a reverse rate constant is less than 0.1%. The forward rate constant is so much larger than the reverse rate constant that the latter is negligible, and the assumption made above to this effect is hence justified.

It has been shown then, that the system without charcoal cloth present may be modelled on three continuous stirred-tank reactors in series. Furthermore, a forward rate constant for adsorption on charcoal cloth at steady state may be calculated, from equilibrium pollutant concentration empirically obtained. Finally a steady state, iterative, adsorption model has been developed.

Chapter 7

Experimental Apparatus

Plate 7.1

The Adsorption Contactors and Coated Driven Rollers

1. Neoprene-rubber coated driven roller
2. Plastic inlet tube
3. Adsorption contactor
4. Perspex support for idler roller in contactor base
5. Polythene dividing wall
6. Undriven roller
7. Bearing for the shaft of the driven rollers
8. Thermocouple (NiCr/NiAl)
9. Outlet from stage 3

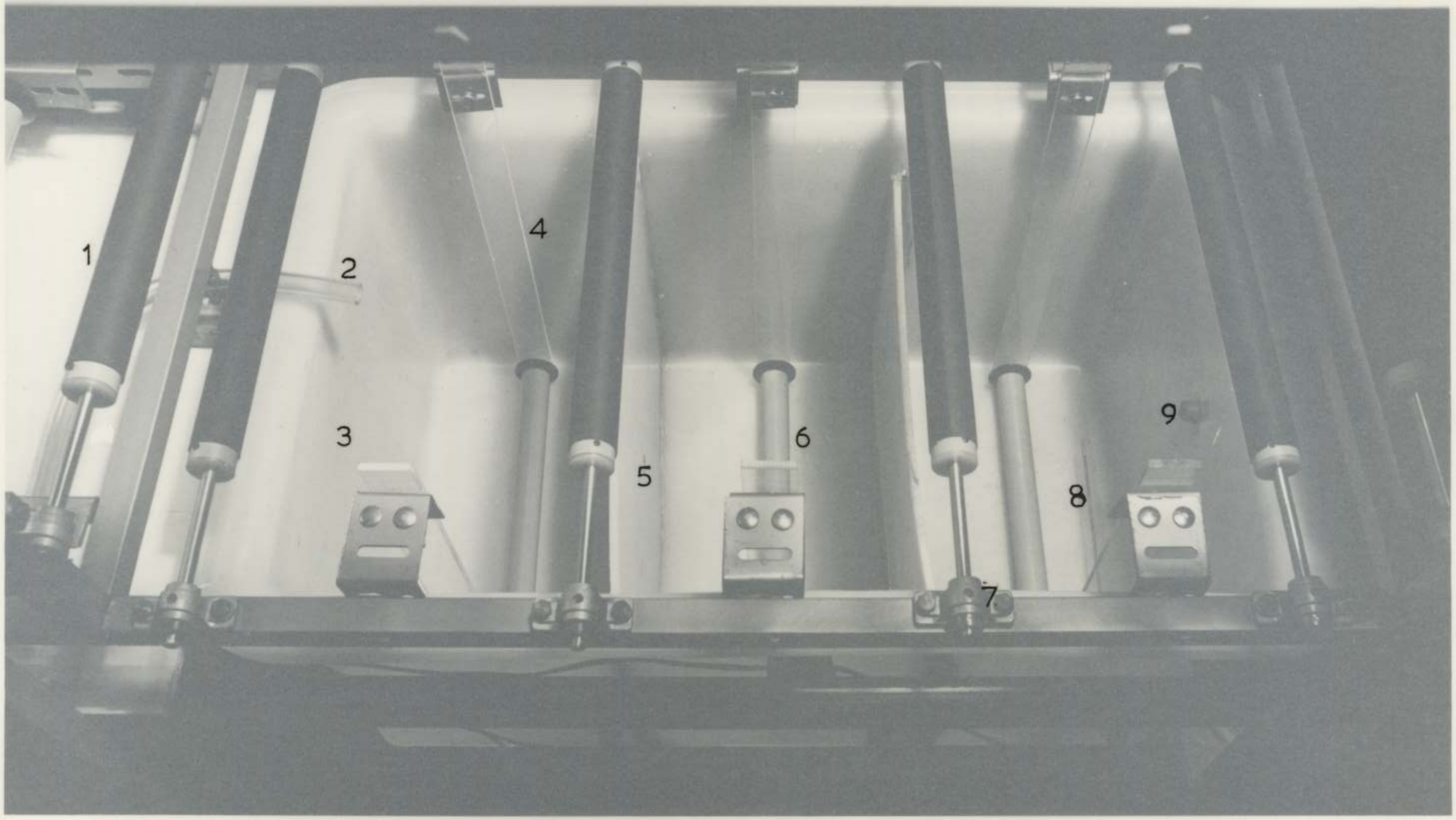
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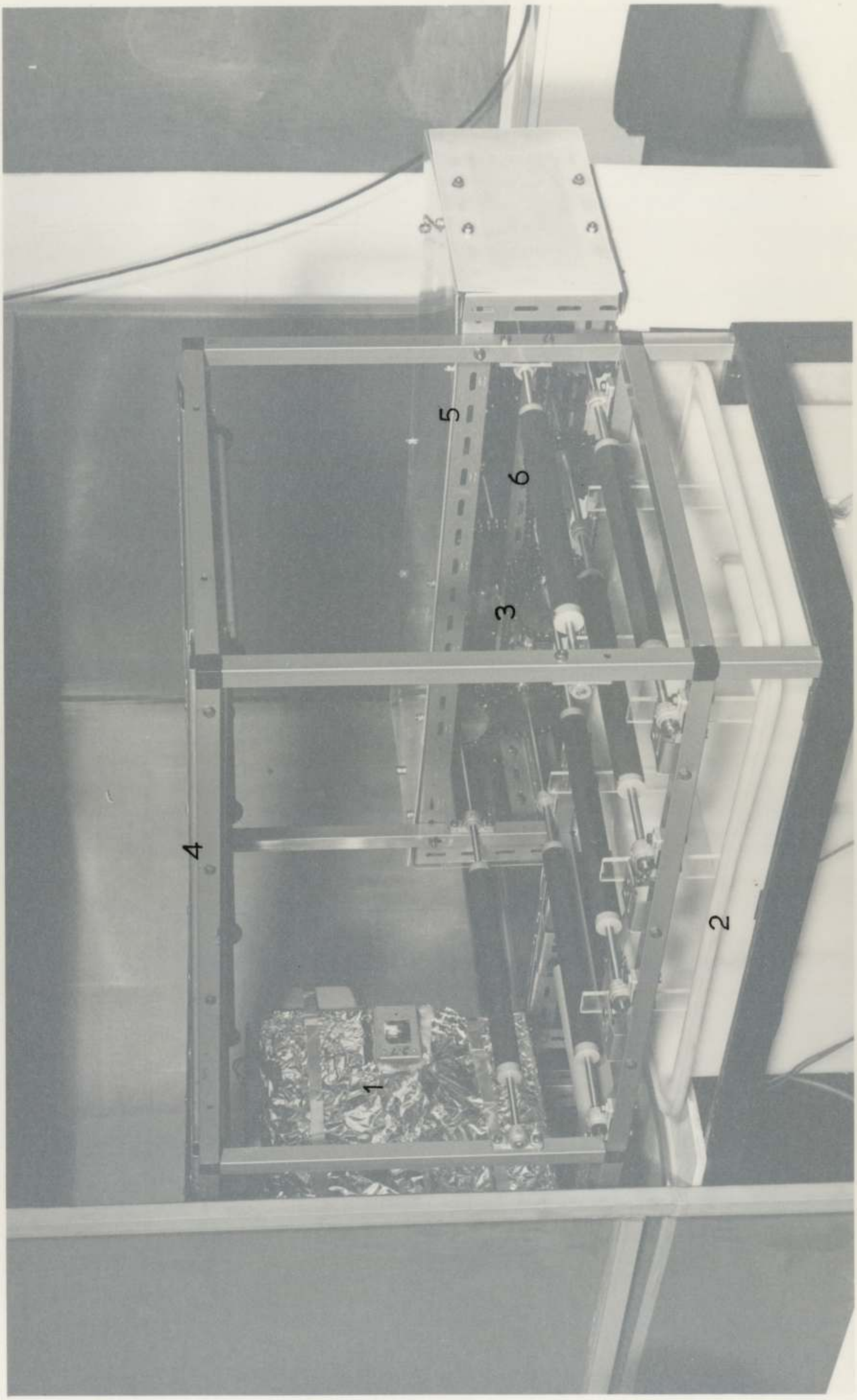
Plate 7.2

A General View of the Continuous Adsorption System

1. Regeneration heater (coated with foil to prevent heat loss).
2. Adsorption contactor
3. Chain drive for the cloth transport system
4. Support for overhead idler rollers
5. Chain guard
6. Driven roller with opposite revolution (see section 7.1.3)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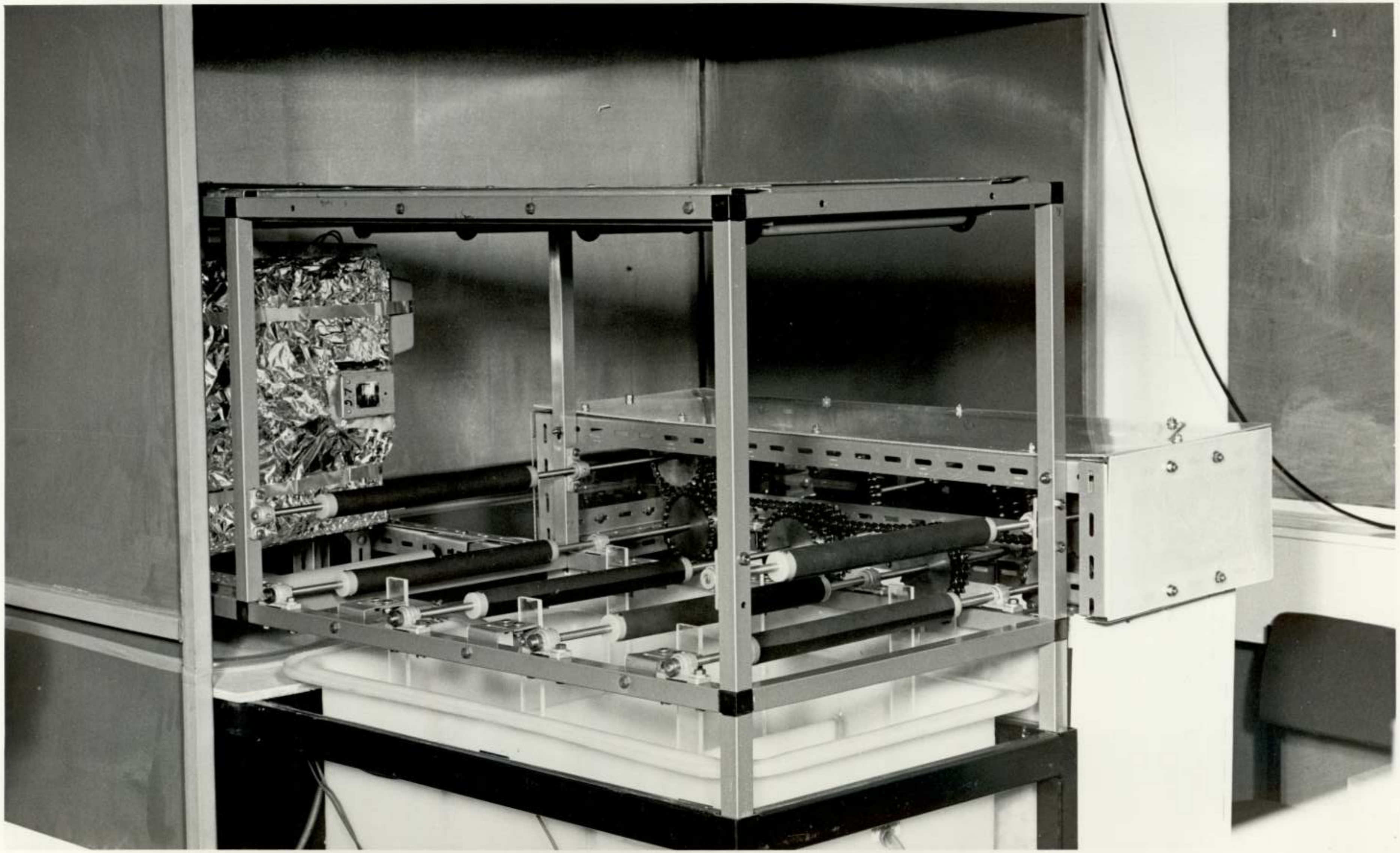
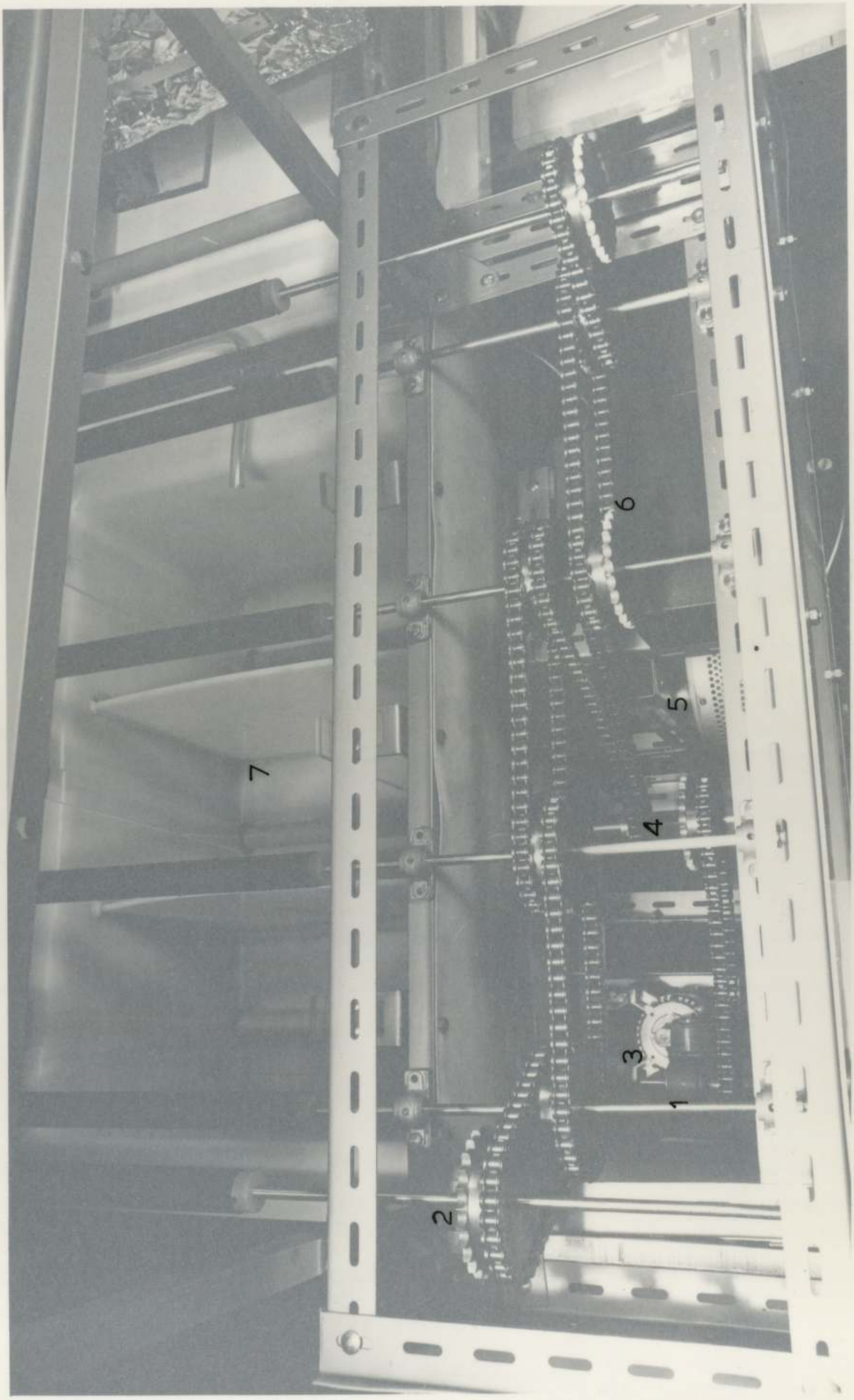


Plate 7.3

The Chain Drive for the Cloth Transport System

1. 6.5 cm diameter driving cog (13 teeth on a 1.25 cm pitch)
2. 11.3 cm diameter driven cog (25 teeth on a 1.25 cm pitch)
3. 5 r.p.m. motor
4. Gearing mechanism
5. Variable speed controller
6. Ether temperature controller for the regenerator
7. Adsorption contactor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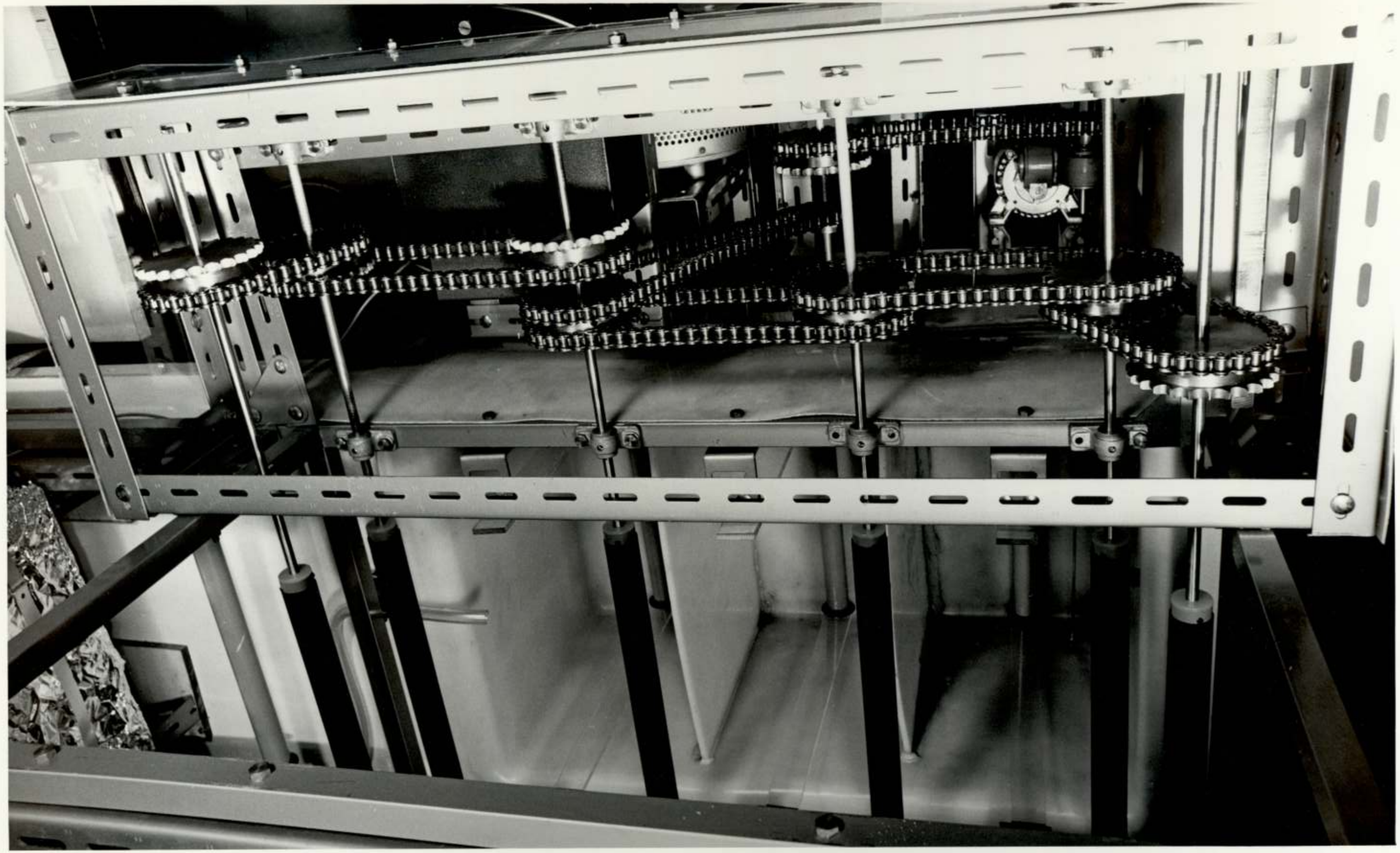
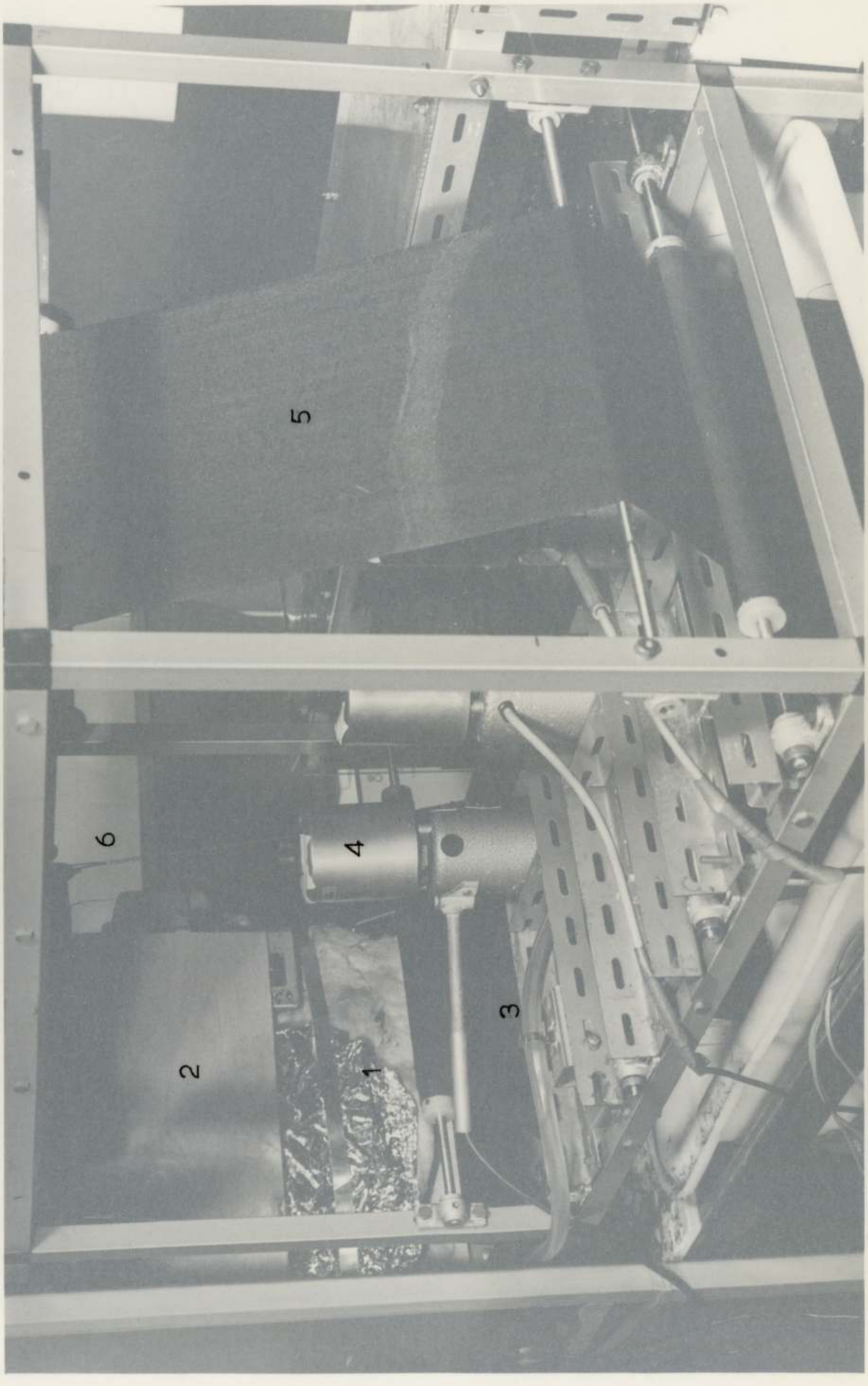


Plate 7.4

A General View of the Continuous Adsorption System
Including Charcoal Cloth

1. The regeneration heater
2. Heat shield
3. Inlet tube to stage 1 stirrer vortex
4. Variable speed controlled stirrer
5. Charcoal cloth (0.3 m wide x 6.5 m long)
6. Cloth tensioning roller (spring loaded)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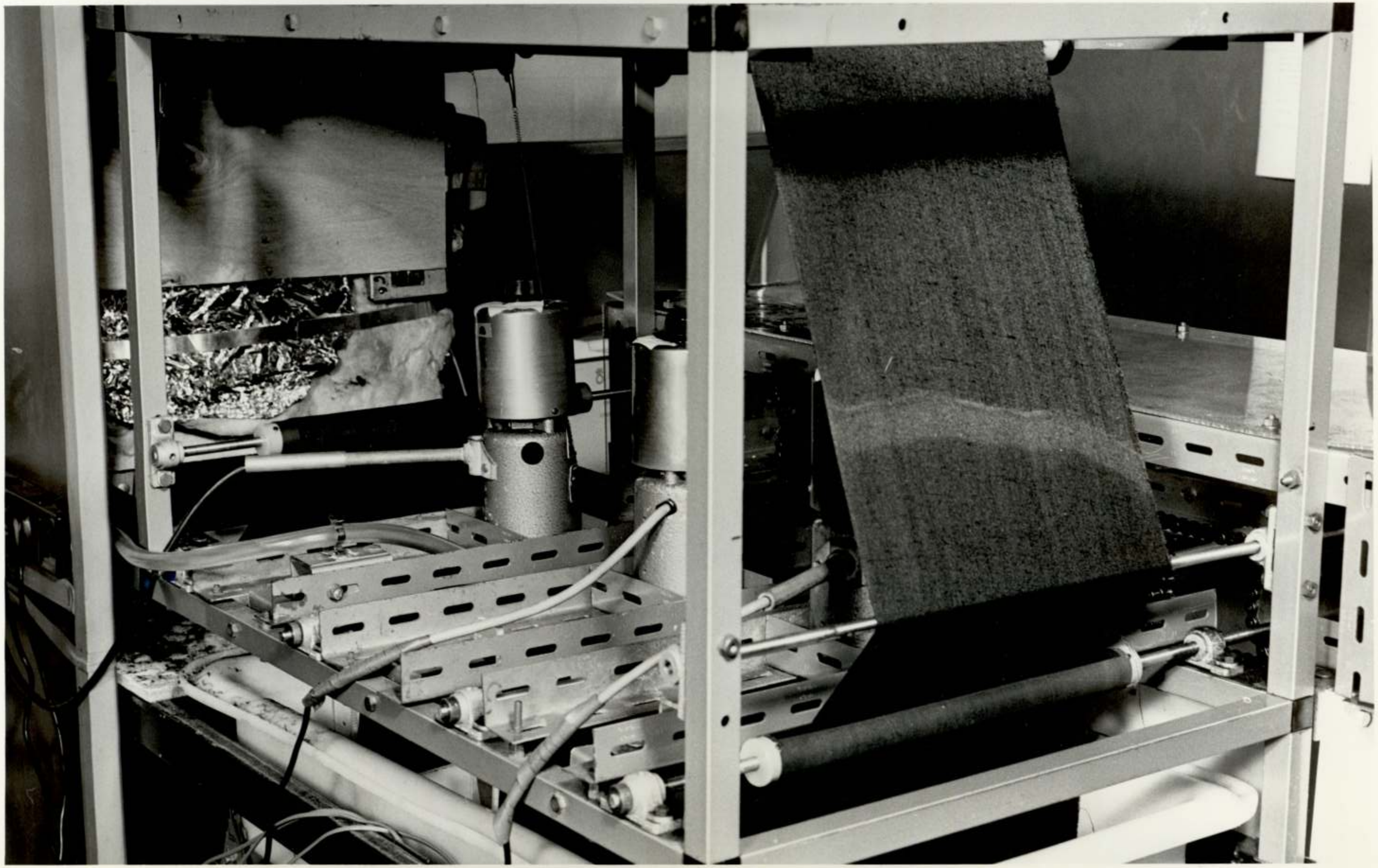

7 Experimental Apparatus

This chapter contains general information concerning the continuous adsorption system. It includes general descriptions of the main items of equipment, related to photographs taken of each one. Also, details of the commissioning of the system are included, although these are mainly with respect to mechanical aspects, since most of the early adsorption experiments are discussed in chapter 8.

7.1 Description of the Continuous Adsorption Equipment

Each section contains basic information about the design of each specific item of equipment, to conduct the desired effluent treatment programme. The system is shown in a schematic form in figure 7.1.

7.1.1 The Adsorption Contactors and Ancillary Equipment

The adsorption contactors were constructed from a standard 110l rectangular polythene tank, as shown in plates 7.1, 7.2 and 7.3 of dimensions 0.74 m x 0.44 m x 0.39 m. The three stages or tanks were made by dividing the tank into equal sections, using polythene dividers as indicated in plate 7.1 and figure 7.1. The dividers were secured using polythene welding on both sides, which is visible in plates 7.1 and 7.3. The join was then

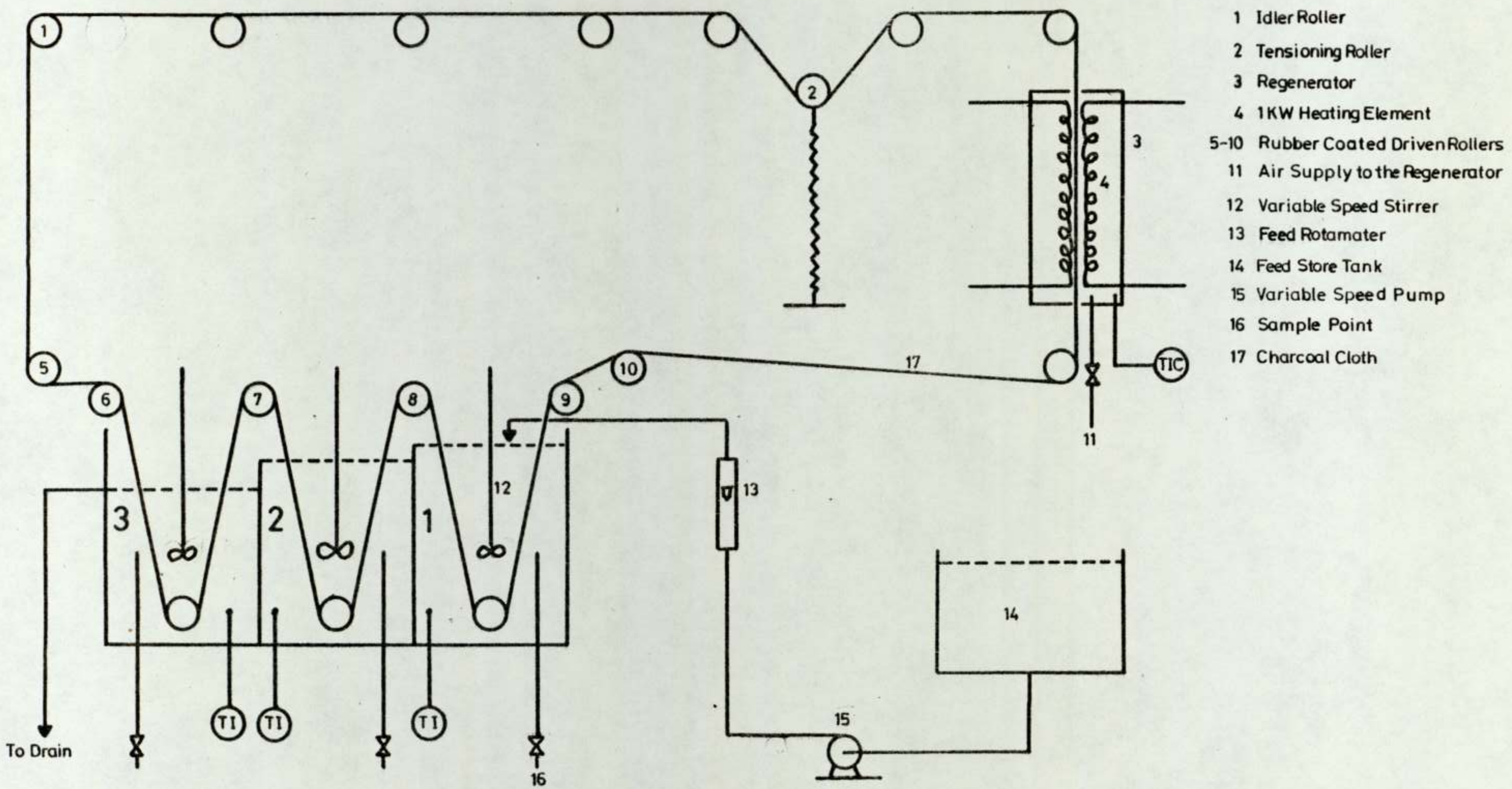

Figure 7.1 The Continuous Adsorption Equipment

covered using an adhesive compound such as 'Araldite'. The liquid originally entered the first contactor through a length of plastic hose mounted as in plate 7.1. However, this was situated behind the cloth and flowing into an area of low turbulence. The inlet was eventually mounted directly onto the support of the stirrer for stage 1, allowing flow directly into the stirrer vortex, plate 7.4. Hence, the pollutant was quickly dispersed throughout the first stage. Flow from stage to stage was achieved using a weir system, created by making one divider slightly smaller than the next, as in figure 7.1 and plates 7.2 and 7.3, giving each stage the following dimensions:

Stage 1 : 0.25 m x 0.44 m x 0.33 m = $3.6 \times 10^{-2} m^3$
Stage 2 : 0.24 m x 0.44 m x 0.31 m = $3.3 \times 10^{-2} m^3$
Stage 3 : 0.25 m x 0.44 m x 0.26 m = $2.9 \times 10^{-2} m^3$

The effluent from tank 3 was then removed using plastic piping and then pumped to the drain, as shown in figure 7.1. A sample point was mounted at the base of each stage, to allow the easy withdrawal of samples.

The only ancillary equipment visible on the plates are the thermocouples and the stirrers. The thermocouples in plate 7.1, were mounted in each stage to allow monitoring of the temperature, since any change in this could alter the adsorption capacity of the cloth. The stirrers, shown in figure 7.1 and plate 7.4, were mounted in the centre of each tank, having 6 cm diameter blades and variable speed control, although being maintained in general at around 20 r.p.s. This was found to be sufficient to provide the necessary turbulence to comply with modelling assumptions. Other ancillaries are concerned with the actual feed water supply. The feed water used in all of the experiments was made in a holding tank, indicated in figure 7.1. The water was then pumped, using a small centrifugal pump, with a variable speed attachment, to allow changes in flowrate, through a size 10 S rotameter and then into tank 1.

7.1.2 The Regeneration System

The regeneration system described is the one giving the most favourable experimental results, as indicated in chapter 8. Two main types of regeneration system were used, firstly one using heat to regenerate the cloth and secondly, one using chemical reaction to remove the pollutants from the cloth surface. The chemical reaction system removed pollutant by reacting it with a 4% solution of sodium hydroxide, in the case of phenol, giving sodium phenate. This was washed from the cloth to a bath where acid could be added and phenol recovered. However, it was found that this system would not regenerate successfully.

The equipment giving better results used a traditional form of regeneration, that is, passing the cloth through a heater and burning off the pollutants. The regeneration heater consisted of two 1 KW elements, supplying radiant heat. These were mounted on a support structure, 15 cm apart and the cloth allowed to pass through, as shown in plate 7.4. The support structure was then covered with sindanyo, a non-harmful asbestos type material and the whole system was then lagged. The temperature in the heater was monitored by NiCr/Ni Al thermocouples, on both sides of the cloth and at the top and base of the regenerator. These thermocouples indicated that while a temperature of 100^{o}C could be maintained at the base of the regenerator, with both elements switched on, convection currents caused this to rise to in excess of 500^{o}C at the top. The temperature was controlled very basically, using a Pye Ether on/off controller, linked to one of the base thermocouples. The regeneration system is illustrated in figure 7.1 and plates 7.2 and 7.4.

7.1.3 The Charcoal Cloth and Transport Mechanism

The charcoal cloth used in these experiments was manufactured from loomstate viscose rayon, made in Rosebank, Northern Ireland giving the batch of cloth its name. The properties of each cloth run used are shown in appendix VI. Basically, for these experiments, the two chief interests were that the cloth was, firstly strong enough to be able to pass around the cloth transport system. Secondly a high degree of activity was necessary, to remove the desired pollutant quantities with no loss in strength. These conditions were met by all of the cloth types used in this experimental programme. Each of the two criteria mentioned were tested on the plant where the charcoal cloth was manufactured. Firstly, the strength was tested by taking 2 cm squares of cloth and pulling them apart in the warp and weft directions. The breaking strength was then given as the strain (in kg cm^{-2} of cloth) required to result in cloth breakage. Secondly, the activity was measured using a silicone-oil heat of wetting test. This was conducted by measuring the amount of heat generated by a known amount of the cloth, when ground and placed into a test tube containing silicone oil. The temperature change was registered using six thermocouples in place within the test tube linked to a chart recorder.

In each experiment, a piece of cloth about 6.5 m long and 0.3 m wide was placed onto the cloth transport system and the loose ends joined using a suitable adhesive material, determined by the regenerator temperature. This completed the cycle and gave a continuous loop of charcoal cloth. The tension was maintained in the cloth during an experiment, by placing a roller over the top of the cloth and attaching springs, fixed to the chassis, to each end of the roller. The system, indicating the charcoal cloth and tensioning device, is shown in plate 7.4.

The cloth transport system consisted of both driven and idler rollers. The undriven rollers were situated at various positions around the cloth loop as shown in figure 7.1. These rollers were approximately 38 cm long and 3 cm in diameter, containing shoulders with clip on bearings for attachment to 'Dexion' structures. Figure 7.1 and plates 7.2 and 7.4 show that these idler rollers were positioned at various intervals around the system, including one at the base of each adsorption contactor, as in plate 7.1. When the design of a motorised transport system was studied, it was considered that for successful adsorption to take place, the cloth would need to be moved through each contactor at a constant slow speed. Using a design as in figure 7.1, one driven roller would have caused uneven transport through the contactors and probably breaking of the cloth due to uneven tensions. It was decided, therefore, to have a driven roller for each section of the adsorber and two more at each end of the system as shown in plate 7.1. The rollers were of the same dimensions as the undriven ones, but covered with neoprene rubber to aid friction on the roller surface. Each driven roller was mounted on a 1 cm diameter stainless steel shaft. The drive system for the rollers is shown in plate 7.3. It was decided that each driven roller would be linked as shown in the plate and driven by a common motor. As explained in chapter 8, it was decided that a residence time for cloth in the adsorption section of about 25 minutes was required to give a favourable cloth to pollutant flowrate ratio and to this end, a 'Parvalux' 5 r.p.m. double reduction worm gear motor was used. Prior to the actual movement of the driven rollers, this motor speed was again geared down twice more by using toothed cogs of 6.5 cm:11.3 cm, with the teeth having a 1.25 cm pitch. The shafts on which the driven rollers were mounted were 1 cm diameter and moved by using 11.3 cm diameter toothed cogs, again with a pitch of 1.25 cm. The chain drive, as shown in plate 7.3 hence maintained the driven rollers at a constant speed of 1.5 r.p.m, giving a cloth residence time in the system of about 25 minutes as required. It was possible to vary the speed of the motor using a variable rheostat control. However, friction in the system limited the range of this variation. Thus, a constant speed was maintained.

7.2 Commissioning

This section is intended, generally to point out teething troubles encountered with the mechanics of the system, at the commissioning stage. Various qualitative experiments were conducted on the cloth, however the bulk of the early experiments on its adsorptive properties are discussed in chapter 8.

7.2.1 Cloth Transport System

Firstly, uncarbonised rayon was placed in the system and the cloth transport started, with the net result that the cloth was able to be continuously moved around the loop without any breakage. The same experiment was then conducted using activated charcoal cloth, but the cloth tore very easily and also slack cloth occurred on the return section of the loop. It was discovered that the cloth tore at one roller moving in a counter rotation to the others. However, the drive action of the rubber coated rollers was so effective that the counter rotation caused the cloth to tear; hence this roller was disconnected. The slack cloth in the return section of the loop was tightened by using a spring tensioning roller, as described in the previous section.

7.2.2 Adsorption Contactors

These were tested, firstly by putting water into each of the sections in turn and testing for leaks, then filling the whole adsorber with water and again testing for leaks. It was found that the polythene welds needed to be substantially reinforced and then bound, using a strong adhesive to prevent any leakage from section to section.

The stirrers were tested by filling the adsorber with water, switching on the stirrers and injecting a dye into the stirrer vortex. It was apparent that very good mixing could be obtained and that the dye reached stage 3 within 5 minutes. The same experiment using charcoal cloth indicated that most of the dye could be removed in the first adsorber section. It also indicated that organics could be removed by the system and presented a good basis for continuing the experimental programme.

7.2.3 Regeneration System

The heater was first tested for temperature and control, with the net result that the on/off temperature controller could maintain a temperature in excess of 100^{o}C at the heater base and 500^{o}C at the top. It was envisaged that this would cause any excess water to be evaporated and the resultant steam could form a reactivating agent. However, these high temperatures, when used with charcoal cloth, caused severe burning and difficulties in joining the loop together.

It was thought that passing air through the furnace, as a reactivation agent, would lower the temperature and increase regeneration, but this was unsuccessful. However, it was found that a better regeneration could be obtained by using only one regenerator element, as explained in chapter 8. This caused the temperature in the furnace to drop, thus removing problems caused by burning and joining. It was thought that with two elements operating, the rate of heating was excessive, while with only one element working, a steady rise in temperature occurred. This lower rate of heating resulted in better volatilisation and decomposition of the phenolic compounds and eventual breakdown in the heater exhaust. The higher heating rate achieved with two elements caused carbonisation of the phenols, blocking the pore structure.

Hence, mechanically, the system worked very well, however, further development would require several changes. Firstly, the partitions in the adsorption contactor would require either welding in much more efficiently or a stainless steel tank with welded partitions would be required. A more precise way of maintaining tension in the system would be required. The regeneration heater would need redesigning, as it was only intended to establish whether, in this type of equipment, a successful regeneration could be obtained.

Chapter 8

Operation of the Continuous Adsorption Equipment

8 Operation of the Continuous Adsorption Equipment

8.1 Mixing Characteristics of the System

The system operates dynamically, as mentioned in chapter 6, so that, if there is any chemical present in the contactors at the same time as the charcoal cloth, it will be adsorbed, prior to saturation. Hence, no chemical concentration may be 'held' in the contactors in the presence of charcoal cloth, making the measurement of absolute amounts of adsorption difficult. It was hence necessary to be able to estimate what the concentration in the contactors would be in the absence of charcoal cloth, so that when cloth was introduced to the system, a measure of the amount of adsorption taking place could be calculated. As explained in chapter 6, this was achieved by modelling the system on a step change to three continuously stirred contactors in cascade. The experimental procedure adopted to verify the mixing model and the results obtained are presented and discussed in the next three sections.

8.1.1 Experimental Procedure and Results

The adsorption contactor section is shown in Figure 7.1 and discussed in chapter 7. It consists of three contactors, each containing a stirrer and facilities for withdrawing samples from the base through a sampling valve. The contactors are connected by a weir and the final effluent flows to the sewer.

At the beginning of each experiment a stock solution of the chemical to be investigated was made and stored in tanks. (Phenol was used throughout the mixing tests and most of the adsorption tests, as explained in chapter 4 and 5). The contactors were then filled with clean water and the stirrers switched on and maintained at a speed of about 20 r.p.s. The phenol solution was then pumped from the stock tank, through a rotameter and into the vortex of the stirrer in the first tank, at a given flowrate. This provided immediate mixing, as indicated at the commissioning stage by the use of coloured dyes. Periodically, throughout the experiment, samples were withdrawn from each tank and analysed, so that the build up of pollutant concentration in each tank could be monitored. The experiments were terminated, as the concentration of chemical in the first tank approached that in the stock solution. An experiment was also conducted with plain uncarbonised rayon, the base material for charcoal cloth, in the contactors, to test the physical mixing properties of the system with cloth present.

The flowrate used for the experiments was 3.2×10^{-5} ms^{-1}, obtained from preliminary experiments at the commissioning stage as the optimum flowrate, giving a residence time of about 50 minutes in the contactors.

The chemical concentration used was about 0.1 kgm^{-3} (100 mg/l) as indicated in chapter 4. The results are presented in appendix I, tables 3 and 4, from which it may be seen that the concentration values obtained at various intervals throughout the experiments, are reproducible to within about 5% of each other. This is an indication that the tanks are well mixed and that no 'pockets' of chemical are causing concentration fluctuations. The concentration profiles obtained are shown in figure 8.1 and it can be seen that these follow traditional lines for this type of system, as shown in figure 6.4. The profiles are all of the type:- $(1-\exp^{-nt})$, reaching around 92%, 83% and 66% of the initial or maximum concentration for tanks 1-3 respectively; compared with predicted values of 95%, 84% and 68% for each tank after 1 hour. The inclusion of the untreated rayon in each tank in experiment PCRMCRB11, does not hinder the mixing process, since the concentration obtained compares very well with those for the previous experiments. This is illustrated in figure 8.1, from which it is noticeable that the results from experiment PCRMCRB11 follow the profiles of experiments PCRMCRB8 and 10, to within the limits of experimental error.

8.1.2 Comparison of the Experimental Results with the Mixing Model

It was clear from the experimental results that the system, with continuous stirring, yields reproducible

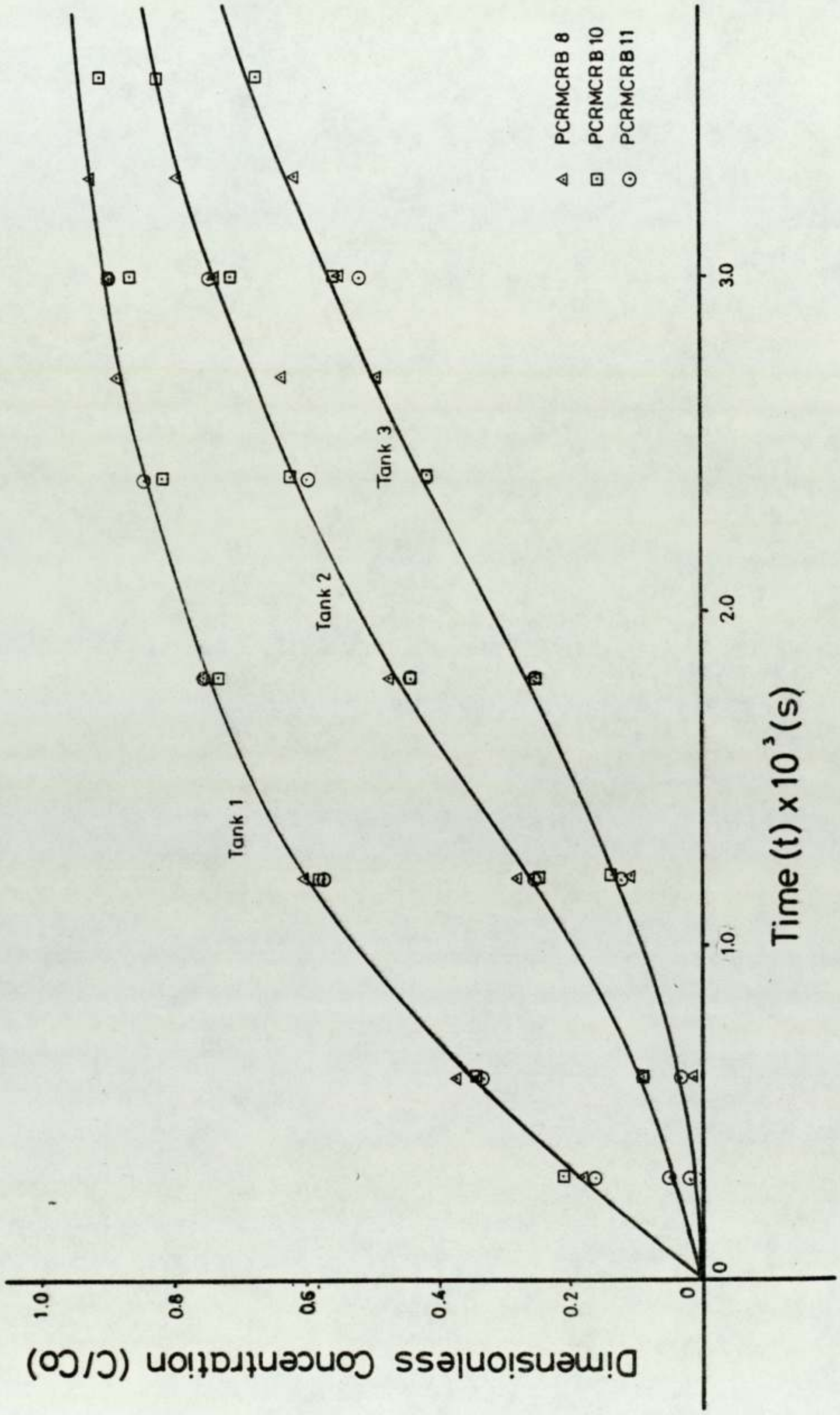

Figure 8.1 Concentration Profiles for Mixing Experiments Compared with Values for Flow around Uncarbonised Rayon Cloth

results. The mixing model had predicted a set of concentration profiles similar to those found under experimental conditions; it was now necessary to see how similar these were for a given set of circumstances. Appendix IV presents both the experimental and theoretical concentrations in tabular form. However, figure 8.2 shows graphically a comparison between the profiles of experiments PCRMCRB8 and 10 and those predicted by the mixing model, but it is apparent that these are slightly below the values predicted by the model. This is also true when a comparison is made between profiles obtained from experiment PCRMCRB11 and the mixing model, as indicated by figure 8.3. In general however, a reasonable comparison with theory appears to have been achieved.

8.1.3 Discussion

It is clear from the results that the apparatus produces reproducible concentration profiles for the mixing process, both with and without cloth present. This is adequately illustrated by figure 8.1, from which it is apparent that the concentration profile for each tank, could describe any one of the three sets of experimental results. The presence of the uncarbonised rayon also does little to affect the mixing taking place in each tank. The possibility of stagnant areas throughout the tanks had been studied at the commissioning

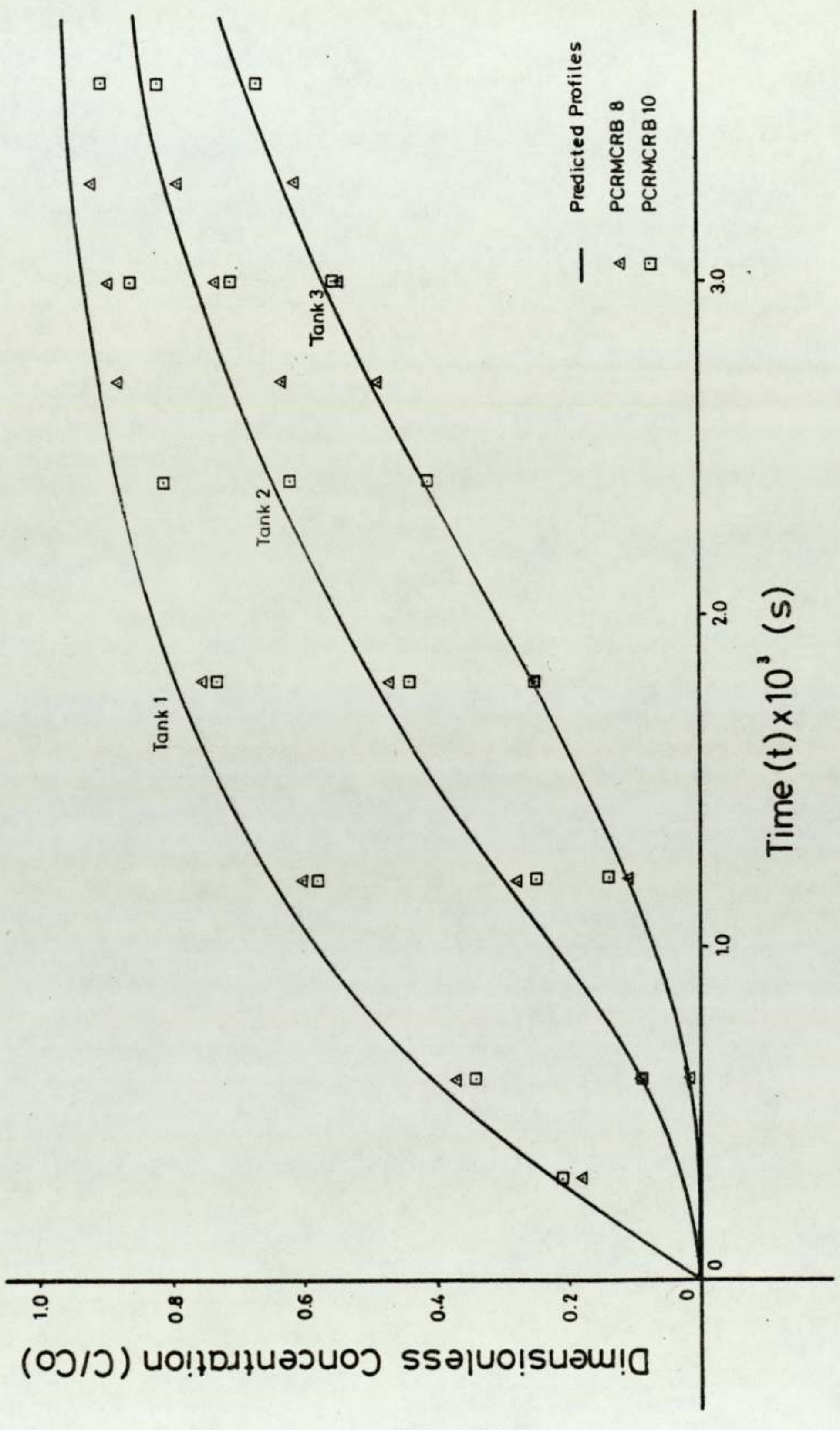

Figure 8.2 A Comparison between Predicted Concentration Profiles from the Mixing Model and Experimental Values

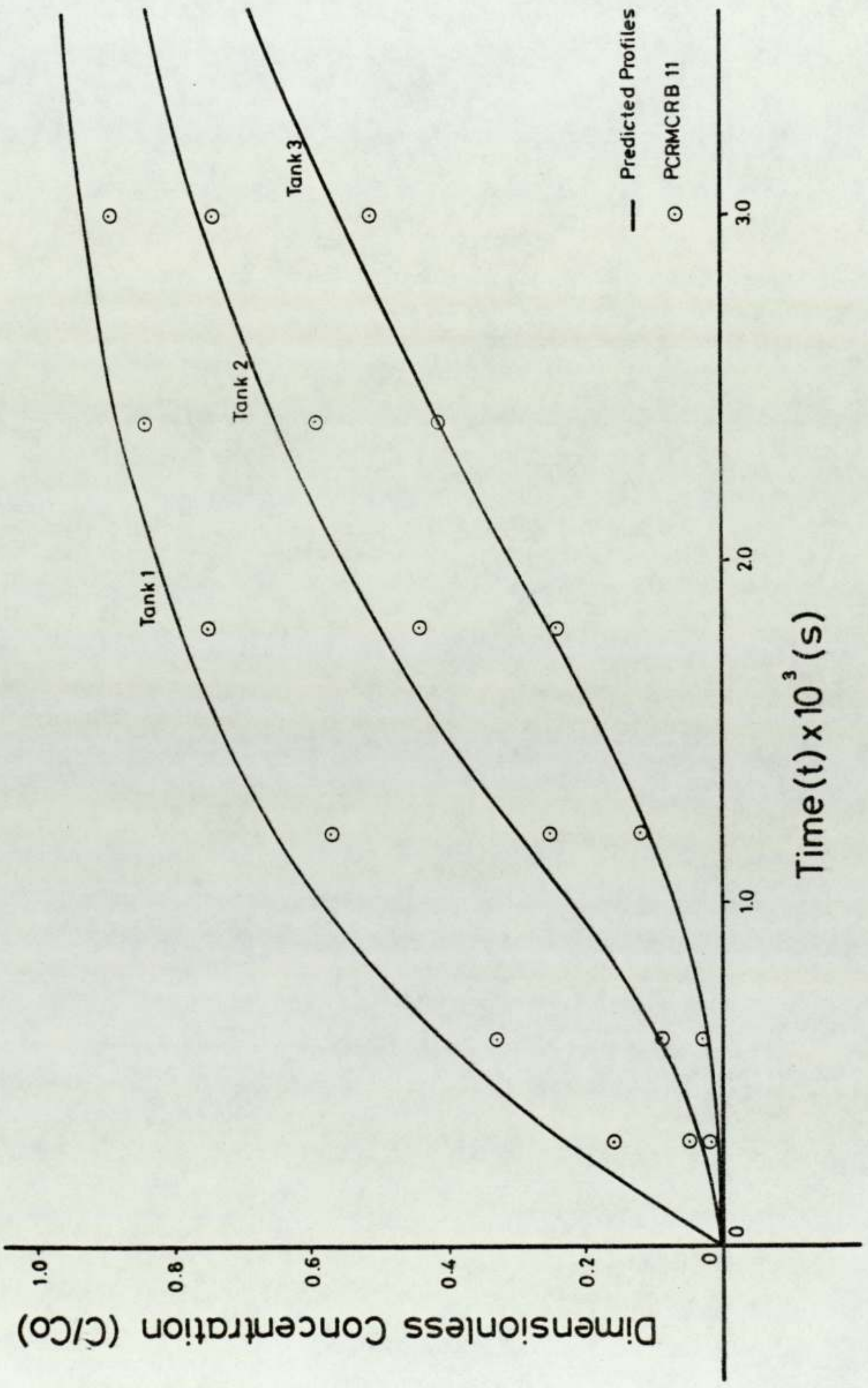

Figure 8.3 A Comparison between Concentration Profiles Predicted by the Mixing Model and Experimental Values obtained for Flow around the Cloth

stage using coloured dyes. These indicated that the high turbulence, created in each tank by the stirrers, caused complete mixing. During initial experiments on the mixing properties of the system using phenol, this was again checked by sampling simultaneously at different points in each tank; the concentration did not vary significantly from one sample point to another. The samples for subsequent experiments were extracted from the centre of the bath, through a sample tube, having first made sure that each one did not contain any liquid from previous samples. Hence, by making sure that the liquid in each tank was sufficiently turbulent, (by using a stirrer speed of about 20 r.p.s) and that the sample lines were clean prior to each sample being taken, it was possible to greatly reduce any error due to concentration fluctuations and sampling technique.

Figures 8.2 and 8.3 show a comparison between the concentration profiles obtained from experiments PCRMCRB8-11 and those predicted, for the same conditions, by the mixing model. A difference in values is evident from these concentration profiles. The premise for modelling mixing in the continuous system was a step change to three continuously stirred, well mixed, contactors. Taking the predicted profile as the perfectly mixed case, then the experimental profiles give an indication of the degree of mixing, which in most cases appears to be around 90%. The difference in the two profiles was not entirely attributable to the degree of mixing; several other factors could be responsible. The feed to the first tank was supplied by a variable speed centrifugal pump and monitored by a rotameter giving rise to moderate variations in flowrate. It was also true that due to the weir system, connecting the tanks, direct flow from tank to tank, without mixing could occur. In an effort to prevent this, the feed was introduced to the system via the stirrer vortex in tank 1, with better results.

In general however, the results point to the system being well mixed and agreeing with the premise for mathematical modelling, the effects of which are twofold. Firstly, the 'mixing' concentration of a chemical may be predicted for each tank, at any time during an adsorption experiment, allowing the calculation of the amount of adsorption. Secondly, during the development of the steady state mathematical model, it was stipulated that the contactors must be well stirred, to eliminate film diffusion resistances, as indicated by Weber (14) and Weber and Morris (21). The reaction rate also remains steady, according to Weber and Morris at high stirrer speeds.

8.2 Operation of the Continuous System with the Charcoal Cloth in a Stationary Mode

Having established a basis for calculating the maximum concentration in each tank without any cloth present, it was necessary to assess the performance of the cloth in an adsorption situation. As a preliminary exercise to running the system continuously, it was decided to investigate the adsorptive properties of the cloth in a stationary mode.

8.2.1 Arrangement of the System and Experimental Results

A length of cloth about 0.3 metres wide was passed through the adsorption section of the system, as shown in Figure 7.1, secured at each end and maintained under slight tension, to avoid ripping on the stirrer blades. The contactors were then filled with clean water and the stirrers set at a steady speed of 20 r.p.s. At the start of an experiment, polluted water was introduced to the first tank and then allowed to flow to subsequent tanks, after treatment, over a weir. The same flow rate and concentration as for the mixing experiments, were used, that is $3.2 \times 10^{-5}\ m^3 s^{-1}$ and $0.1\ kgm^{-3}$ (100 mg/l). The treated water was allowed to run out of the third tank to drainage. The temperature of the liquid in each tank was monitored periodically using thermocouples.

Only two experiments using the cloth in a stationary mode were conducted, since these were merely intended to determine the possibility of using charcoal cloth in the proposed contactor arrangement. Also, phenol was used as the pollutant chemical under investigation.

The results of these experiments indicated that reductions in concentration from the mixing model case, of 30%, 55% and 60% for tanks 1 to 3 respectively could be obtained. In general for the whole system, the concentration was reduced by about 92%. The reproducibility of the results was very good and to within the limits obtained by the mixing experiments for repeatability. The concentration profiles obtained for PCRSTCRB2 are compared in figure 8.4 to the mixing model profiles, from which it may be seen that similarities exist in the shapes. The reduction in concentration from tank to tank is now clearly seen. The results are tabulated and presented in appendix I, table 1.

8.2.2 Discussion

In preliminary experiments on the adsorption of phenol onto activated charcoal cloth, an initial phenol concentration of about 1 kgm^{-3} (1000 mg/l) was used. However, this concentration saturated the cloth very rapidly and would require a contactor system much larger than the present one or a liquid feedrate substantially lower than the already small flowrate. Subsequent investigations into the adsorption capacity of the cloth, as described in Chapter 4, revealed that a feed concentration of 0.1 kgm^{-3} (100 mg/l) would be more suitable, which proved to be the case. It is also true

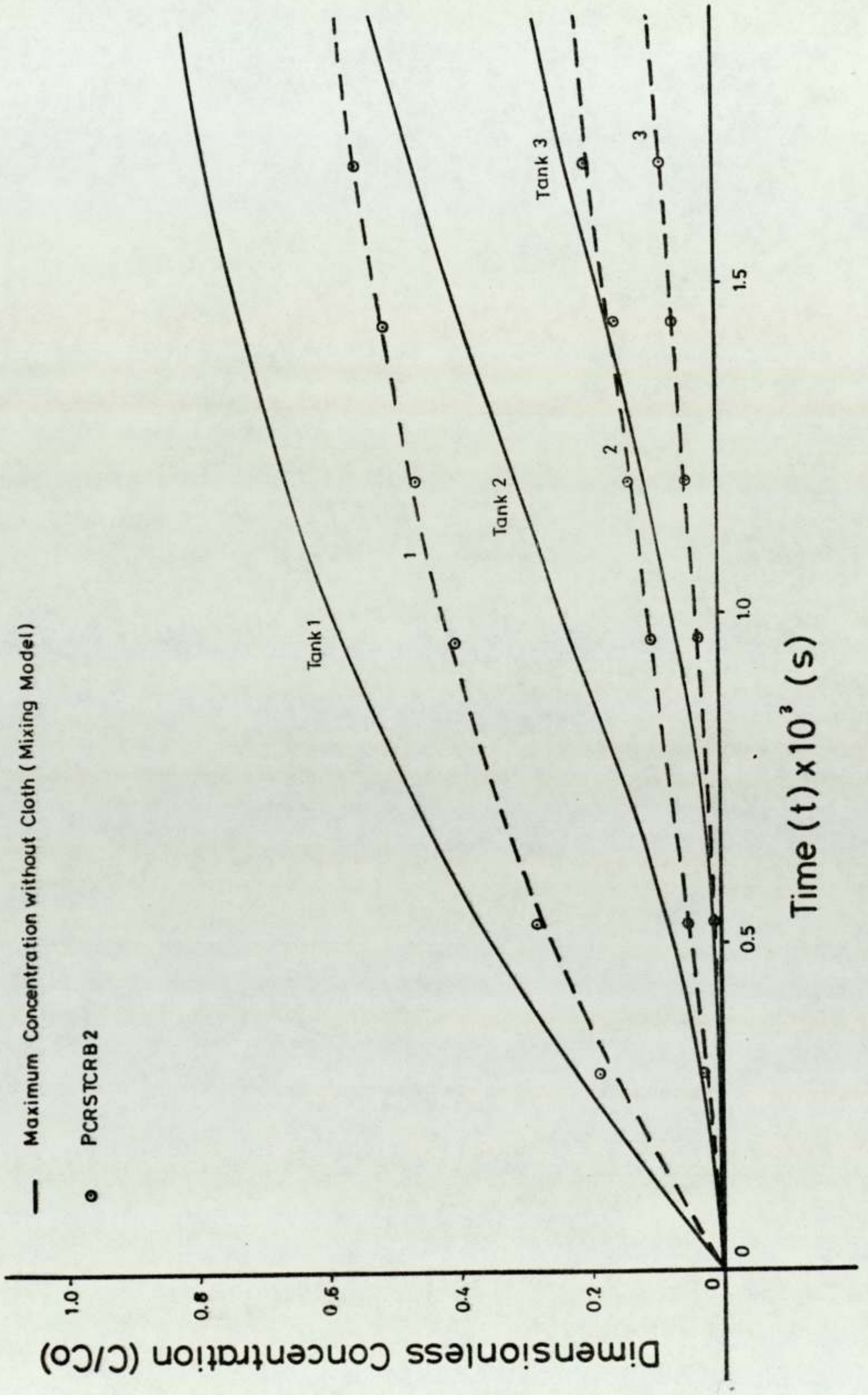

Figure 8.4 Concentration Profiles showing the Reduction in Concentration of Phenol obtained by using Charcoal Cloth in a Stationary Mode

that many industrial effluents contain phenol concentrations of about this magnitude as indicated by Henshaw (78).

The overall reduction of 92% across the system in 30 minutes was large for such a short period, compared with granular columns however, the dilution of the pollutant in the original clean water still accounts for a reduction of 75%, at this time. Hence, an overall improvement in the final effluent quality of 17% was attributable to the cloth. More encouraging at this stage, was the fact that between 30 and 60% reduction in concentration from the mixing model values, could be obtained in each tank. This indicated that the adsorption of phenol from water in a continuous system, using the same configuration should give even better results.

The reproducibility was good, as already mentioned, especially in tank 1, where the feed is introduced to the stirrer vortex, thereby forcing it out through the cloth in this contactor very rapidly. The good mixing around the cloth in each tank as indicated in the previous section, by experiment PCRMCRB11, could account for the reproducibility and the similarity in adsorption profiles. The repeatability does in fact point to a fairly even distribution of cloth activity from experiment to experiment. Also, to avoid any change in adsorption due to temperature, this was monitored throughout each experiment, with a thermocouple in each tank.

Of particular note, is the reduction in concentration achieved by the cloth in such a short time, which is shown with more effect in figure 8.4. This seems to agree with the findings of Maggs and Smith (29), that charcoal cloth adsorbs much faster than granular charcoal, since small scale qualitative experiments with granules of charcoal did not adsorb nearly so quickly.

The results from this section indicated, that using the intended contactor configuration for the continuous system, but with the cloth in a stationary mode, significant improvements in effluent quality could be obtained. It was hence decided to proceed to the study of the system with continuous cloth recycling.

8.3 Continuous Recycling of the Charcoal Cloth without Regeneration

Having been able to obtain good results from the system with the cloth in a stationary mode, it was decided to test the cloth and the equipment in their true design capacity, as a continuous system, thus providing an analogy to a moving bed system of granular charcoal and using the continuous properties of the cloth.

8.3.1 Operation of the Continuous Recycling Method

The system was set up as described in chapter 7, that is the complete continuous adsorption system. A length of cloth about 6.5 m long and 0.3 m wide, was passed through each contactor of the adsorption section, around the roller transport system, through the regeneration section and rejoined, making a continuous loop. The loop was maintained in tension, to promote enough friction on the driven rollers to sustain an even cloth transport around the system. A steady speed for cloth transport of 2.5×10^{-3} ms^{-1} was maintained, by using a variable speed motor to drive the rollers, hence allowing for any fluctuations in load etc. This gave a cloth residence time in the contactors, of about 20 minutes. Then as before, the contactors were filled with clean water and the stirrers maintained at a constant speed of 20 r.p.s. Several types of experiment were then carried out. Firstly the continuous system and cloth recycling were tested, to see if this type of operation was feasible for experiments varying in length from 30 minutes to about 2 hours. It was thought, as will be explained in the discussion, that most of the adsorption took place in tank 1, with tanks 2 and 3 acting mainly as polishing stages or overspill tanks in the event of a sudden increase in pollution load. Hence, several experiments were conducted with cloth in tank 1 only, to check this theory. These results also provided initial information for the calculation of the rate constant in the steady state adsorption model, since this constituted one stage, of an 'n' stage system. Using a continuous loop of cloth as the adsorption medium, leads to its eventual saturation in a recycling situation. The ultimate aim is to regenerate the cloth and provide a continuous source of fresh cloth until its breakdown due to mechanical wear occurs, which is discussed in section 8.4. However to test the efficiency of the regeneration process it would be necessary to pass a continuous length of fresh cloth through the system for an extended period to simulate the cloth regeneration. This was in fact achieved by passing a continuous length of unreacted cloth through the system for 2 hours and 30 minutes, hence representing the ideal regeneration situation. In each of the above experiments the actual procedure was as for the mixing and stationary tests, with the feed entering the stirrer vortex of tank 1. The feed concentration was 0.1 kgm^{-3} (100 mg/l) as before, (although a lower concentration of 0.05 kgm^{-3} (50 mg/l) was also investigated with a liquid flowrate of 3.2×10^{-5} m^3s^{-1} giving a residence time for the liquid of 50 minutes in the system, compared to that of 20 minutes for the cloth. Phenol was used mainly as the polluting chemical, as with previous experiments. At the beginning of each experiment the polluted water was allowed to enter tank 1, the cloth transport was started, and samples were taken at various intervals to allow the concentration profile to be determined.

Experiments were also conducted at feed flowrates of 0.5 and 1.5 x the above value of 3.2×10^{-5} m^3s^{-1}, to determine the effects of an increase or decrease in pollutant flowrate at the same cloth speed. Finally, the adsorption of 2-chlorophenol was investigated to test the effects that a different chemical pollutant has on the adsorbing system.

8.3.2 Experimental Results

Initially, it was decided to run the continuous system with charcoal cloth recycling for 30 minutes, to compare with the results already obtained during stationary tests. Findings from the four initial experiments, as shown in appendix I, table 2, were that better effluent levels than before could now be obtained. Reductions of around 44%, 79% and 85% on average, for tanks 1-3 respectively were obtained from the concentration predicted by the mixing model after 30 minutes. An overall reduction of about 96% was obtained, an increase of 4% on the figure obtained with stationary cloth. These results while not quite as reproducible as previous experiments, due to the inherent problems associated with moving the cloth, were extremely encouraging and much better than those obtained for the stationary experiments. Figure 8.5 shows a graphical comparison between the results obtained, for the mixing model, the stationary cloth and continuous cloth recycling. It is easy to see from these profiles the marked reduction in effluent levels of phenol from one case to the next. Of note again is the fact that the concentration profiles, while all having a different range of values, have the same basic shape. This is almost certainly due to the pollutant mixing into the system as described by the mixing model and appears to hold in a modified form in the adsorption situation. However, it was clear that the cloth had barely moved around a complete loop in such a short time. Hence, due to the success of the early experiments, the period for each experiment was increased to 1 hour. By running the system for 1 hour periods the cloth was allowed to cycle once, with some of it passing through the contactors twice, due to the cycle time of 45 minutes. The results obtained for these experiments are shown in appendix I, tables 2, 3 and 8 and with the exception of PCRMCRB5 are reproducible to the 30 minutes value with the previous experiments. The concentration profiles obtained from these experiments are shown in figure 8.6, from which it may now be more clearly seen that a familiar pattern is emerging, that is, a similar one to the mixing model. By studying the results it was clear that the reductions obtained from the mixing model values were now 47%, 79% and 86% on average, respectively for each tank, which

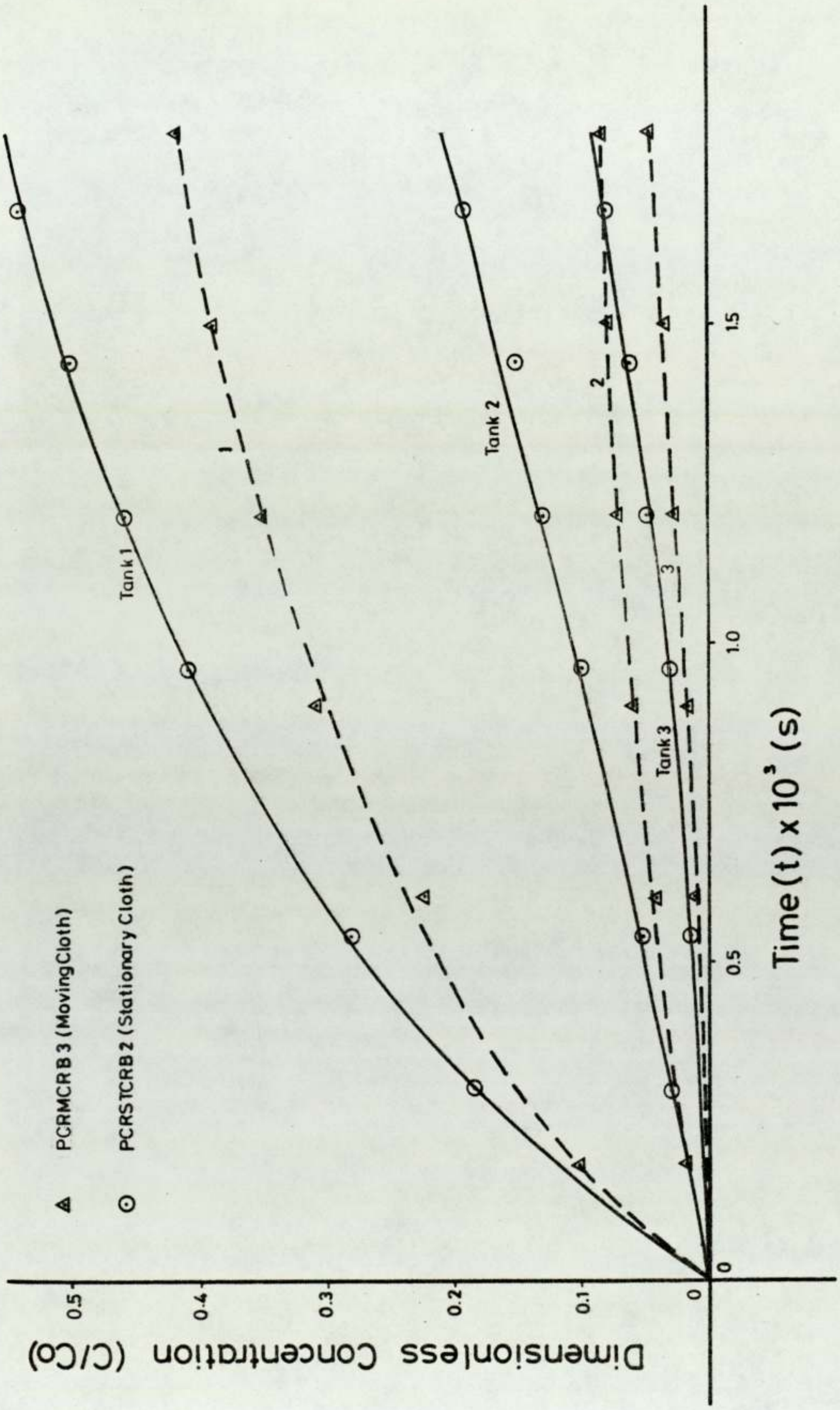

Figure 8.5 Concentration Profiles showing the Reduction in Concentration obtained by using Continuous Cloth Recycling

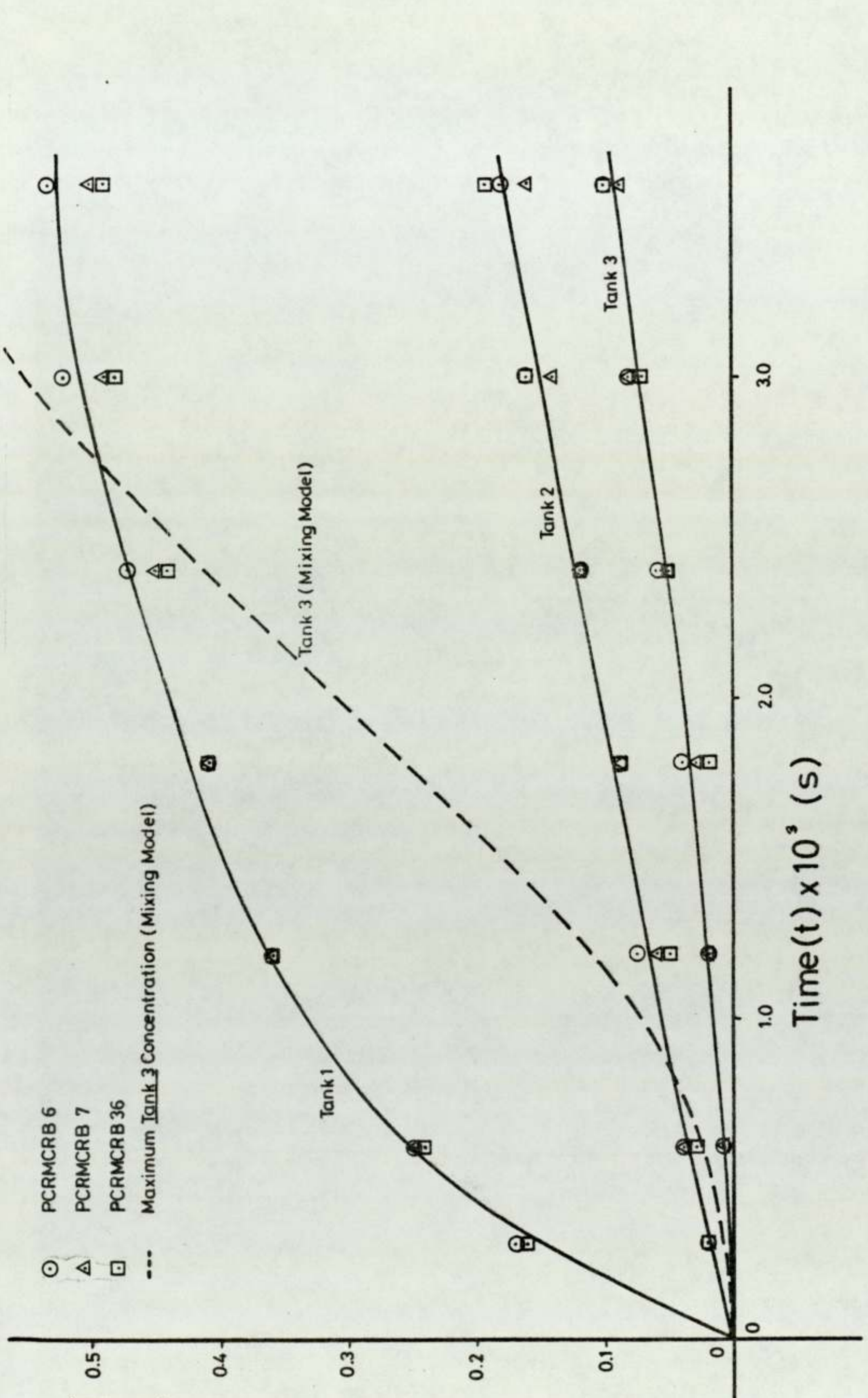

Figure 8.6 Comparison between Experiments using Continuous Cloth Recycling, showing the Reduction in Concentration

is more easily seen in figure 8.6. The overall reduction in concentration obtained across the system on average, was 90%, worse in fact than that obtained in the 30 minute experiments. However, the contribution to this reduction made by the dilution effects from mixing in the original unpolluted water, was 32%, representing a 58% overall decrease in concentration due to the charcoal cloth. The results were reproducible, in general, to less than 10% after 1 hour.

It was apparent that the improvement in overall performance would continue, until equilibrium was reached in tank 3. Also that at some point the improvement in each tank would decrease as an equilibrium stage was attained. Hence, it was decided to increase the time period for each experiment to between 2 hours and 2 hours and 30 minutes, to allow equilibrium to be attained. The results of these experiments are shown in appendix I, tables 12 and 13. As with experiment PCRMCRB5, the results of experiment number PCRMCRB51 were not reproducible, when compared with PCRMCRB6,7 and 36. However, PCRMCRB53, a repeat experiment achieved a much better and more acceptable agreement with the earlier experiments, with a reproducibility of less than 10% after 1 hour. Unfortunately a steady rise in the concentration profiles in each tank was obtained, due to the continuous recycling of used cloth in the system. Reductions from the mixing model values were 37%, 59% and 73% for each tank respectively, a reduction in performance from the 1 hour experiments, due to the fact that the cloth had been recycled three times during the course of the experiment and was nearing saturation towards the end, causing a net build up of concentration in each tank. The overall reduction in concentration had also fallen to 73% but showed an increase in removal due to the cloth since the dilution effects at more than 1 hour and 30 minutes were relatively small. It was thought that with more cloth adsorption capacity, overall reductions of greater than 90% would be obtained and an equilibrium adsorption situation obtained. Hence, it was decided to conduct an experiment using a continuous length of unused charcoal cloth to provide an ideal condition, whereby all of the cloth entering tank 3 was fully active. The results of experiment PCRMCRB42 are tabulated in appendix I, tables 9 and 10; however, they are more easily seen in figure 8.7, as concentration profiles, in comparison with experiment PCRMCRB53. This graph shows what a significant improvement in effluent concentration may be obtained by the continued renewal of charcoal cloth entering tank 3. Reductions in concentration from the mixing figures were 61%, 85% and 94% respectively; with an overall reduction of 94%, totally attributable to the cloth, since dilution effects may be neglected.

The next set of experiments concerned with the continuous recycling of charcoal cloth, without

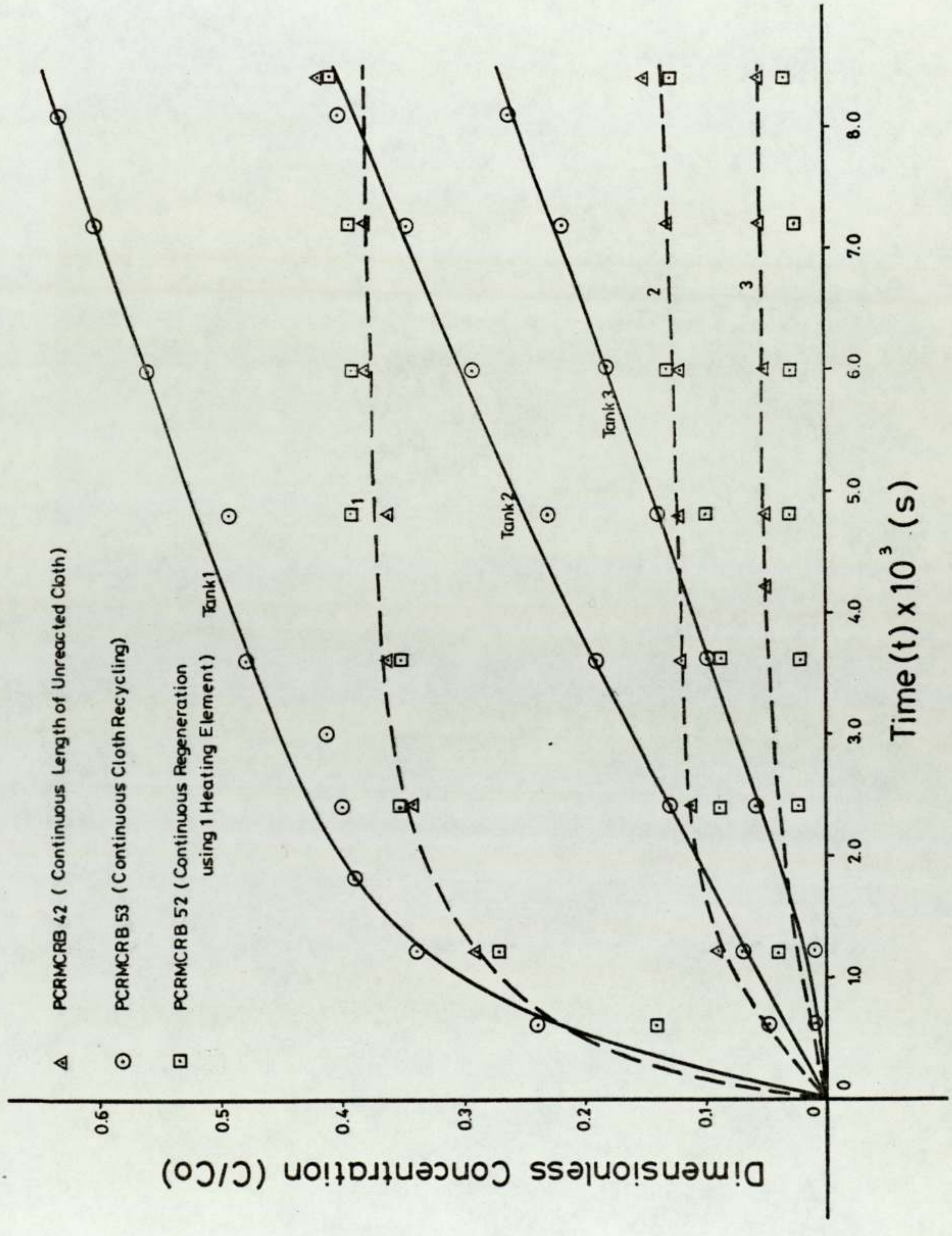

Figure 8.7 A Comparison between Continuous Cloth Recycling with and without Regeneration and the use of a Continuous Length of Unreacted Cloth

regeneration, was a small one. This was intended to determine whether most of the adsorption load was taken by tank 1, also, to provide data from one contactor as an ideal stage in an 'n' stage process for the initial development of the steady state model. The results are presented in appendix I, tables 4-6. It was clear from these results that in the absence of any carry over on the cloth from tanks 2 and 3, the concentration in tank 1 after 1 hour was about 46% of the feed concentration. Using this figure in early development of the steady state model provided good results, although, as explained in chapter 6 (p.114), the effects due to carry over were found to be small. The figures obtained from cloth regeneration also provided better results. Of more interest was the fact that the apparatus could give a reasonable effluent quality, although not desirable, when operating with one tank alone. This set of experiments also served to indicate that the removal of pollutants in tank 1 was equal to that in the other two tanks added together.

A further set of experiments was conducted to test the effects on the system, of changing feed conditions, that is, fluctuations in feed flowrate or concentration. Also, to see if different feedrates could produce a better effluent quality while fully utilising the cloth capacity. Feed rates of 0.5 and 1.5 x the current feedrate and a feed concentration of 0.5 x the current feed concentration were used, with a time period for each experiment of 1 hour.

The results are tabulated in appendix I, table 8-10. Firstly, a feedrate of 0.5 x the current one presented little difficulty to the system and in fact most of the reduction in concentration could be achieved in tank 1, with tank 2 as a polishing stage due to a residence time of 100 minutes in the liquid phase. Reductions from the mixing values obtained in each tank were 70%, 88% and 87% respectively after 1 hour. The profiles for these experiments are shown in figure 8.8. An overall reduction of about 97% was obtained from this set of experiments, of which more than 75% was due to the dilution effects of the system. At the higher flowrate, reductions from the mixing values were 31%, 60% and 72% respectively, again shown in the form of concentration profiles in figure 8.9. The profiles, as before, have the same characteristic curve as the mixing system. An overall reduction of about 72% was obtained of which only 10% was attributable to dilution effects. The results obtained by reducing the feed concentration by half were similar to those for experiments using one contactor only, indicating that several cycles could be carried out before the adsorption capacity was exhausted.

Finally, a short set of experiments was conducted using 2-chlorophenol in place of phenol. All other conditions were as for the phenol experiments using cloth recycling. A liquid feedrate of 3.2 x 10^{-5} m^3s^{-1} and a cloth speed of 2.5 x 10^{-3} ms^{-1} were used, with a feed concentration of 0.1 kgm^{-3} (100 mg/l). It was expected

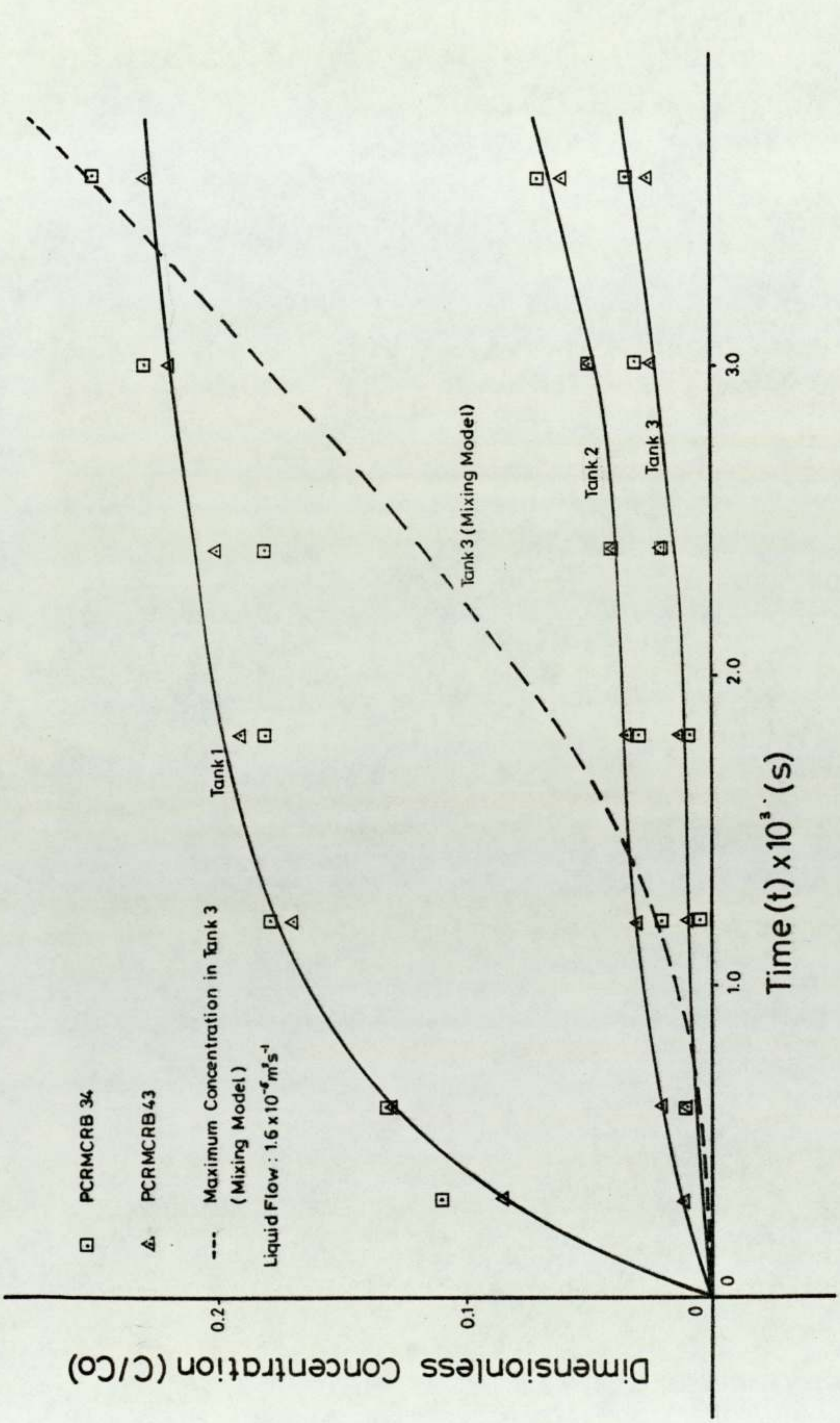

Figure 8.8 Concentration Profiles obtained using Half the Normal Liquid Rate, showing the Reduction in Concentration

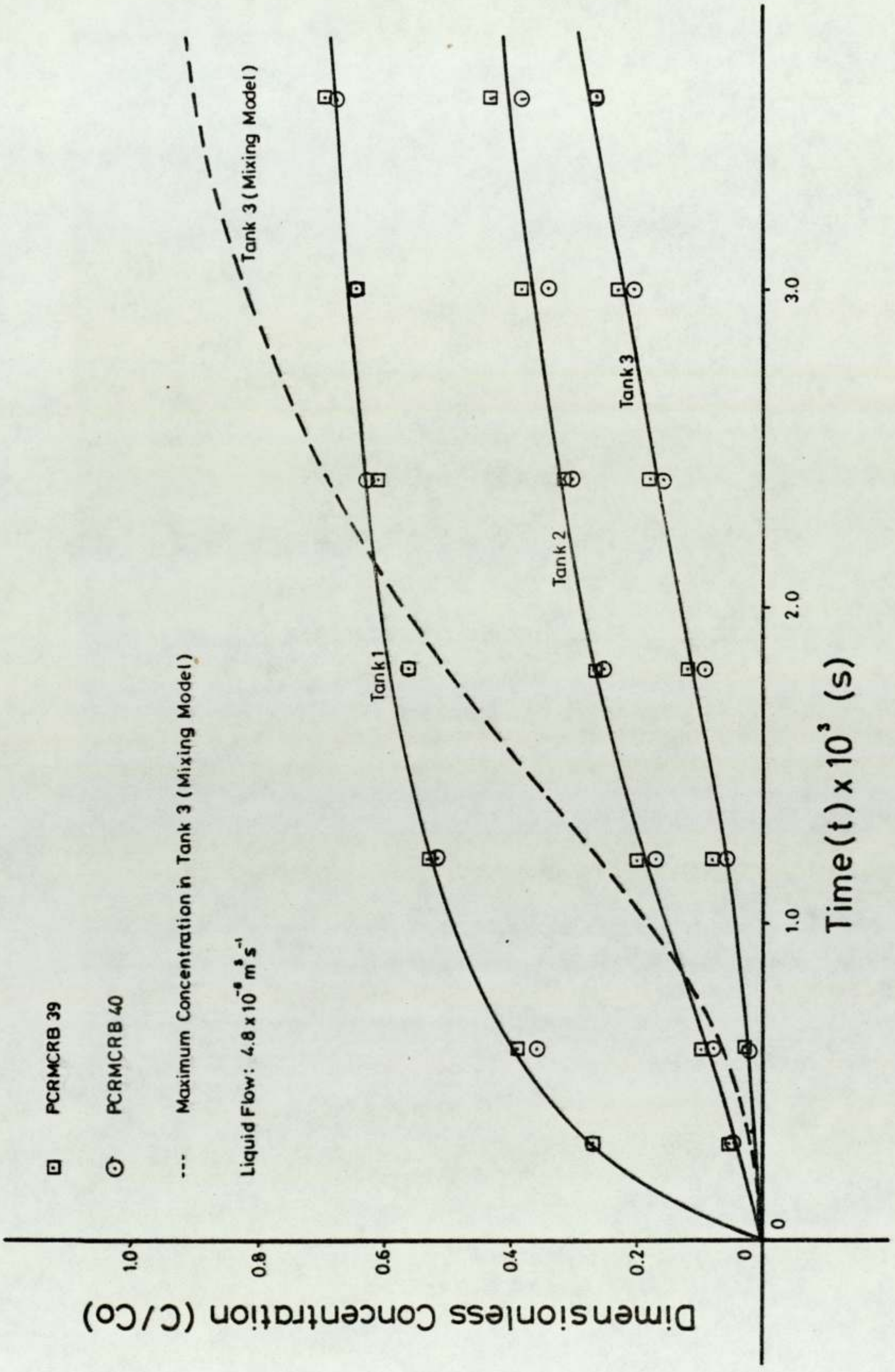

Figure 8.9 Concentration Profiles obtained using One and a Half Times the Normal Liquid Rate, showing the Reduction in Concentration

that since the adsorption capacity of charcoal cloth was more than two and a half times as great for 2-chlorophenol than for phenol, the system would remove it to a much greater extent. The results are presented in appendix I, table 14. It was clear, from these results that the system could remove far larger amounts of 2-chlorophenol than phenol, in fact the reductions from mixing values were 54%, 86% and 90% respectively, after more than two hours. Concentration profiles for the system are shown in figure 8.10. An overall reduction of more than 90% was attained, attributable to the cloth alone, neglecting dilution effects. This indicated that almost total removal of 2-chlorophenol should be possible with a regeneration scheme.

8.3.3 Discussion

In general during the experimentation involving continuous cloth recycling without regeneration, several problems were encountered with the actual system. It is possible that these had some effect on the reproducibility of results from experiment to experiment. Problems were encountered with the tank partitions which in some cases split during an experiment, however, using strong adhesives such as 'Araldite', to bind the polythene welding, reduced this problem somewhat. After considerable

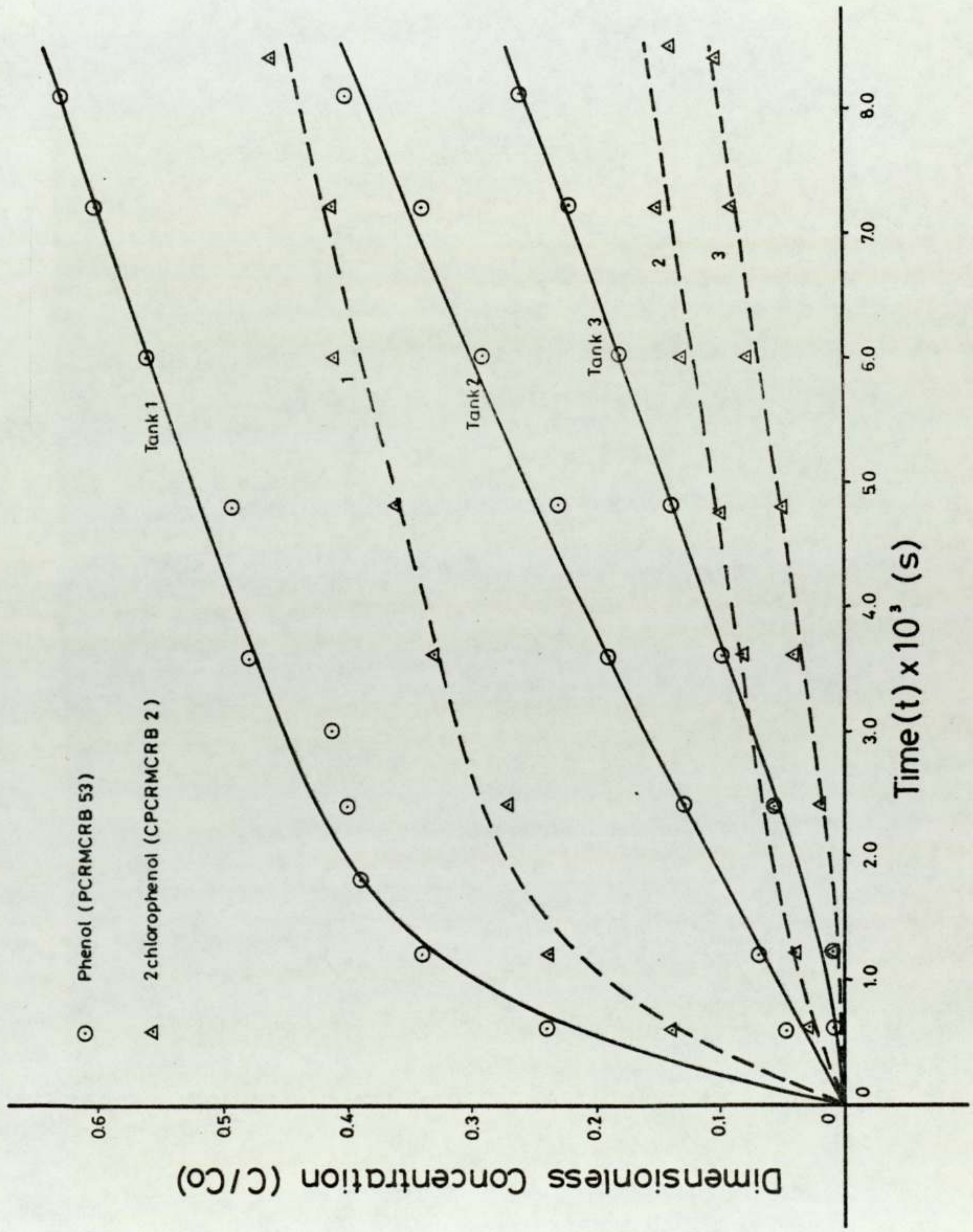

Figure 8.10 The Effect on Concentration Profiles of Changing from Phenol to a more Adsorptive Polluting Compound

initial problems in trying to join the ends of the charcoal loop together using such things as staples and sewing with steel wire, it was found that an impact adhesive survived best, in the water. Several problems were encountered with the actual cloth transport mechanism. The primary source of trouble was ripping of the cloth, not due to tension but to it being caught on the stirrer blades. This was caused by failure of the tensioning device, which was a spring supported roller and a constant watch was needed to check the springs throughout an experiment. One possible reason for fluctuations in results was the fact that although the cloth was driven by separate rollers throughout the contactor system, when the rollers were wet, slippage occurred. An attempt was made to prevent this by coating each roller with rubber, which while greatly reducing the slipping, did not completely remove it.

In the first set of experiments, that is those to see if the system could remove phenol with continuous cloth recycling, a cloth to liquid residence time ratio of 5:2 was used. This provided sufficiently more water per given time than cloth, since Weber and Morris (21) had suggested that fresh solution at the carbon surface enhances adsorption. The constant speed stirring action also helped to maintain a perpetual movement of fluid around the cloth. The first set of experiments gave encouraging results with regard to the possibility of using charcoal cloth recycling for pollution control. However, it must be realised that over such a short period as 30 minutes, much of the reduction in concentration was due to dilution effects. In the 60 minute tests a different picture began to emerge, with more of the reduction being due to the cloth. The continuous recycling of the cloth without regeneration, however, meant that continued improvement in effluent quality beyond an experimental time period of 1 hour was not possible, due to the continued saturation of the cloth. This is apparent if the reductions in concentration are studied for PCRMCRB6 and then compared to those for PCRMCRB53. It is obvious that while the cloth is passed around the system, after a peak removal at about 1 hour, with a reasonable effluent quality, a fall off may easily be noted in tank 3. Again however, it must be said that the reductions in concentration obtained over a 2 hour period in experiment PCRMCRB53 were very encouraging and could be improved with regeneration.

Experiment PCRMCRB42 as stated before, was considered as the ideal case, with a continuous length of unused cloth passing through the system for more than 2 hours. The results obtained should indicate the best which could be obtained from the system for the given operating conditions, assuming that the entering cloth was fully activated. An overall reduction of about 94% was obtained indicating that an efficient regeneration system coupled to the adsorption system, should be able to achieve at least the same reduction.

Experiments using only one tank proved that although a significant reduction in effluent concentration could be achieved, the additional reduction in the further stages was necessary to achieve practically valuable removal. It was thought however, that the two additional tanks were needed as a final polishing stage, the main pollution load was removed in tank 1 as expected.

In an effort to test the system under varying conditions, experiments were conducted using different feedrates and feed concentrations. It was not possible to radically change the cloth speed, due to friction in the system, involved in moving the complex roller system. Furthermore, such changes would probably not be of great significance in improving the removal levels. It also served as a test for load changes in the system. Firstly in the case of the feedrate of 1.6×10^{-5} m^3s^{-1}, half the original, it was clear that the system would cope with this flowrate, in fact most of the pollutant removal was achieved in tank 1. However, the residence time of liquid in the system was now doubled to 100 minutes, or more than two complete cycle times of the cloth. The reduction in concentration on first inspection looked impressive but it must be remembered that the majority of this was due to dilution effects, from mixing. This lower liquid flowrate did not offer a viable alternative process feedrate since the capacity of the cloth was not utilised sufficiently, due to the high liquid residence time. Hence, spare cloth capacity was passing around the system, when a higher flowrate would have been effective. An increase in flowrate to 4.8 x 10^{-5} m^3s^{-1} came closer to full use of the cloth capacity. Here, it was apparent that the cloth was becoming saturated after only 1 hour, again due to the residence times, since the liquid residence time approached that of the cloth in the contactors. The similarity of the liquid and cloth residence times in the contactors was evident, since pollutant was finding its way straight through the system and into tank 3, more easily than before. The reductions in concentration were not as encouraging as for the lower feedrate; however, they were almost all attributable to the cloth. Again, an efficient regeneration system could improve the final effluent quality significantly but due to the similarity of residence times in the contactors, the cloth would not be able to remove the pollutant fast enough. Hence, this feedrate would provide a better alternative process feedrate than the lower one, if coupled with an efficient regeneration system; however, it is slightly above the optimum value. Operation of the system with a feed concentration of half of the original value, had the same effect as the lower feedrate experiments, with not enough of the cloth adsorption capacity being utilised. It is of note that the dimensionless concentration after 60 minutes should be the same as for PCRMCRB6, however, it was found to be lower. This again, is an indication that in run PCRMCRB6 at 0.1 kgm^{-3} (100 mg/l) feed concentration, the cloth was beginning to become saturated after one complete cycle. However, from the concentration values in tank 1 for experiments PCRMCRB44 and 45 it is evident that compared to PCRMCRB6, extra capacity is available. Hence, a feed concentration of 0.05 kgm^{-3} (50 mg/l) would not utilise the full potential of the cloth capacity. From earlier commissioning studies, a feed concentration of substantially higher than 0.1 kgm^{-3} (100 mg/l) causes rapid saturation of the cloth.

Finally, the equipment was tested with a different chemical from the phenol used hitherto. 2-chlorophenol was used, since it is in itself a toxic pollutant, as explained in chapter 2, also since charcoal cloth has an adsorption capacity for it of about two and a half times as great as for phenol. The reductions in concentration obtained were extremely impressive with an overall reduction of greater than 90%, without regeneration, compared to around 75% in a similar situation for phenol. The concentration profiles in figure 8.10 show these reductions very clearly. This indicated that with regeneration almost total removal could be obtained. It was hence apparent that the system could remove more 2-chlorophenol than phenol, due to reasons discussed in chapters 4 and 5.

Hence, operating the system with continuous cloth recycling provided reasonable effluent concentrations and indicated that a system with a continuous band of cloth moving around a loop could be mechanically feasible. However, several initial problems with the system were encountered, such as cloth breakage etc. as explained earlier in this section and illustrated by the results from experiments PCRMCRB5 and 51, which have lower concentration profiles than similar experiments such as PCRMCRB6 and 53. This was due to a break in the seal between the tanks causing more dilution than usual. By reducing these problems the results obtained could be repeated reasonably confidently generally to around 10% from experiment to experiment. It may be noted in some experiments that a spread in many of the values for tank 3 and some values for tank 2 was obtained. The cause of this was the detector of the chromatographic analyser, since its repeatability became very suspect at extremely low concentrations as explained in chapter 3. Cloth slippage, as already mentioned, may also contribute to a small change in values from time to time.

It was found that the flowrate of 3.2×10^{-5} m^3s^{-1} and feed concentration of 0.1 kgm^{-3}, were very close to being optimum values for the system, since the cloth speed could not be changed due to friction in the drive to the rollers, to compensate for any change in feed conditions.

Finally, it was found that other chemicals than phenol could be successfully removed from water, with an indication that as its adsorption capacity increases, then so does the scope for removal of a chemical from water using this system. This is in keeping with traditional theory as indicated in chapter 4 and 5.

Overall, it was apparent that for the system to be economically viable, a regeneration scheme was necessary. Experiment PCRMCRB42 served to indicate that overall reductions in concentration of better than 94% were possible for phenol, with regeneration. It also appeared that almost total removal of 2-chlorophenol could be achieved this way. Hence, it was decided to design and test a regeneration section of the system.

8.4 Continuous Recycling and Regeneration of the Charcoal Cloth

The results from experiment PCRMCRB42 indicated that a steady flow of fresh charcoal cloth into the adsorption system could improve, to acceptable levels, the quality of effluent streams, containing substantial phenolic concentrations. It was however, not practicable or economical to conduct this type of operation, hence it was decided to study the effects of cloth regeneration on the performance of the system.

8.4.1 The Application of Regeneration Schemes

The pollutants removed from water are very rarely in a recoverable state and hence the most popular form of regeneration is by breaking these chemicals down using heat. The cloth would then be reactivated using normal reactivating agents such as carbon dioxide or air. Another form of regeneration involves the reaction of the adsorbed chemical with an acid or alkali, such as caustic soda.

Both of the above methods were tried in the experimental programme, although regeneration using heat was the more favoured method, as explained later. The system was arranged as shown in figure 7.1 and discussed in section 8.1, 8.2 and 8.3. However, unlike in the previous experiments, the cloth was recycled through an electric heater, consisting of two 1 KW elements, after leaving tank 1. The regenerator was operated with either one or both elements operating and with or without air passing through the system. After regeneration the cloth was then passed back to tank 3. Alternatively, the cloth entered a small bath containing a 4% solution of sodium hydroxide, on leaving tank 1, then passed through a wash stage and again back to tank 3, following a method suggested by Himmelstein, Fox and Winter (109). The experimental method adopted was as for section 8.3.

8.4.2 Experimental Results

The results for these experiments are presented in tabular form in appendix I.

As indicated above, experiments were conducted with the regenerator operating as either one or two elements and with or without excess air passing through the system. Firstly, the system was operated with both heater elements working, giving an average temperature at the top of around 400°C and about 100°C at the bottom. However, at these temperatures various problems were encountered with the cloth, for instance, at the top temperature, the join in the carbon roll would break, also burning of the cloth occurred. However, it was found, as shown in figure 8.11, that good regeneration could be obtained along with significant overall improvements in effluent quality, at comparable cloth flowrates. This is especially noticeable in the cases of PCRMCRB26 and 31, where overall improvements of around 94% from the mixing values were obtained. Although a small amount of the reduction is due to dilution. Also, noticeable improvements in the effluent levels in each tank were obtained compared to the case without regeneration, with improvements (in effluent concentration) of 20%, even in tank 1, where the largest pollution load occurred. Since the use of two elements at such high temperatures caused many problems, especially with cloth burning, it was decided to try to cool the inside of the heater using air, as an activating agent. Although the air cooled the system, it did not have the desired effect as indicated by PCRMCRB32 and shown in figure 8.11, in fact the results obtained were similar to those already given without air. Another effect, was that the inclusion of excess air promoted burning of the cloth, especially at some weaker patches throughout the cross section of the cloth which showed up as rather large holes. It was therefore decided to investigate chemical regeneration using a bath of 4% sodium hydroxide solution, as suggested by Himmelstein et al. (10). However, even after extensive washing of the cloth,

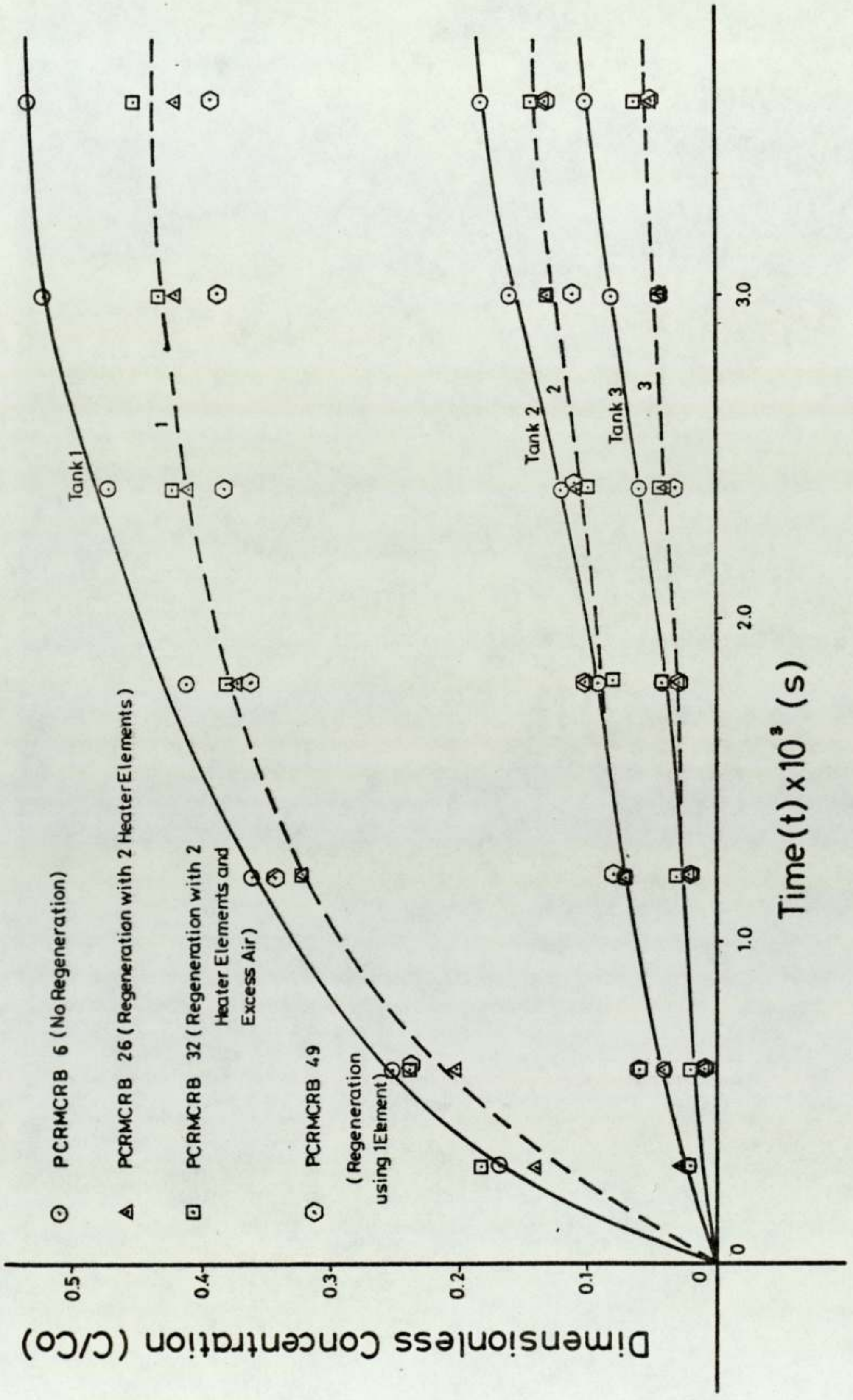

Figure 8.11 A Comparison between Concentration Profiles for Experiments with and without Regeneration

the effluent levels obtained were higher than without any regeneration at all and the cloth life reduced significantly, this is indicated by experiments PCRMCRB46 and 47.

Finally, it was decided to investigate the properties of the heater for the case with only one element working. This had the effect of lowering the heat input to the system, while still maintaining relatively high temperatures at the top of the heater. The result is shown in figure 8.11, where the values obtained from PCRMCRB49 are comparable with those for 26 while only using half as much power. Figure 8.7 indicates that over a longer period, using only one heating element as the regenerator, effluent levels similar to those for PCRMCRB42 could be obtained, that is, approaching the original cloth state. Hence, for phenol in water at a feed concentration of about 0.1 Kgm^{-3} (100 mg/l), overall removals of 95% could be obtained using heat regeneration. Similar experiments were also conducted using 2-chlorophenol as the polluting chemical with one heater element. An overall removal of 98% with regeneration was obtained, indicated by experiment CPCRMCRB4. Improvements on the figures without regeneration were quite significant, with a 30% improvement even in tank 1.

8.4.3 Discussion

It is clear from the results, thatthe quality of the effluent from tank 3 can be greatly increased by including a regenerator in the continuous system. However, many problems were encountered and more exist before a reproducible regenerator system is found.

Firstly, the use of two elements in the heater proved to be impracticable, since the cloth became very weak after one pass through the heater and also had a tendency to burn very easily. The high temperatures also caused the compound joining the cloth together to burn, causing breaks. These problems were dealt with by using only one heater element, in which case the cloth could be cycled for much longer periods. Although it is true that the capability of a given sample of cloth to regenerate again, falls off rapidly as the number of regenerations increases. Therefore in an industrial situation, the furnace would not be used continuously, but for a fraction of a cycle or a given number of cycles. The use of air as an activating agent proved to be of little use. It was however, presumed that the steam raised in the heater by the evaporation of water carried over by the cloth, played a part in the regeneration process, since steam is a well-known reactivating agent.

It may be argued that by burning the pollutants from the surface of the carbon, an air pollution hazard is being created. However, Gralan and Smith (127) have shown that under the influence of external energy (ultra-voilet light), phenol breaks down to carbon dioxide and water. It is probable that the heat supplied by the regenerator, achieves this breakdown much more rapidly. It is also probable that 2-chlorophenol is converted to carbon dioxide and hydrogen chloride. In the case of higher molecular weight compounds, an afterburner would be supplied to promote further breakdown at much higher temperatures, of the regenerator exit gases. Hence, using a heat regenerator system, it is possible to obtain very high overall levels of removals of phenolic compounds from water.

8.5 Discussion of the Results from the Continuous Cloth Recycling Experiments compared with Results from the Steady State Mathematical Model

The experimental and calculated concentration values for continuous cloth recycling may be found in appendix III.

Due to the number of variables involved as the cloth moves around the system; it was explained, in chapter 6, that a complex numerical method would be required to completely model the adsorption process taking place on the cloth. Hence, within the overall aim of the experimental programme, it was decided that at this stage, a more general model would be of greater use. It was found that after a certain time, as with the mixing model, the concentration in each tank attained a pseudo-steady state, that is its increase reduced to almost zero. Hence, eliminating concentration as one of the time dependent variables. The model was therefore, based on this steady state concentration.

As indicated in chapter 6, the steady state mathematical model contains a rate term which was calculated from empirical data supplied by the experimental equipment. Since most of the mass transfer took place in tank 1, where the largest pollutant concentration existed, it was decided to use the steady state value obtained in tank 1 to calculate the rate term and to use this for each tank assuming that the rate is the same throughout the system. It was originally intended to obtain a value for the rate term from experiments PCRMCRB14-21, using only one tank, then to use this value throughout the complete experimental programme. However, the value of the rate term was very sensitive to the steady state concentration value used for its calculation and as explained later, this could vary from experiment to experiment. The rate term was hence calculated from the results of each separate experiment, for this experimental programme.

When the concentration values obtained at steady state, for experiments without cloth regeneration, were substituted into the mathematical model, very little agreement with experimental values was obtained, as shown by the experimental representation of experiment PCRMCRB6 in appendix III, for instance. It appeared from these results that mathematical modelling of the system at steady state would not be possible. The regeneration cycle of the adsorption system was then introduced and as its efficiency improved, a better agreement was obtained between experimental and calculated concentrations, as shown by the experimental representation of PCRMCRB26. Hence it was thought that on this basis, the best agreement with the model would be obtained by a perfect regeneration system, returning uncontaminated cloth after each cycle to the contactors. Using the regeneration heater at present in the system, complete regeneration was not feasible. However, it was possible to simulate perfect regeneration by feeding a length of unreacted charcoal cloth continuously into the system, as in experiment PCRMCRB42, assuming that unreacted cloth properties are the same as those of totally regenerated cloth. The calculated results obtained for this experiment from the model, as shown in appendix III, agreed very well with those obtained in practice. This indicated that a highly efficient regeneration process, coupled with the adsorption system, could be successfully modelled. Each set of values therefore appears twice in appendix III, firstly as 'EXPERIMENTAL' results and then as 'IDEAL' results. The 'EXPERIMENTAL' results indicate the comparison between calculated and experimental concentration values using the steady state concentration obtained from the stated experiment. The 'IDEAL' results indicate the calculated and experimental concentration values which would be obtained in an ideal situation, using PCRMCRB42 as the ideal case, where a perfect regeneration is obtained.

The tables in appendix III, therefore indicate varying degrees of agreement with the mathematical model. As stated above, in the normal situation, using three tanks, with no regeneration, very little agreement is obtained. But as the regeneration efficiency improves, then so does agreement with the model. In some cases the 'IDEAL' situation has been omitted since a close agreement was obtained between the two sets of values, by using experimental values only. It is clear from appendix III, by following the ideal case, that for a given value of the steady state and good regeneration, the rate term does, in fact, remain reasonably constant.

It is apparent that the carry-over of solute from cycle to cycle, can also have a significant effect on the modelling of the system. For example, experimental concentration values for PCRMCRB34 agree very well with predicted concentration values, using EXPERIMENTAL data only and without regeneration. However, in the case of experiments PCRMCRB6 and 38, which use flowrates of twice and three times that of run number 34, respectively; no agreement between experimental and calculated values for concentrations using EXPERIMENTAL data, was obtained. Hence, since the flowrate used in experiment PCRMCRB34 was so small, the cloth remained reasonably active, for several cycles, representing the regenerated case in experiments using higher flowrates. Whereas, in experiments PCRMCRB6 and 38, too much of the cloth activity was used up in one cycle, not allowing a steady state to be achieved. This was then 'carried over' from cycle to cycle, in the absence of regeneration. It is true that without regeneration, given sufficient time, regeneration would be required in experiment PCRMCRB36 also. A similar case exists between experiment PCRMCRB6 and 45 where different feed concentrations were used.

Hence, the system may be modelled at steady state, provided that an efficient regeneration system is used, or if the amount of pollutant carried around the system on the cloth, over a significant time period, is small. A better agreement between experimental and predicted concentration values is obtained, with a regeneration cycle, since a more realistic steady state value is obtained. Since, when concentration profiles are plotted for the experiments using regeneration it is apparent that after a short time the concentration increase subsides and steady state is obtained. However, without regeneration, although the rise in concentration slows down considerably, after the initial rapid rise, it nevertheless continues to increase albeit at a much slower rate.

Chapter 9

Conclusions and Recommendations

9 Conclusions and Recommendations

The objectives of the experimental programme may be divided into approximately four areas:

i) The study of the adsorption capacity of the cloth, establishing whether the cloth could remove any pollutants and to what extent.

ii) The physical construction and commissioning of the experimental apparatus, to establish if it were possible to continuously transport charcoal cloth under the desired conditions.

iii) The development and testing of mathematical models to describe the system and enable future workers to scale the system up to process size.

iv) The experimental programme to verify the predicted performance of the cloth and that it would remove pollutants from water, to the desired extent in the test equipment. Also, to test the mathematical models for agreement with experimentally determined data.

It was evident at a very early stage that the cloth did not have the same adsorptive capacity under process conditions, as had been achieved in the laboratory. Capacities of around 0.9 kg phenol/kg cloth had been quoted (6,29) while only a third of this figure had been obtained in practice. It was later found, however, that to achieve the adsorption capacities obtained in the laboratory, an extensive cleaning process had been undertaken to enable the cloth to be sufficiently wetted. Mere contact with the atmosphere can cause fall off of adsorption capacity when the cloth is thoroughly clean. It was hence decided that under the circumstances and bearing in mind the scale of the operation, it would not be economically feasible to clean the cloth under process conditions. Although certain values of capacity around 0.5kg phenol/kg cloth had been obtained, it was concluded that, under process conditions, the cloth had a capacity of 0.3 kg phenol/kg cloth and around 0.7 kg 2 chlorophenol/kg cloth. This agreed with traditional absorption theory, in that 2 chlorophenol is less soluble in water, than phenol and as such should be adsorbed more readily. Comparison with figures from the literature (74) and similar experiments, indicated that although the process capacity of the cloth for phenol was relatively small, it was much larger than for granular charcoal under similar conditions. Thus, it was evident that the charcoal cloth could adsorb, in substantial quantities, the phenolic compounds used as test pollutants in the experimental programme.

The continuous adsorption equipment was hence constructed and tested using normal rayon cloth and activated charcoal cloth. It was necessary to have rubber coated motorised rollers for each adsorber section to enable constant cloth motion and reduce cloth tearing due to excess tension. To maintain a small amount of overall tension in the system, a tensioning device was used. It was necessary to operate the regenerator at the lowest temperature possible, to prevent the cloth burning. However, it was discovered that low temperature regeneration could provide a much more active cloth. Hence, the adsorption system as described in chapter 7 could continuously transport cloth around an adsorption cycle, containing an adsorber section and facilities for regeneration.

The adsorption contactors each contained a stirrer to aid mixing of the pollutant within the adsorber, to promote contact between cloth and pollutant and to provide sufficient turbulence to neglect adsorption resistances due to films on the cloth surface. The system, without any cloth present, was modelled on a three stage continuous stirred tank reactor, having a step change to tank 1. The adsorption system agreed very well with the equations developed from this model. However, profiles indicated that the experimental concentration values were always slightly less than calculated values. It was decided that this was a measure of the mixing achieved in each tank and was usually greater than 90%. Mixing experiments with cloth present showed that the physical presence of inert cloth had no effect on the concentration profiles and did not promote stagnant concentration areas. In general then, a good agreement was obtained by assuming a step change to three continuously stirred tank reactors as the basis for the mixing model.

Before the adsorption mechanism for the mathematical model with cloth adsorption could be ascertained the cloth surface properties were studied. It was found, by using scanning electron micrograph techniques, that at similar magnifications, while a largely porous structure on granular charcoal could easily be seen, no visible pores could be found in charcoal cloth even at high magnifications. Hence, it was proved that no macropores existed in charcoal cloth. In fact, by closer study of the high magnification micrographs, at greater than 10000 x magnification, the pore structure was noticed to give some of the micrographs a 'hazy' appearance. A study of transmission micrographs taken by Bailey, Creasy and Robins (13) and comparison with the stereo micrographs, indicated that most of the pores in charcoal cloth were micropores, having widths of much less than 1 nm. This indicated that the pores were of molecular dimensions and that larger molecules, such as phenolic compounds, would have difficulty in diffusing into or through these pores. It was assumed therefore, that pore transport played little part in the adsorption kinetics of phenolic compounds on activated charcoal cloth. The stereo electron micrographs also indicated two possible ways in which the phenolic compounds adsorb onto charcoal cloth. Firstly, the chemical adsorbs onto the surface, followed by more phenol attaching itself to the ensuing crystals, forming a nucleation site. Also, the micrographs indicated that the strands of cloth possessed longitudinal corrugations. It was noticed, in some cases, that during the course of a reaction these corrugations could be filled. Analysis by a Kevex X-ray microanalyser discounted the presence of any inorganics and hence it was assumed that the corrugations were filled by phenol. Therefore, for mathematical modelling purposes it was assumed that all adsorption takes place either on the surface of the cloth or in pores very close to the surface, which is a very fast reaction. This assumption was further supported by Maggs and Smith (29), who indicated that the experimental adsorption rate on charcoal cloth was exceptionally fast.

Due to the fact that several variables in the continuous adsorption system were time dependent, at the start of an experiment, it was decided to limit early mathematical modelling of the system to the steady state situation, to avoid extremely complex numerical solutions. At steady state, the concentration in each stage of the adsorber does not change significantly with time and hence this may be assumed to be constant. The kinetics were assumed to be surface reaction dependent, as explained above and on this basis an iterative model was developed to predict the steady state concentration in each stage of the adsorber for a given set of conditions. The experimental steady state concentration in tank 1 was used to predict the rate term. It was found that for normal experiments, without regeneration, very little agreement between experimental and predicted concentrations was obtained. However, as the efficiency of the regeneration process increased then so did the agreement between experimental and predicted results. The best agreement was obtained by passing unused cloth continuously into the system, representing an ideal regenerated state. In fact, it was apparent that this was so, since with totally regenerated cloth, a true steady state could be obtained due to reduced carry-over of pollutant and hence, the rate term did not vary significantly. Therefore, the steady state model holds, as long as only exceptionally small amounts of pollutants are removed without regeneration or in the normal case with an efficient regeneration system. It must be accepted that total regeneration is very difficult to obtain, but the results have shown that as the figures approach this value, then a better reliability may be expected from the steady state mathematical model. In general, it was found that the adsorption equipment could, to a reasonably reproducible degree, remove substantial amounts of phenol from polluted water, without regeneration. In fact, up to 80% removal of phenol and greater than 90% of 2 chlorophenol was obtained, when compared to the situation without any cloth present, as supplied by data from the mixing model. It was discovered that after an initial rapid rise in concentration, a pseudo-steady state situation was obtained, whereby the increases in concentration were small. Of interest also was the fact that most of the pollution load was adsorbed by the cloth in tank 1, the first in the cascade, with tanks 2 and 3 acting as polishing stages, removing between them only as much as tank 1. In fact, tank 3 only acted as an emergency stage in the event of pollutant flows accidentally increasing. At the allowable cloth throughput of 2.5 x 10^{-3} kgs^{-1}, it was found that a liquid flowrate of 3.2 x 10^{-5} m^3s^{-1} provided the optimum removals. Since a liquid flowrate of 0.5 times the optimum, while being treated successfully, did not fully utilise the cloth capacity. However, at this flowrate, the equipment could be operated for longer periods prior to regeneration. Also, at a liquid flowrate of 1.5 times the optimum, the cloth adsorption capacity was exhausted too rapidly and even with an efficient regeneration system, some pollutant would find its way through the system. It was also obvious that in the treatment of reduced feed concentrations, the cloth could be allowed to cycle several times prior to regeneration being required.

By conducting an experimental run using only unused cloth at the cloth inlet, it was found that phenol removals of around 95% could be obtained. Hence, it was decided that regeneration would be necessary as part of any water treatment scheme using this type of system. High temperature regeneration, using two 1 KW heating elements, caused the cloth to burn and tear, with no great increase in the performance of the system. However, regeneration with only one 1 KW heater and at a subsequently lower temperature, gave results approaching those obtained by passing unused cloth through the system. The improvement was believed to be due to lack of formation of surface carbon. Using this type of regeneration system also reduced wear on the cloth and no burning or tearing occurred. This single element regeneration was a great improvement in respect of its effect on the adhesive bond for joining the cloth and the reduction in energy required for the same amount of reactivation. The adsorption system, utilising a regenerator with one 1 KW heating element, could hence obtain continuous reductions in feed concentration for phenol and 2 chlorophenol of 90 and 98% respectively.

Although successful results have been obtained using the current apparatus, future work involving this system would require modifications. Firstly, the use of three separate tanks or compartments connected by small diameter piping would prevent the possibility of back mixing. A more sophisticated drive system for the cloth would allow a study of the effects of running at different cloth speeds. A regenerator furnace containing only one heat source would be adequate and operate at a lower temperature. The inclusion of a steam facility would be useful since steam acts as a good reactivating agent and also effective sealing of the regenerator from external air would prevent cloth burning. The installation of an afterburner would prevent air pollution from the regenerator.

It is necessary to conduct more testing of the steady state mathematical model, at different cloth and liquid flowrates, using a better regenerator, to obtain more information about the rate term under these various conditions. A detailed study of modelling the system in the unsteady state would also be necessary. This could be based on methods used by Bell (4) and Bell and Molof (33), who have studied the effects of changing adsorption rates in stirred tank reactors, using granular charcoal and linear alkylbenzenesulphonates.

This experimental programme has enabled a study to be made of the continuous removal of phenolic compounds from water, using activated charcoal cloth. By using a regenerator and then subsequently recycling the cloth, these removals may be radically increased.

The basis for a mathematical model has been established and this has indicated the further investigations required to develop this model to describe the system more fully.

NOMENCLATURE

b	Langmuir constant related to adsorption energy	m^3kg^{-1}
B	B.E.T. constant related to adsorption energy	-
C	Concentration of adsorbate in solution	kgm^{-3}
Ce	Equilibrium concentration of adsorbate in solution	kgm^{-3}
Cm	Maximum concentration of adsorbate in solution (Temkin)	kgm^{-3}
Cs	Saturation concentration of adsorbate in solution	kgm^{-3}
Cos	Concentration of occupied active sites on wet charcoal cloth	m^{-3}
C_T	Total number of active sites on wet charcoal cloth	m^{-3}
Cu	Concentration of unoccupied active sites on wet charcoal cloth	m^{-3}
DG	Ratio of solid phase and fluid phase concentration of adsorbate at saturation	-
k	Forward rate constant used in the steady state mathematical model	$m^3kg^{-1}s^{-1}$
k_d	Reverse rate constant used in the steady state mathematical model	$m^3kg^{-1}s^{-1}$
k_f	Mass transfer coefficient for film diffusion	ms^{-1}
k_s	Mass transfer coefficient for internal surface diffusion	ms^{-1}
K	Equilibrium constant	s^{-1}
K_f	Equilibrium constant for film diffusion	s^{-1}

K_F	Freundlich constant	-
Ks	Equilibrium constant for internal surface diffusion	s^{-1}
l	Length	m
L	The length of charcoal cloth contained in one contactor	m
m	Mass flowrate of charcoal cloth	kgs^{-1}
M	The amount of adsorbent added to an isotherm test	kg
n	A constant (empirical exponent, contactor number)	-
p	The mass of phenol per occupied site	kg
Q^o	Langmuir monolayer capacity	-
r^o	Equilibrium modulus (1/(1+bCo))	-
S	The actual concentration of adsorbate in the particles of adsorbent (Temkin)	kgm^{-3}
Sm	The concentration of adsorbate in the particle in equilibrium with Cm (Temkin)	kgm^{-1}
t	Time	s
u	The volumetric flowrate of liquid through the adsorption system	m^3s^{-1}
v	The cloth velocity	ms^{-1}
V	The volume of the adsorption contactors	m^3
w	Width of charcoal cloth	m
x	u/V	s^{-1}
X	Amount of solute adsorbed in isotherm testing	kg

y	Mass of pollutant per unit mass of wet cloth	$kg\ kg^{-1}$
y^*	Mass of pollutant per unit mass of wet cloth under saturation conditions	$kg\ kg^{-1}$
z	Thickness of charcoal cloth	m
α	Effective area for mass transfer per unit volume of bed or reactor	m^{-1}
δl	Incremental length	m
$\overline{\varepsilon}$	Interparticle void ratio or porosity in an expanded bed	-
ρ_o	Density of charcoal cloth	kgm^{-3}
ρ_e	Density of an expanded bed	kgm^{-3}
ξ	Intraparticle void ratio	-
τ	Time from first entry of solution to an adsorption column	s

Subscripts

O	Feed tank (initial conditions of concentration)
1	First stage contactor
2	Second stage contactor
3	Third stage contactor

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APPENDIX I

EXPERIMENTAL RESULTS FROM THE CONTINUOUS TREATMENT SYSTEM

Experimental Notation:

P : The polluting chemical is phenol

CP : The polluting chemical is 2 chlorophenol

CR : Continuous Treatment System

MC : The Charcoal Cloth is in motion

STC : The Charcoal Cloth is stationary

RB : The type of Rayon used to make the cloth is Rosebank

For cloth notation see Appendix VI

The type of experiment carried out is explained as follows:

Stationary : There is cloth in each of the three tanks only and it is not in motion

Continuous : There is cloth in the whole system including the regenerator and it is moving

Blank : There is no cloth in the system, these experiments are used to test the mixing model

The cloth velocity is constant at 2.5×10^{-3} ms^{-1} and stirrer speeds are constant at 20 r.p.s.

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^3 s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRSTCRB2	A119RBNS7B	3.2	1.68	Stationary	100.0	0.30	18.5	0.185	3.0	0.030	0.0	0.000	None
						0.72	34.4	0.344	7.1	0.071	2.6	0.026	
						1.68	53.8	0.538	19.0	0.190	8.4	0.084	None
PCRSTCRB3	A119RBNS7B	3.2	1.68	Stationary	124.6	0.30	20.8	0.200	3.8	0.36	0.0	0.000	None
						0.72	36.1	0.348	8.3	0.080	3.6	0.035	None
						1.68	57.9	0.559	22.3	0.215	6.6	0.064	None
PCRSTCRB4	-	3.2	1.62	Blank	96.1	0.30	25.0	0.261	3.1	0.031	0.0	0.000	None
						0.90	53.9	0.561	15.2	0.158	2.3	0.024	None
						1.62	74.8	0.778	47.3	0.492	11.8	0.123	None
PCRMCRB1	A119RBNS7B	3.2	1.8	Continuous	106.8	0.30	16.8	0.157	2.9	0.027	0.0	0.000	None
						0.90	32.3	0.303	7.7	0.072	1.6	0.015	None
						1.80	43.4	0.407	11.6	0.109	3.9	0.036	None

Table 1

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^3 s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB2	A119RBNS7B	3.2	1.8	Continuous	93.4	0.30	19.9	0.212	3.3	0.036	0.0	0.000	None
						0.90	33.1	0.355	6.9	0.074	2.5	0.027	None
						1.80	45.6	0.488	11.1	0.118	4.0	0.043	None
PCRMCRB3	A119RBNS7A	3.2	1.8	Continuous	101.1	0.48	19.3	0.191	3.0	0.029	0.0	0.000	None
						0.00	31.3	0.310	5.7	0.056	1.6	0.016	None
						1.80	42.4	0.419	8.6	0.085	4.5	0.045	None
PCRMCRB4	A119RBNS7A	3.2	1.8	Continuous	102.3	0.30	17.5	0.171	1.7	0.017	0.0	0.000	None
						0.90	32.5	0.318	6.1	0.060	1.4	0.000	None
						1.80	45.8	0.448	10.3	0.101	2.8	0.027	None
PCRMCRB5	A119RBNS7A	3.2	3.9	Continuous	104.2	0.60	27.4	0.263	5.2	0.050	1.1	0.011	None
						1.80	35.8	0.344	8.6	0.083	3.1	0.030	None
						3.60	46.8	0.449	16.3	0.156	9.1	0.088	None

Table 2

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^3 s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRMCRB6	A119RBNS7A	3.2	3.9	Continuous	104.5	0.70	25.7	0.246	4.3	0.045	1.3	0.013	None
						1.80	43.2	0.414	9.6	0.092	3.9	0.037	None
						3.60	55.0	0.526	18.9	0.181	10.0	0.096	None
PCRMCRB7	A119RBNS7A	3.2	3.9	Continuous	115.1	0.60	28.8	0.251	4.3	0.038	0.9	0.008	None
						1.80	47.7	0.415	20.0	0.087	3.5	0.030	None
						3.60	58.0	0.604	18.8	0.163	10.5	0.091	None
PCRMCRB8	-	3.2	3.3	Blank	101.0	0.60	37.9	0.375	8.7	0.086	2.4	0.024	None
						1.80	75.4	0.747	47.2	0.468	25.4	0.251	None
						3.30	92.7	0.918	80.0	0.793	61.8	0.612	None
PCRMCRB9	-	3.2	3.9	Blank	101.2	0.60	33.3	0.327	9.8	0.097	1.7	0.016	None
						1.80	74.9	0.740	49.1	0.485	27.8	0.274	None
						3.60	94.4	0.934	86.4	0.854	66.3	0.655	None

Table 3

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^{3}s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB10	–	3.2	3.9	Blank	103.2	0.6	34.9	0.338	9.2	0.089	4.9	0.047	None
						1.8	75.0	0.727	45.3	0.439	25.5	0.247	None
						3.6	92.4	0.895	84.4	0.817	69.3	0.671	None
PCRMCRB11	Untreated Ravello	3.2	3.0	Blank	102.8	0.6	33.6	0.327	8.8	0.086	3.0	0.029	None
						1.8	76.4	0.754	43.8	0.426	25.0	0.243	None
						3.0	91.7	0.893	76.0	0.739	52.8	0.514	None
PCRMCRB14	A126RBNS30	3.2	3.6	Continuous	103.1	0.6	24.5	0.237	–	–	–	–	2 x 1KW Heaters R L T 573 563 B 338 358
				One Tank		1.8	38.7	0.375	–	–	–	–	
						3.6	46.0	0.446	–	–	–	–	
PCRMCRB15	A126RBNS30	3.2	3.6	Continuous	101.6	1.8	22.0	0.217	–	–	–	–	None
				One Tank		1.8	37.1	0.365	–	–	–	–	None
						3.6	44.7	0.440	–	–	–	–	None

Table 4

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^{3}s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB16	A126RBNS30	3.2	3.6	Continuous	101.2	0.6	22.1	0.218	–	–	–	–	None
				One Tank		1.8	38.7	0.382	–	–	–	–	None
						3.6	48.5	0.479	–	–	–	–	None
PCRMCRB17	A126RBNS30	3.2	3.6	Continuous	99.7	0.6	21.8	0.218	–	–	–	–	None
				One Tank		1.8	35.9	0.360	–	–	–	–	None
						3.6	44.0	0.441	–	–	–	–	None
PCRMCRB18	A126RBNS30	3.2	3.6	Continuous	101.8	0.6	22.0	0.216	–	–	–	–	None
				One Tank		1.8	36.9	0.362	–	–	–	–	None
						3.6	50.8	0.499	–	–	–	–	None
PCRMCRB19	A126RBNS30	3.2	3.6	Continuous	102.5	0.6	22.1	0.216	–	–	–	–	None
				One Tank		1.8	37.7	0.368	–	–	–	–	None
						3.6	49.1	0.479	–	–	–	–	None

Table 5

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	m^3s^{-1}	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRMCRB20	A126RBNS30	3.2	3.6	Continuous	98.9	0.6	22.1	0.223	-	-	-	-	None
				One Tank		1.8	33.8	0.342	-	-	-	-	None
						3.6	43.8	0.443	-	-	-	-	None
PCRMCRB21	A126RBNS30	3.2	3.3	Continuous	100.0	0.6	21.2	0.212	-	-	-	-	1 x 1KW Heater R L T 463 688 B 318 413
				One Tank		1.8	33.8	33.8	-	-	-	-	
						3.3	34.7	0.347	-	-	-	-	
PCRMCRB23	A126RBNS30	3.2	3.6	Continuous	113.5	0.6	32.3	0.284	-	-	-	-	2 x 1KW Heater R L T 678 568 B 360 345
						1.8	51.9	0.457	13.6	0.120	4.9	0.043	
						3.6	56.3	0.496	19.9	0.175	8.1	0.072	
PCRMCRB26	A126RBNS30	3.2	3.6	Continuous	106.8	0.6	21.8	0.204	4.1	0.038	0.9	0.008	2 x 1KW Heater R L T 738 594 B 388 358
						1.8	39.5	0.372	10.3	0.096	3.6	0.034	
						3.6	45.2	0.423	14.4	0.134	5.6	0.052	

Table 6

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	m^3s^{-1}	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRMCRB27	A126RBNS30	3.2	3.6	Continuous	108.6	0.6	22.5	0.207	5.0	0.046	0.4	0.004	2 x 1KW Heater
						1.8	43.7	0.402	12.4	0.114	3.6	0.033	R L T 728 573
						3.6	51.4	0.473	18.6	0.171	8.2	0.076	B 388 353
PCRMCRB28	A126RBNS28	3.2	3.6	Continuous	103.6	0.6	25.5	0.246	4.0	0.039	0.0	0.000	2 x 1KW Heater
						1.8	42.1	0.407	12.3	0.119	4.1	0.040	R L T 748 573
						3.6	43.5	0.420	15.9	0.154	7.0	0.067	B 398 359
PCRMCRB30	A126RBNS28	3.2	3.6	Continuous	102.4	0.6	28.0	0.274	4.3	0.042	1.1	0.011	2 x 1KW Heater
						1.8	44.6	0.435	10.4	0.101	2.9	0.029	R L T 758 623
						3.6	45.5	0.445	13.0	0.127	5.0	0.049	B 408 363
PCRMCRB31	A126RBNS30	3.2	3.6	Continuous	101.1	0.6	25.5	0.252	4.5	0.044	1.0	0.010	2 x 1KW Heater
						1.8	42.0	0.415	12.2	0.120	3.5	0.036	R L T 803 613
						3.6	41.6	0.456	14.7	0.146	5.1	0.051	B 463 398

Table 7

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^{3}s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB32	A126RBNS28	3.2	3.6	Continuous	96.7	0.6	22.9	0.237	6.1	0.063	1.8	0.019	2 x 1KW Heaters + $6.2x10^{-4}$ $M^{3}S^{-1}$ Air R L T 618 613 B 348 343
						1.8	36.5	0.377	8.0	0.082	3.6	0.037	
						3.6	43.4	0.449	13.6	0.141	6.1	0.063	
PCRMCRB34	A126RBNS28	1.6	3.6	Continuous	103.5	0.6	13.9	0.134	1.1	0.010	0.0	0.000	None
						1.8	18.2	0.176	3.1	0.030	1.0	0.010	None
						3.6	26.3	0.254	8.2	0.070	3.6	0.035	None
PCRMCRB36	A126RBNS28	3.2	3.6	Continuous	106.4	0.6	26.0	0.295	3.4	0.032	0.0	0.000	None
						1.8	44.0	0.413	9.5	0.090	2.3	0.022	None
						3.6	52.5	0.494	20.3	0.191	10.8	0.101	None
PCRMCRB37	A130RBNS48	1.6	3.6	Continuous	125.9	0.6	16.0	0.127	0.0	0.000	0.0	0.000	None
						1.8	25.5	0.202	1.7	0.014	0.0	0.000	None
						3.6	30.5	0.242	5.1	0.040	1.9	0.015	None

Table 8

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	m^3s^{-1}	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB38	A130RBNS48	4.8	3.6	Continuous	104.2	0.6	44.4	0.426	7.3	0.070	1.2	0.012	None
						1.8	66.4	0.638	15.9	0.153	9.1	0.087	None
						3.6	72.6	0.697	35.9	0.344	21.9	0.211	None
PCRMCRB39	A126RBNS28	4.8	3.6	Continuous	108.1	0.6	42.1	0.389	11.3	0.105	2.8	0.026	None
						1.8	60.8	0.562	27.8	0.258	13.5	0.125	None
						3.6	74.4	0.688	46.5	0.430	28.4	0.262	None
PCRMCRB40	A126RBNS28	4.8	3.6	Continuous	100.0	0.6	35.9	0.359	8.4	0.084	2.3	0.023	None
						1.8	56.1	0.561	24.5	0.245	9.5	0.095	None
						3.6	67.2	0.672	37.6	0.376	27.1	0.271	None
PCRMCRB42	A131RBNS53	3.2	9.6	Continuous	106.5	0.6	24.5	0.230	5.0	0.047	0.0	0.000	Continuous
				Unused		1.8	33.3	0.312	11.2	0.105	0.0	0.000	Length of Unused
				Cloth		3.6	38.1	0.358	12.3	0.116	0.0	0.000	Cloth

Table 9

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^{3}s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRMCRB42	A131RBNS53					5.4	40.0	0.375	13.7	0.128	5.2	0.049	Passed through the system
						7.2	40.4	0.380	14.2	0.133	5.6	0.053	
						9.6	41.3	0.388	15.9	0.149	6.6	0.062	
PCRMCRB43	A131RBNS52	1.5	3.6	Continuous	103.3	0.6	13.3	0.129	1.8	0.018	0.0	0.000	None
						1.8	19.2	0.186	3.5	0.033	1.3	0.013	None
						3.6	23.8	0.230	6.2	0.060	4.7	0.045	None
PCRMCRB44	A131RBNS53	3.2	3.6	Continuous	53.5	0.9	12.0	0.225	0.0	0.000	0.0	0.000	None
						1.8	16.9	0.316	4.6	0.085	1.7	0.031	None
						3.6	20.5	0.383	8.5	0.159	4.1	0.076	None
PCRMCRB45	A131RBNS52	3.2	3.6	Continuous	45.2	0.6	9.7	0.214	-	-	-	-	None
						1.8	14.6	0.322	-	-	-	-	None
						3.6	18.3	0.404	7.2	0.158	3.4	0.054	None

Table 10

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^{3}s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	s	–	kmg^{-3}	–	K
PCRMCRB47	A131RNBS52	3.2	3.6	Continuous	98.8	0.9	27.5	0.279	5.2	0.053	1.2	0.012	4% NaOH
						1.8	42.7	0.432	14.9	0.151	5.4	0.055	Solution
						3.6	55.1	0.558	22.6	0.229	10.4	0.105	and Wash
PCRMCRB49	A131RBNS52	3.2	3.6	Continuous	115.5	0.6	27.4	0.237	4.4	0.038	1.2	0.010	1 x 1KW Heater
						1.8	42.1	0.364	11.2	0.097	3.6	0.031	R L T 743 383
						3.6	45.6	0.395	15.7	0.136	6.2	0.054	B 323 313
PCRMCRB50	A131RBNS62	3.2	6.6	Continuous	100.6	0.6	21.7	0.216	4.1	0.041	1.2	0.012	1 x 1KW Heater
						1.8	37.9	0.377	10.3	0.103	4.0	0.040	R L T 748 393
						3.6	45.8	0.455	16.0	0.159	6.6	0.066	B 318 313
						5.4	48.5	0.482	18.0	0.179	7.2	0.071	
						7.6	50.8	0.505	19.2	0.191	7.5	0.075	
PCRMCRB51	A131RBNS52	3.2	9.0	Continuous	99.8	0.6	11.2	0.112	2.6	0.026	3.3	0.035	None

Table 11

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^3 s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
PCRMCRB51	A131RBNS52					1.8	35.6	0.357	8.4	0.084	3.3	0.033	None
						3.6	42.0	0.421	15.5	0.155	8.0	0.080	None
						5.4	48.8	0.490	22.9	0.229	12.2	0.122	None
						7.2	56.4	0.565	28.1	0.281	16.2	0.162	None
						9.0	58.4	0.585	34.2	0.343	21.1	0.222	None
PCRMCRB52	A131RBNS52	3.2	9.0	Continuous	105.0	0.6	14.4	0.137	3.7	0.036	1.1	0.011	1 x 1KW Heater R L T 738 388 B 323 308
						1.8	32.9	0.313	7.5	0.71	2.3	0.021	
						3.6	36.5	0.349	9.5	0.090	1.6	0.016	
						5.4	39.9	0.380	11.8	0.113	2.8	0.027	
						7.2	40.9	0.390	-	-	2.6	0.025	
						9.0	45.0	0.429	17.0	0.162	4.9	0.046	
PCRMCRB53	A131RBNS52	3.2	8.1	Continuous	98.8	0.6	23.6	0.210	4.6	0.047	0.7	0.007	None

Table 12

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
–	–	$x10^{-5}$	$x10^{3}$	–	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	–	$x10^{-3}$	–	$x10^{-3}$	–	Temp
–	–	$m^{3}s^{-1}$	s	–	kgm^{-3}	s	kgm^{-3}	–	kgm^{-3}	–	kgm^{-3}	–	K
PCRMCRB53	A131RBNS52					1.8	38.3	0.388	10.1	0.102	3.6	0.036	None
						3.6	47.0	0.475	19.0	0.192	9.7	0.098	None
						5.4	51.2	0.518	26.0	0.263	16.0	0.162	None
						7.2	59.3	0.601	33.7	0.341	21.7	0.220	None
						8.1	61.8	0.626	40.0	0.405	26.0	0.263	None
PCRMCRB54	A131RBNS52	3.2	7.2	Continuous	98.3	0.6	21.0	0.214	3.6	0.036	0.5	0.005	None
						1.8	36.0	0.366	8.5	0.086	2.7	0.027	None
						3.6	43.9	0.450	17.1	0.174	8.8	0.090	None
						5.4	48.8	0.496	22.0	0.223	13.8	0.140	None
						7.2	58.2	0.592	29.0	0.295	20.3	0.206	None

Table 13

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^{3}s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
CPCRMCRB1	A13RBNS52	3.2	3.6	Continuous	96.9	0.6	16.4	0.170	1.4	0.015	0.5	0.005	None
						1.8	24.5	0.252	4.1	0.042	1.4	0.010	None
						3.6	31.3	0.322	7.5	0.077	3.2	0.033	None
CPCRMCRB2	A131RBNS52	3.2	8.4	Continuous	96.2	0.6	14.3	0.149	2.9	0.030	0.4	0.004	None
						1.8	25.2	0.262	5.0	0.052	1.4	0.015	None
						3.6	31.4	0.327	7.7	0.080	3.7	0.038	None
						5.4	38.0	0.395	10.2	0.106	6.3	0.065	None
						7.2	38.1	0.406	14.2	0.147	8.7	0.091	None
						8.4	44.4	0.461	13.4	0.140	10.1	0.105	None
CPCRMCRB3	A131RBNS52	3.2	3.6	Continuous	90.9	0.6	14.4	0.158	1.6	0.018	0.8	0.009	1 x 1KW Heater R L T 728 378 B 323 308
						1.8	24.2	0.266	4.3	0.047	1.4	0.015	
						3.6	25.8	0.283	4.6	0.051	1.5	0.016	

Table 14

Expt. No.	Cloth No.	Liquid Flow Rate	Expt. Duration	Type of Experiment	Feed Concentration (Co)	Time From Start	Tank 1		Tank 2		Tank 3		Regeneration Details
							Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	Conc. (C)	$\frac{C}{Co}$	
-	-	$x10^{-5}$	$x10^{3}$	-	$x10^{-3}$	$x10^{3}$	$x10^{-3}$	-	$x10^{-3}$	-	$x10^{-3}$	-	Temp
-	-	$m^{3}s^{-1}$	s	-	kgm^{-3}	s	kgm^{-3}	-	kgm^{-3}	-	kgm^{-3}	-	K
CPCRMCRB4	A131RBNS52	3.2	7.8	Continuous	92.7	0.6	10.8	0.117	1.3	0.014	0.6	0.006	1 x 1KW Heater R L T 743 388 B 333 313
						1.8	21.9	0.236	3.6	0.039	1.2	0.013	
						3.6	26.0	0.281	4.9	0.53	1.4	0.015	
						5.4	27.5	0.297	4.4	0.047	1.6	0.017	
						7.2	27.3	0.294	5.5	0.060	1.7	0.019	
						7.8	29.6	0.320	5.7	0.062	1.8	0.019	

Table 15

APPENDIX II

LISTING OF THE COMPUTER PROGRAM FOR THE STEADY STATE MODEL

This appendix contains the computer program used for the iterative solution of the steady state model. The program has been made as general as possible to allow for changes in the system, such as the number of tanks, liquid flow rate or the cloth adsorption capacity.

When information about the system has been entered into the computer, the first stage of the program is the calculation of the forward rate constant to be used in the calculation. The iteration then starts and continues until a given tolerance limit is reached. At this point in the program, the concentrations of solute in both the solid and liquid phases are printed, followed by the specified and calculated feed concentrations. At the end of this section, a set of results from experiment PCRMCRB6 is presented, as an example of the output from the computer program.

LISTING OF THE STEADY STATE MODEL (PAGE 1)

```
5  REM        COMPUTER PROGRAM FOR STEADY STATE MODELLING OF THE
10  REM        CONTINUOUS TREATMENT SYSTEM
15  DIM C(50),P(50),Y(50)
20  INPUT U1: REM        LIQUID FLOW RATE (CU.M/S)
25  INPUT T: REM        TOLERANCE LIMIT ON CALCULATED FEED CONC. (KG/CU.M)
30  INPUT F: REM        SPECIFIED FEED CONCENTRATION (KG/CU.M)
35  INPUT C1: REM        ESTIMATED TANK 1 STEADY STATE CONCENTRATION
40  REM        FOR CALCULATION OF THE RATE CONSTANT (KG/CU.M)
45  INPUT C(1): REM        STARTING VALUE OF THE CONCENTRATION IN TANK 3
50  REM        FOR ITERATION IN THE STEADY STATE MODEL (KG/CU.M)
55  INPUT E: REM        CLOTH ADSORPTION CAPACITY (KG/KG)
60  INPUT V: REM        CLOTH VELOCITY (M/S)
65  INPUT N: REM        NUMBER OF TANKS
70  INPUT S: REM        STEP LENGTH FOR ITERATIONS (KG/CU.M)
75  F1=.89E-04: REM        MASS FLOW RATE OF THE CLOTH (KG/S)
80  REM        INPUT OF LENGTHS OF CLOTH IN EACH TANK (M)
85  FOR I=1,N
90  READ P(I)
95  NEXT I
100  DATA .52,.625,.69
105  Y1=0
106  Y(I)=0
110  REM        CALCULATION OF THE FORWARD RATE CONSTANT
115  Y2=(U1/F1)*(F-C1)+Y1
120  R1=LOG(E/(E-Y2))*(V/(P(N)*C1))
125  REM        THE STEADY STATE MODEL
130  FOR I=1,N
```

LISTING OF THE STEADY STATE MODEL (PAGE 2)

```
135  Y( I+1 )=E-((E-Y( I ))/(EXP((R1*P( I )*C( I ))/V)))
140  C( I+1 )=(F1/U1 )*( Y( I+1 )-Y( I ) )+C( I )
145  NEXT I
150  IF C(N+1 )>F GOTO 170
155  IF F-C(N+1 )<T GOTO 181
160  C( 1 )=C( 1 )+S
165  GOTO 130
170  IF C(N+1 )-F<T GOTO 181
175  C( 1 )=C( 1 )-S
180  GOTO 130
181  PRINT
182  PRINT "CLOTH VELOCITY = ",V,"M/S"
183  PRINT
185  PRINT "LIQUID FLOW RATE =",U1,"CU.M/S"
190  PRINT
195  PRINT "CLOTH CAPACITY =",E,"KG/KG"
200  PRINT
205  PRINT "ESTIMATED TANK 1 CONCENTRATION =",C1,"KG/CU.M"
210  PRINT
215  PRINT "FORWARD RATE CONSTANT =",R1,"CU.M/KG.S"
220  PRINT
225  PRINT "  TANK NO.  LIQUID CONC. LEAVING    CLOTH CONC. ENTERING "
230  PRINT "                   KG/CU.M                       KG/KG       "
235  PRINT
240  FOR I=1,N
245  PRINT I,C(N+1-I),TAB(40),Y(I)
250  NEXT I
255  PRINT
```

LISTING OF THE STEADY STATE MODEL (PAGE 3)

```
260  PRINT "SPECIFIED FEED CONC. =",F."KG/CU.M"
265  PRINT
270  PRINT "CALCULATED FEED CONC. =",C(N+1),"KG/CU.M"
275  PRINT
280  PRINT "TO WITHIN + OR - ",T,"KG/CU.M"
285  PRINT
290  END
```

Nomenclature (Computer Program Only)

C	Concentration of pollutant in the liquid phase.	kgm^{-3}
C(1)	Starting value of the pollutant concentration in Tank 3 for iteration in the steady state model.	kgm^{-3}
C1	Tank 1 pollutant concentration used for the calculation of the rate constant.	kgm^{-3}
E	Cloth adsorption capacity.	kg (pollutant) kg (cloth)$^{-1}$
F	Specified feed concentration of the pollutant.	kgm^{-3}
F1	Mass flow rate of the charcoal cloth.	kgs^{-1}
N	Number of tanks in the adsorption section.	-
P	Length of cloth in each tank.	m
R1	Forward rate constant.	$m^3kg^{-1}s^{-1}$
S	Step length for iterations of the program (in concentration units).	kgm^{-3}
T	Tolerance limit placed on the difference between the calculated and specified feed concentrations of pollutant.	kgm^{-3}
U1	Liquid flow rate.	m^3s^{-1}
V	Charcoal cloth velocity.	s^{-1}
Y	Pollutant concentration on the charcoal cloth.	kg (pollutant) kg (cloth)$^{-1}$
Y1	Pollutant concentration on the charcoal cloth entering Tank 1, for the forward rate constant calculation.	kg (pollutant) kg (cloth)$^{-1}$
Y2	Pollutant concentration on the charcoal cloth leaving Tank 1, for the forward rate constant calculation.	kg (pollutant) kg (cloth)$^{-1}$

```
A SAMPLE SET OF RESULTS FOR THE STEADY STATE MODEL
(EXPERIMENTAL RESULTS OF RUN NO. PCRMCR86 )


CLOTH VELOCITY =                   .25E-02      M/S
LIQUID FLOW RATE =                 32E-04       CU.M/S
CLOTH CAPACITY =                      .299      KG/KG
ESTIMATED TANK 1 CONCENTRATION =           .57E-01       KG/CU.M
FORWARD RATE CONSTANT =      .373859E-02  CU.M/KG.S
  TANK NO.  LIQUID CONC. LEAVING    CLOTH CONC. ENTERING
                 KG/CU.M                  KG/KG

     1          .561609E-01                  0
     2          .320149E-01               .449973E-02
     3          .195E-01                  .131814E-01
SPECIFIED FEED CONC. =             .1045    KG/CU.M
CALCULATED FEED CONC. =            .100918  KG/CU.M
TO WITHIN + OR -              .5E-02        KG/CU.M

290 EXIT
```

APPENDIX III

PROPERTIES OF THE SYSTEM FOR AND RESULTS OBTAINED FROM THE STEADY STATE MATHEMATICAL MODEL

Notes:

1. Phenol was the polluting chemical in experiments P/---

2. 2-Chlorophenol was the polluting chemical in experiments CP/---

3. Most of the results have both experimental and ideal values. Experimental values are based on recorded results of experiment PCPMCRB42 where a continuous length of unused cloth was passed through the system.

4. Some of the results use experimental data only, this is because the values obtained from these results, using the model, approach those of the ideal situation.

5. It may be noted in some experimental results for tanks 2 and 3 in regenerated experiments, that values given are the same as for the ideal case, becuase the experimental figures approached the ideal situation, from the model, very well.

Experiment Number	Charcoal Cloth Run Code Number	Liquid Flow Rate	Cloth Velocity	Cloth Capacity	Number of Contactors	Tank 1 Concentration For Rate Calculation	Forward Reaction Rate	Value Used For Tank 1 Estimate	Regeneration
-	-	$x10^{-5}$	$x10^{-3}$	kg(Adsorbate)	-	$x10^{-3}$	$x10^{-3}$	-	-
-	-	m^3s^{-1}	ms^{-1}	$kg(Cloth)^{-1}$	-	kgm^{-3}	$m^3kg^{-1}s^{-1}$	-	-
PCRMCRB5	A119RBNS7	3.2	2.5	0.299	3	50.0	4.884	Experimental	None
PCRMCRB5	A119RBNS7	3.2	2.5	0.299	3	46.0	7.100	Ideal	None
PCRMCRB6	A119RBNS7	3.2	2.5	0.299	3	57.0	3.739	Experimental	None
PCRMCRB6	A119RBNS7	3.2	2.5	0.299	3	40.8	7.077	Ideal	None
PCRMCRB7	A119RBNS7	3.2	2.5	0.299	3	61.6	3.911	Experimental	None
PCRMCRB7	A119RBNS7	3.2	2.5	0.299	3	44.9	7.117	Ideal	None
PCRMCRB14	A126RBNS30	3.2	2.5	0.299	1	46.0	5.603	Experimental	Regeneration
PCRMCRB14	A126RBNS30	3.2	2.5	0.299	1	40.2	7.089	Ideal	Regeneration
PCRMCRB15	A126RBNS30	3.2	2.5	0.299	1	44.5	5.792	Experimental	None
PCMCRB14	A126RBNS30	3.2	2.5	0.299	1	39.6	7.089	Ideal	None
PCRMCRB16	A126RBNS30	3.2	2.5	0.299	1	49.0	4.794	Experimental	None
PCRMCRB16	A126RBNS30	3.2	2.5	0.299	1	39.5	7.071	Ideal	None

Table 1

Experiment Number	Specified Feed Concentration	Calculated Feed Concentration	Tolerance Limit on Feed	Tank 1 Concentration (Experimental)	Tank 1 Concentration (Calculated	Tank 2 Concentration (Experimental)	Tank 2 Concentration (Calculated)	Tank 3 Concentration (Experimental)	Tank 3 Concentration (Calculated)
-	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}	x10^{-3}
-	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}
PCRMCRB5	104.2	100.5	5	50.0	49.3	17.4	24.8	12.9	13.5
PCRMCRB5	104.2	102.7	5	40.6	46.0	15.6	16.7	6.3	7.5
PCRMCRB6	104.5	100.9	5	57.0	19.1	32,0	10.8	10.8	19.6
PCRMCRB6	104.5	101.2	5	40.8	40.5	15.7	16.6	6.3	7,5
PCRMCRB7	115.1	111.8	5	61,6	61.2	20.8	34.3	15.0	20.5
PCRMCRB7	115.1	114.7	5	44.9	46.1	17.3	18.9	6.9	8.5
PCRMCRB14	103.1	98.7	5	46.0	44.0	-	-	-	-
PCRMCRB14	103.1	98.8	5	40.2	38.5	-	-	-	-
PCRMCRB15	101.6	97.1	5	44.5	42.5	-	-	-	-
PCRMCRB15	101.6	97.6	5	39.6	38.0	-	-	-	-
PCRMCRB16	101.2	97.1	5	49.0	47.0	-	-	-	-
PCRMCRB16	101.2	97.4	5	39.5	38.0	-	-	-	-

Table 2

Experiment Number	Charcoal Cloth Run Code Number	Liquid Flow Rate	Cloth Velocity	Cloth Capacity	Number of Contactors	Tank 1 Concentration For Rate Calculation	Forward Reaction Rate	Value Used For Tank 1 Estimate	Regeneration
-	-	$x10^{-5}$	$x10^{-3}$	kg(Adsorbate)	-	$x10^{-3}$	$x10^{-3}$	-	-
-	-	m^3s^{-1}	ms^{-1}	$kg(Cloth)^{-1}$	-	kgm^{-3}	$m^3kg^{-1}s^{-1}$	-	-
PCRMCRB17	A126RBNS30	3.2	2.5	0.299	1	44.5	5.593	Experimental	None
PCRMCRB17	A126RBNS30	3.2	2.5	0.299	1	38.9	7.072	Ideal	None
PCRMCRB18	A126RBNS30	3.2	2.5	0.299	1	52.0	4.303	Experimental	None
PCRMCRB18	A126RBNS30	3.2	2.5	0.299	1	39.7	7.083	Ideal	None
PCRMCRB19	A126RBNS30	3.2	2.5	0.299	1	50.0	4.726	Experimental	None
PCRMCRB19	A126RBNS30	3.2	2.5	0.299	1	40.0	7.077	Ideal	None
PCRMCRB20	A126RBNS30	3.2	2.5	0.299	1	44.5	5.508	Experimental	None
PCRMCRB20	A126RBNS30	3.2	2.5	0.299	1	38.6	7.066	Ideal	None
PCRMCRB21	A126RBNS30	3.2	2.5	0.299	1	35.0	8.425	Experimental	Regeneration
PCRMCRB23	A126RBNS30	3.2	2.5	0.299	3	57.5	4.393	Experimental	Regeneration
PCRMCRB23	A126RBNS30	3.2	2.5	0.299	3	44.3	7.106	Ideal	Regeneration
PCRUMCRB26	A126RBNS30	3.2	2.5	0.299	3	46.0	5.980	Experimental	Regeneration

Table 3

Experiment Number	Specified Feed Concentration	Calculated Feed Concentration	Tolerance Limit on Feed	Tank 1 Concentration (Experimental)	Tank 1 Concentration (Calculated)	Tank 2 Concentration (Experimental)	Tank 2 Concentration (Calculated)	Tank 3 Concentration (Experimental)	Tank 3 Concentration (Calculated)
-	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$
-	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}
PCRMCRB17	99.7	95.3	5	44.5	42.5	-	-	-	-
PCRMCRB17	99.7	94.9	5	38.9	37.0	-	-	-	-
PCRMCRB18	101.8	97.0	5	52.0	49.5	-	-	-	-
PCRMCRB18	101.8	97.5	5	39.7	38.0	-	-	-	-
PCRMCRB19	102.5	98.5	5	50.0	48.0	-	-	-	-
PCRMCRB19	102.5	98.7	5	40.0	38.5	-	-	-	-
PCRMCRB20	98.9	94.5	5	44.5	42.5	-	-	-	-
PCRMCRB20	98.9	94.5	5	38.6	37.0	-	-	-	-
PCRMCRB21	100.0	95.8	5	35.0	33.5	-	-	-	-
PCRMCRB23	113.5	111.4	5	57.5	57.8	19.9	30.7	8.1	17.5
PCRMCRB23	113.5	114.4	5	44,3	46.0	19.9	18.9	8.1	8.5
PCRMCRB26	106.8	106.4	5	46.0	47.0	14.4	21.3	5.6	10.5

Table 4

Experiment Number	Charcoal Cloth Run Code Number	Liquid Flow Rate	Cloth Velocity	Cloth Capacity	Number of Contactors	Tank 1 Concentration For Rate Calculation	Forward Reaction Rate	Value Used For Tank 1 Extimate	Regeneration
-	-	$x10^{-5}$	$x10^{-3}$	kg (Adsorbate)	-	$x10^{-3}$	$x10^{-3}$	-	-
-	-	$m^3 s^{-1}$	ms^{-1}	$kg (Cloth)^{-1}$	-	kgm^{-3}	$m^3 kg^{-1} s^{-1}$	-	-
PCRMCRB26	A126RBNS30	3.2	2.5	0.299	3	41.7	7.083	Ideal	Regeneration
PCRMCRB27	A126RBNS30	3.2	2.5	0.299	3	52.3	4.856	Experimental	Regeneration
PCRMCRB27	A126RBNS30	3.2	2.5	0.299	3	42.4	7.089	Ideal	Regneration
PCRMCRB28	A126RBNS38	3.2	2.5	0.299	3	45.0	5.863	Experimental	Regeneration
PCRMCRB28	A126RBNS28	3.2	2.5	0.299	3	40.3	7.095	Ideal	Regeneration
PCRMCRB30	A126RGNS28	3.2	2.5	0.299	3	45.0	5.759	Experimental	Regeneration
PCRMCRB30	A126RBNS28	3.2	2.5	0.299	3	39.9	7.095	Ideal	Regeneration
PCRMCRB31	A126RBNS30	3.2	2.5	0.299	3	47.0	5.186	Experimental	Regeneration
PCRMCRB31	A126TBNS30	3.2	2.5	0.299	3	39.4	7.089	Ideal	Regeneration
PCRMCRB32	A126RBNS28	3.2	2.5	0.299	3	44.0	5.391	Experimental	Regeneration
PCRMCRB32	A126RBNS28	3.2	2.5	0.299	3	37.7	7.073	Ideal	Regeneration
PCRMCRB34	A126RBNS28	1.6	2.5	0.299	3	25.0	7.007	Experimental	None

Table 5

Experiment Number	Specified Feed Concentration	Calculated Feed Concentration	Tolerance Limit on Feed	Tank 1 Concentration (Experimental)	Tank 1 Concentration (Calculated)	Tank 2 Concentration (Experimental)	Tank 2 Concentration (Calculated)	Tank 3 Concentration (Experimental)	Tank 3 Concentration (Calculated)
-	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$
-	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}
PCRMCRB26	106.8	107.6	5	41.7	43.2	14.4	17.7	5.6	8.0
PCRMCRB27	108.6	106.7	5	52.3	52.6	18.6	26.6	8.2	14.5
PCRMCRB27	108.6	107.8	5	42.4	43.2	18.6	17.8	8.2	8.0
PCRMCRB28	103.4	98.6	5	45.0	43.9	19.9	20.1	7.0	10.0
PCRMCRB28	103.4	101.6	5	40.3	40.6	15.9	16.7	7.0	7.5
PCRMCRB30	102.4	100.5	5	45.0	45.2	13.0	20.9	5.0	10.5
PCRMCRB30	102.4	101.6	5	39.9	40.6	13.0	16.7	5.0	7.5
PCRMCRB31	101.1	97.8	5	47.0	46.5	14.7	22.7	5.1	12.0
PCRMCRB31	101.1	101.5	5	39.4	40.5	14.7	16.6	5.1	7.5
PCRMCRB32	96.7	95.3	5	44.0	44.3	13.6	21.2	6.1	11.0
PCRMCRB32	96.7	94.8	5	37.7	37.8	13.6	15.5	6.1	7.0
PCRMCRB34	103.5	108.7	10	25.0	26.6	7.2	6.8	3.6	2.0

Table 6

Experiment Number	Charcoal Cloth Run Code Number	Liquid Flow Rate	Cloth Velocity	Cloth Capacity	Number of Contactors	Tank 1 Concentration For Rate Calculation	Forward Reaction Rate	Value Used For Tank 1 Estimate	Regeneration
-	-	$x10^{-5}$	$x10^{-3}$	kg(Adsorbate)	-	$x10^{-3}$	$x10^{-3}$	-	-
-	-	$m^3 s^{-1}$	ms^{-1}	$kg(Cloth)^{-1}$	-	kgm^{-3}	$m^3 kg^{-1} s^{-1}$	-	-
PCRMCRB36	A130RBNS48	3.2	2.5	0.299	3	53.5	4.451	Experimental	None
PCRMCRB36	A130RBNS48	3.2	2.5	0.299	3	41.5	7.094	Ideal	None
PCRMCRB37	A130RBNS48	1.6	2.5	0.299	3	31.5	6.721	Experimental	None
PCRMCRB38	A130RBNS48	4.8	2.5	0.299	3	74.0	2.743	Experimental	None
PCRMCRB39	A126RBNS28	4.8	2.5	0.299	3	76.0	2.843	Experimental	None
PCRMCRB40	A126RNBS28	4.8	2.5	0.299	3	68.5	3.094	Experimental	None
PCRMCRB42	A131RBNS53	3.2	2.5	0.299	3	41.6	7.077	Experimental	All Virgin Cloth: Ideal
PCRMCRB43	A131RBNS52	1.6	2.5	0.299	3	24.5	7.178	Experimental	None
PCRMCRB44	A131RBNS53	3.2	2.5	0.299	3	21.0	6.878	Experimental	None
PCRMCRB45	A131RBNS52	3.2	2.5	0.299	3	18.7	6.275	Experimental	None
PCRMCRB49	A131RBNS52	3.2	2.5	0.299	3	46.0	6.874	Experimental	Regeneration
PCRMCRB49	A131RBNS52	3.2	2.5	0.299	3	45.0	7.113	Ideal	Regeneration

Table 7

Experiment Number	Specified Feed Concentration	Calculated Feed Concentration	Tolerance Limit on Feed	Tank 1 Concentration (Experimental	Tank 1 Concentration (Calculated)	Tank 2 Concentration (Experimental)	Tank 2 Concentration (Calculated)	Tank 3 Concentration (Experimental)	Tank 3 Concentration (Calculated)
-	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$
-	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}
PCRMCRB36	106.4	101.1	5	53.5	53.5	20.3	28.2	10.8	16.0
PCRMCRB36	106.4	101.6	5	41.5	40.6	16.0	16.7	6.4	7.5
PCRMCRB37	125.9	123.4	10	31.5	31.3	5.0	8.3	1.9	2.5
PCRMCRB38	104.2	99.2	5	74.0	71.7	35.9	52.5	21.9	40.0
PCRMCRB39	108.1	103.2	5	76.0	73.9	46.5	53.6	28.4	40.5
PCRMCRB40	100.0	95.8	5	68.5	66.8	37.6	47.3	27.1	35.0
PCRMCRB42	106.5	107.5	5	41.6	43.1	15.9	17.7	6.6	8.0
PCRMCRB43	103.3	114.5	15	24.5	27.0	6.2	7.0	4.7	2.0
PCRMCRB43	53.5	53.1	5	21.0	21.1	8.5	8.7	4.1	4.0
PCRMCRB45	45.2	45.6	2.5	18.7	19.1	7.2	8.3	2.4	4.0
PCRMCRB49	115.5	114.4	5	46.0	46.9	15.7	19.6	6.2	9.0
PCRMCRB49	115.5	115.1	5	45.0	46.2	15.7	18.9	6.2	8.5

Table 8

Experiment Number	Charcoal Cloth Run Code Number	Liquid Flow Rate	Cloth Velocity	Cloth Capacity	Number Contactors	Tank 1 Concentration For Rate Calculation	Forward Reaction Rate	Value Used For Tank 1 Eetimate	Regeneration
–	–	$x10^{-5}$	$x10^{-3}$	kg(Adsorbate)	–	$x10^{-3}$	$x10^{-3}$	–	–
–	–	m^3s^{-1}	ms^{-1}	$kg(Cloth)^{-1}$	–	kgm^{-3}	$m^3kg^{-1}s^{-1}$	–	–
PCRMCRB51	A131RBNS52	3.2	2.5	0.299	3	59.5	3.025	Experimental	None
PCRMCRB51	A131RBNS52	3.2	2.5	0.299	3	38.9	7.084	Ideal	None
PCRMCRB52	A131RBNS52	3.2	2.5	0.299	3	46.0	5.796	Experimental	Regeneration
PCRMCRB53	A131RBNS52	3.2	2.5	0.299	3	62.5	2.587	Experimental	None
PCRMCRB53	A131RBNS52	3.2	2.5	0.299	3	38.5	7.084	Ideal	None

Table 9

Experiment Number	Specified Feed Concentration	Calculated Feed Concentration	Tolerance Limit on Feed	Tank 1 Concentration (Exeprimental	Tank 1 Concentration (Calculated)	Tank 2 Concentration (Experimental)	Tank 2 Concentration (Calculated)	Tank 3 Concentration (Experimental)	Tank 3 Concentration (Calculated)
-	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$	$x10^{-3}$
-	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}	kgm^{-3}
PCRMCRB51	99.8	94.9	5	59.5	57.5	34.2	35.7	22.2	23.5
PCRMCRB51	99.8	95.0	5	38.9	37.9	15.0	15.5	6.0	7.0
PCRMCRB52	105.0	101.5	5	46.0	45.5	17.0	21.0	5.0	10.5
PCRMCRB53	98.8	94.3	5	62.5	60.5	40.0	39.7	26.0	27.5
PCRMCRB53	98.8	95.0	5	38.5	37.9	14.8	15.5	5.9	7.0

Table 10

APPENDIX IV

COMPARISON OF EXPERIMENTAL RESULTS AND THEORY FOR THE MIXING MODEL

Notes:

1. The flowrate used to test the model was $3.2 \times 10^{-5}\ m^3 s^{-1}$

2. $x_1 = \frac{u}{V_1} = 0.087\ s^{-1}$: V_1 = Volume of Tank 1 = $3.643 \times 10^{-2}\ m^3$

   $x_2 = \frac{u}{V_2} = 0.096\ s^{-1}$: V_2 = Volume of Tank 2 = $3.316 \times 10^{-2}\ m^3$

   $x_3 = \frac{u}{V_3} = 0.1104\ s^{-1}$: V_3 = Volume of Tank 3 = $2.872 \times 10^{-2}\ m^3$

Experiment Number	Time From Start	Feed Concentration (Co)	Tank 1		Tank 2		Tank 3	
			Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$
-	$x10^3$	$x10^{-3}$	-	-	-	-	-	-
-	s	kgm^{-3}	-	-	-	-	-	-
PCRMCRB8	0.3	101.3	0.230	0.182	0.031	0.045	0.003	0.008
	0.6		0.406	0.375	0.105	0.086	0.021	0.024
	0.9		0.543	0.536	0.198	0.185	0.058	0.063
	1.2		0.648	0.598	0.298	0.276	0.113	0.120
	1.5		0.729	0.668	0.396	0.383	0.180	0.170
	1.8		0.790	0.747	0.486	0.486	0.254	0.251
	2.1		0.839	0.804	0.570	0.524	0.333	0.354
	2.7		0.904	0.886	0.704	0.635	0.485	0.486
	3.0		0.926	0.899	0.757	0.734	0.555	0.540
	3.3		0.943	0.918	0.801	0.793	0.618	0.612

Table 1

Experiment Number	Time From Start	Feed Concentration (Co)	Tank 1		Tank 2		Tank 3	
			Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$
-	$x10^{-3}$	$x10^{-3}$	-	-	-	-	-	-
-	s	kgm^{-3}	-	-	-	-	-	-
PCRMCRB9	0.3	101.2	0.230	0.430	0.031	0.060	0.003	0.000
	0.6		0.406	0.329	0.105	0.097	0.021	0.016
	0.9		0.543	0.484	0.198	0.187	0.058	0.017
	1.2		0.648	0.593	0.299	0.238	0.113	0.127
	1.5		0.729	0.656	0.396	0.392	0.180	0.196
	1.8		0.791	0.740	0.488	0.485	0.254	0.274
	2.1		0.839	0.777	0.570	0.572	0.333	0.359
	2.4		0.876	0.821	0.642	0.639	0.410	0.443
	2.7		0.904	0.847	0.704	0.718	0.485	0.522
	3.0		0.926	0.887	0.757	0.759	0.555	0.589
	3.3		0.943	0.908	0.801	0.792	0.618	0.591
	3.6		0.956	0.934	0.838	0.854	0.676	0.655

Table 2

Experiment Number	Time From Start	Feed Concentration (Co)	Tank 1		Tank 2		Tank 3	
			Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$
-	$x10^3$	$x10^{-3}$	-	-	-	-	-	-
-	s	kgm^{-3}	-	-	-	-	-	-
PCRMCRB10	0.3	103.2	0.230	0.206	0.031	0.038	0.003	0.036
	0.6		0.406	0.338	0.105	0.089	0.021	0.047
	0.9		0.543	0.459	0.198	0.166	0.058	0.075
	1.2		0.684	0.581	0.299	0.251	0.113	0.135
	1.5		0.729	0.669	0.396	0.363	0.180	0.223
	1.8		0.791	0.727	0.488	0.439	0.254	0.247
	2.1		0.879	0.784	0.570	0.544	0.333	0.345
	2.4		0.876	0.806	0.642	0.620	0.410	0.412
	2.7		0.904	0.829	0.704	0.672	0.485	0.486
	3.0		0.926	0.858	0.757	0.713	0.555	0.553
	3.3		0.943	0.869	0.801	0.807	0.618	0.622
	3.6		0.956	0.895	0.838	0.817	0.676	0.671

Table 3

Experimental Number	Time From Start	Feed Concentration (Co)	Tank 1		Tank 2		Tank 3	
			Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$
-	$x10^3$	$x10^{-3}$	-	-	-	-	-	-
-	s	kgm^{-3}	-	-	-	-	-	-
PCRMCRB11	0.3	102.8	0.230	0.161	0.031	0.052	0.003	0.019
	0.6		0.406	0.327	0.105	0.086	0.021	0.029
	0.9		0.543	0.452	0.198	0.169	0.058	0.083
	1.2		0.648	0.565	0.299	0.250	0.113	0.115
	1.5		0.729	0.665	0.396	0.359	0.180	0.165
	1.8		0.791	0.754	0.488	0.426	0.254	0.243
	2.1		0.839	0.804	0.570	0.508	0.333	0.333
	2.4		0.876	0.840	0.642	0.588	0.410	0.405
	2.7		0.904	0.866	0.704	0.667	0.485	0.470
	3.0		0.926	0.893	0.757	0.739	0.555	0.514

Table 4.

Experiment Number	Time From Start	Feed Concentration (Co)	Tank 1		Tank 2		Tank 3	
			Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$	Calculated $\frac{C}{Co}$	Experimental $\frac{C}{Co}$
-	$x10^3$	$x10^{-3}$	-	-	-	-	-	-
-	s	kgm^{-3}	-	-	-	-	-	-
PCRSTCRB4	0.30	96.1	0.230	0.261	0.031	0.032	0.003	0.000
	0.60		0.406	0.433	0.105	0.059	0.021	0.000
	0.90		0.543	0.561	0.198	0.158	0.058	0.024
	1.20		0.648	0.680	0.298	0.254	0.113	0.052
	1.50		0.729	0.766	0.396	0.337	0.180	0.079
	1.62		0.755	0.778	0.434	0.492	0.209	0.123

Table 5

APPENDIX V

RESULTS OF ADSORPTION EQUILIBRIA EXPERIMENTS FOR ACTIVATED CHARCOAL CLOTH AND GRANULAR CHARCOAL

Details of the cloth and granular charcoal used may be found in Appendix VI

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	$kg\ Carbon^{-1}$	$kg\ Carbon^{-1}$
RB3 (Control)	A119RBNS7A	Phenol	0.0	104.0	0.0	-	0.175
(1)			86.6	49.0	11.0	0.127	
(2)			169.5	17.1	17.4	0.102	
(3)			285.5	5.0	19.8	0.069	
(4)			465.6	1.4	20.5	0.044	
(5)			764.0	1.0	20.6	0.027	
RB4 (Control)	A126RBNS30	Phenol	0.0	104.0	0.0	-	0.205
(1)			24.2	82.7	4.3	0.176	
(2)			42.5	68.1	7.2	0.169	
(3)			110.8	33.8	14.0	0.127	
(4)			245.5	8.9	19.0	0.078	
(5)			517.5	3.5	20.1	0.039	

Table 1

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB4 (6)	A127RBNS30	Phenol	650.4	1.6	20.5	0.032	0.205
(7)			973.5	1.1	20.6	0.021	
(8)			1252.0	0.8	20.7	0.017	
RB5 (Control)	A126RBNS30	Phenol	0.0	85.3	0.0	-	0.540
(1)			14.5	58.5	5.4	0.370	
(2)			32.5	43.3	8.4	0.259	
(3)			60.4	30.9	10.9	0.180	
(4)			115.0	0.9	16.9	0.147	
RB6 (Control)	A126RBNS30	Phenol	0.0	102.8	0.0	-	0.300
(1)			5.4	94.2	1.7	0.317	
(2)			13.4	85.6	3.4	0.256	
(3)			28.7	72.8	6.0	0.209	

Table 2

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	$kg Carbon^{-1}$	$kg Carbon^{-1}$
RB6 (4)	A126RBNS30	Phenol	39.0	67.1	7.1	0.183	0.300
(5)			60.4	51.1	10.3	0.171	
(6)			80.8	41.1	12.3	0.141	
RB7 (Control)	A126RBNS30	Phenol	0.0	120.4	0.0	-	0.220
(1)			41.3	79.6	8.2	0.198	
(2)			157.4	17.7	20.6	0.131	
(3)			244.0	4.1	23.3	0.095	
(4)			517.0	0.4	24.0	0.046	
RB8 (Control)	A126RBNS30	Phenol	0.0	125.0	0.0	-	0.305
(1)			45.1	71.3	10.8	0.284	
(2)			103.0	22.7	20.5	0.199	
(3)			222.4	4.5	24.1	0.108	

Table 3

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB8 (4)	A126RBNS30	Phenol	477.1	0.3	25.0	0.052	0.305
RB9 (Control)	A126RBNS30	Phenol	0.0	121.6	0.0	-	0.480
(1)			52.3	45.7	15.2	0.290	
(2)			91.1	25.8	19.2	0.210	
(3)			199.1	8.0	22.7	0.114	
(4)			454.7	0.8	24.2	0.053	
RB10 (Control)	A126RBNS30	Phenol	0.0	107.3	0.0	-	0.360
(1)			32.3	63.2	8,8	0.273	
(2)			100.0	14.0	18.7	0.187	
(3)			207.2	1.9	21.1	0.102	
(4)			348.8	0.4	21.4	0.061	

Table 4

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB11 (Control)	A126RBNS30	Phenol	0.0	106.5	0.0	-	0.300
(1)			28.7	69.2	7.5	0.260	
(2)			60.4	41.1	13.1	0.217	
(3)			103.0	15.8	18.1	0.176	
(4)			244.3	2.7	20.8	0.085	
(5)			391.6	0.9	21.1	0.054	
RB12 (Control)	A126RBNS30	Phenol	0.0	102.4	0.0	-	0.355
(1)			52.2	46.1	11.3	0.216	
(2)			75.1	30.6	14.4	0.191	
(3)			93.1	22.8	15.9	0.171	
(4)			181.4	5.9	19.3	0.106	
(5)			377.5	2.4	20.0	0.053	

Table 5

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB13 (Control)	A126RBNS30	Phenol	0.0	107.9	0.0	-	0.275
(1)			12.6	87.8	4.0	0.318	
(2)			19.9	82.0	5.2	0.260	
(3)			50.8	54.3	10.7	0.211	
(4)			147.1	6.4	20.3	0.138	
(5)			265.2	1.5	21.3	0.080	
RB14 (Control)	A126RBNS30	Phenol	0.0	106.4	0.0	-	0.257
(1)			13.3	90.3	3.2	0.243	
(2)			20.2	83.1	4.7	0.230	
(3)			37.2	65.1	8.3	0.222	
(4)			92.7	34.1	14.5	0.156	
(5)			158.7	10.9	19.1	0.120	

Table 6

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB15 (Control)	A126RBNS30	Phenol	0.0	107.1	0.0	-	0.295
(1)			10.2	92.9	2.8	0.278	
(2)			25.2	74.0	6.6	0.263	
(3)			53.5	49.9	11.4	0.214	
(4)			92.1	29.1	15.6	0.169	
(5)			201.5	6.3	20.2	0.100	
RB16 (Control)	A126RBNS30	Phenol	0.0	96.6	0.0	-	0.215
(1)			11.9	84.3	2.5	0.207	
(2)			21.5	77.8	3.8	0.175	
(3)			48.8	47.8	9.8	0.200	
(4)			100.5	20.7	15.2	0.151	
(5)			240.6	1.9	19.0	0.079	

Table 7

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB17 (Control)	A126RBNS30	Phenol	0.0	101.5	0.0	-	0.285
(1)			19.8	76.3	5.0	0.254	
(2)			31.3	61.2	8.1	0.257	
(3)			49.0	48.8	10.5	0.215	
(4)			96.8	24.6	15.4	0.159	
RB18 (Control)	A126RBNS30	Phenol	0.0	100.9	0.0	-	0.300
(1)			15.7	80.6	4.1	0.259	
(2)			36.0	61.7	7.8	0.218	
(3)			67.3	42.0	11.8	0.175	
(4)			106.5	21.1	16.0	0.150	

Table 8

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB19 (Control)	A126RBNS30	Phenol	0.0	101.8	0.0	-	0.250
(1)			21.0	78.7	4.6	0.220	
(2)			33.2	68.8	6.6	0.199	
(3)			65.1	41.9	12.0	0.184	
(4)			120.1	19.4	16.5	0.137	
(5)			215.1	6.6	19.0	0.089	
RB20 (Control)	A126RBNS30	Phenol	0.0	100.3	0.0	-	0.225
(1)			17.0	83.2	3.4	0.201	
(2)			29.2	71.8	5.7	0.195	
(3)			70.4	40.9	11.9	0.169	
(4)			149.1	11.9	17.7	0.119	
(5)			268.2	4.0	19.3	0.072	

Table 9

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB21 (Control)	A126RBNS28	Phenol	0.0	125.3	0.0	-	0.275
(1)			14.0	107.4	3.6	0.266	
(2)			23.5	95.5	5.9	0.253	
(3)			61.6	58.5	13.5	0.217	
(4)			113.2	27.4	19.6	0.173	
(5)			151.5	17.1	21.6	0.143	

Table 10

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg Carbon^{-1}	kg Carbon^{-1}
RB23 (Control)	A130RBNS48	Phenol	0.0	106.2	0.0	-	0.352
(1)			6.4	95.3	2.2	0.341	
(2)			15.3	82.4	4.8	0.312	
(3)			28.8	62.7	8.7	0.302	
(4)			49.9	40.1	13.2	0.265	
(5)			87.1	15.7	18.1	0.208	
(6)			119.6	6.9	19.9	0.166	
(7)			195.8	1.7	20.9	0.107	

Table 11

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
RB24 (Control)	A131RBNS53	2Chloro-	0.0	89.4	0.0	-	0.645
(1)		phenol	12.2	71.9	3.5	0.187	
(2)			23.3	46.8	8.5	0.365	
(3)			29.2	263	12.6	0.432	
(4)			53.8	5.2	16.8	0.313	
(5)			107.8	0.8	17.7	0.164	
RB25 (Control)	A131RBNS53	2Chloro-	0.0	96.5	0.0	-	0.660
(1)		phenol	10.8	67.7	5.8	0.532	
(2)			22.4	36.5	12.0	0.535	
(3)			30.7	18.9	15.5	0.505	
(4)			49.5	5.4	18.2	0.368	
(5)			92.0	3.0	18.7	0.203	

Table 12

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	$kg\ Carbon^{-1}$	$kg\ Carbon^{-1}$
RB26 (Control)	A131RBNS53	2Chloro-	0.0	95.8	0.0	-	0.780
(1)		phenol	11.5	56.6	7.9	0.683	
(2)			23.9	35.9	12.0	0.502	
(3)			33.2	22.9	14.6	0.439	
(4)			41.2	11.0	17.0	0.412	
(5)			84.4	3.1	18.5	0.220	
RB27 (Control)	A131RBNS53	2Chloro-	0.0	97.2	0.0	-	0.705
(1)		phenol	10.7	62.9	6.9	0.641	
(2)			15.3	51.2	9.2	0.602	
(3)			28.5	24.0	14.7	0.514	
(4)			53.9	4.5	18.5	0.344	
(5)			108.2	2.4	19.0	0.175	

Table 13

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
GC1 (Control)	(Granular)	Phenol	0.0	118.9	0.0	-	0.067
(1)			49.2	105.8	2.6	0.053	
(2)			105.6	88.0	6.2	0.059	
(3)			373.9	44.2	14.9	0.040	
(4)			386.4	43.3	15.1	0.039	
(5)			709.4	20.7	19.7	0.028	
GC2 (Control)	(Granular)	Phenol	0.0	125.2	0.0	-	0.083
(1)			64.1	102.8	4.5	0.070	
(2)			128.1	88.0	7.4	0.058	
(3)			311.1	51.9	14.7	0.047	
(4)			427.5	48.0	15.4	0.036	
(5)			730.0	17.1	21.6	0.030	

Table 14

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	$kg\ Carbon^{-1}$	$kg\ Carbon^{-1}$
GC3 (Control)	(Granular)	2Chloro-	0.0	101.6	0.0	-	0.190
(1)		phenol	45.3	74.1	5.5	0.121	
(2)			67.0	57.3	8.8	0.132	
(3)			116.9	38.2	12.7	0.108	
(4)			171.8	26.6	15.0	0.087	
GC4 (Control)	(Granular)	2Chloro-	0.0	97.3	0.0	-	0.264
(1)		phenol	65.6	53.7	8.7	0.133	
(2)			149.3	38.2	11.8	0.079	
(3)			234.6	22.4	15.0	0.064	
(4)			494.6	15.5	16.4	0.033	
(5)			628.1	12.0	17.1	0.027	

Table 15

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
GC5 (Control)	(Granular)	2Chloro-	0.0	97.2	0.0	-	0.163
(1)		phenol	163.1	37.1	12.0	0.074	
(2)			303.1	18.3	15.8	0.052	
(3)			437.3	17.9	15.9	0.036	
(4)			557.5	14.0	16.6	0.030	
(5)			674.8	10.4	17.4	0.026	
GC6 (Control)	(Granular)	2Chloro-	0.0	100.0	0.0	-	0.380
(1)		phenol	209.7	28.7	14.3	0.068	
(2)			346.9	19.2	16.2	0.047	
(3)			617.9	15.2	16.9	0.027	
(4)			765.9	15.0	17.0	0.022	
(5)			1221.2	11.8	17.6	0.014	

Table 16

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsrobed (X)	$\frac{X}{M}$	Adsorption Capacity
-	-	-	x10^{-6}	x10^{-3}	x10^{-6}	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg Carbon^{-1}	kg Carbon^{-1}
GC7 (Control)	(Granular)	Phenol	0.0	97.5	0.0	-	0.096
(1)			134.8	52.1	9.1	0.067	
(2)			287.9	41.2	11.3	0.039	
(3)			590.2	24.9	14.5	0.025	
(4)			927.8	25.4	14.4	0.016	
(5)			1277.0	12.0	17.1	0.013	
GC8 (Control)	(Granular)	Phenol	0.0	102.1	0.0	-	0.060
(1)			201.2	45.3	11.4	0.056	
(2)			431.9	28.2	14.8	0.034	
(3)			624.4	29.9	16.4	0.026	
(4)			824.6	10.4	18.3	0.022	
(5)			1190.8	3.7	19.7	0.017	

Table 17

Experiment Number	Cloth Run Code Number	Chemical	Carbon Dosage (M)	Residual Concentration	Amount of Chemical Adsorbed (X)	$\frac{X}{M}$	Adsorption Capcaity
-	-	-	$x10^{-6}$	$x10^{-3}$	$x10^{-6}$	kg Chemical	kg Chemical
-	-	-	kg	kgm^{-3}	kg	kg $Carbon^{-1}$	kg $Carbon^{-1}$
GC9 (Control)	(Granular)	Phenol	0.0	103.7	0.0	-	0.095
(1)			176.4	50.2	10.7	0.061	
(2)			309.8	33.1	14.1	0.046	
(3)			804.7	16.3	17.5	0.022	
(4)			2141.3	2.4	20.3	0.009	
GC10 (Control)	(Granular)	Phenol	0.0	105.3	0.0	-	0.060
(1)			251.2	38.0	13.5	0.054	
(2)			528.0	22.9	16.5	0.031	
(3)			661.8	22.6	16.6	0.025	
(4)			797.6	8.2	19.4	0.024	
(5)			1682.5	3.1	20.5	0.012	

Table 18

APPENDIX VI

CODE NUMBERS AND PROPERTIES OF ACTIVATED CHARCOAL USED IN EXPERIMENTS ON THE CONTINUOUS APPARATUS AND ADSORPTION EQUILIBRIA

Notes:

1. The heat of wetting is a measure of activity provided by immersing a known weight of carbon in silicone oil. An activated sample releases about 62.8 $kjkg^{-1}$.

2. The code for each cloth sample is as follows:

A	:	The cloth number (rayon)
RB	:	Rosebank, the place or origination of the original rayon
N	:	Place of manufacture of the charcoal cloth, Nancekuke, Cornwall.
S	:	The rayon is sprayed before carbonisation

3. Cloth number A130RBNS40 possessed a chloride content of 2.5% w/w because it had not been washed after activation.

4. The Granular Charcoal used in the equilibria studies was as follows:

Type:	: EXP. grade (supplied by C.D.E., PORTON)
Activity	: In excess of 70 $kjkg^{-1}$
Particle Size	: 1-2 x 10^{-3} m

Charcoal Cloth Run Code Number	Breaking Strength (Warp)	Breaking Strength (Weft)	Heat of Wetting (Left)	Heat of Wetting (Centre)	Heat of Wetting (Right)
-	x10^{2}	x10^{2}	-	-	-
-	kgm^{-1}	kgm^{-1}	kjkg^{-1}	kjkg^{-1}	kjkg^{-1}
A119RBNS7A	1.55	1.49	55.27	55.70	99.65
A119RBNS7B	3.57	1.56	90.85	100.90	74.94
A126RBNS28	1.94	0.16	70.34	79.55	72.85
A126RBNS30	2.28	1.65	78.29	81.46	79.97
A130RBNS48	2.00	1.50	83.74	83.74	83.74
A13RBNS52	3.00	1.75	75.36	66.99	75.36
A131RBNS53	3.00	1.75	75.36	66.99	75.36

Table 1

APPENDIX VII

HANDLING AND SAFETY MEASURES FOR PHENOL AND 2-CHLOROPHENOL

Phenol Hazards (Colourless, crystalline solid)

a. The vapour irritates the skin and eyes.

b. Skin contact causes softening and whitening, followed by painful burns.

c. Rapid skin absorption which causes headache, dizziness, rapid and difficult breathing, weakness and eventual collapse.

d. Oral contact causes severe burns, abdominal pains, nausea, vomiting and internal damages.

e. Inhalation of vapour over long periods of time causes digestive disturbances, nervous disorders, skin eruptions and damage to liver and kidneys.

f. Dermatitis may result from prolonged contact with weak solutions.

2-Chlorophenol Hazards (Pale brown liquid)

As for phenol

The solutions used for the experiments were dilute (about $0.1 kgm^{-3}$ (100mg/l)). However, since these solutions were mixed 'in situ' and remembering the toxicity of phenols, the following handling techniques and safety measures were employed:

a. Safety glasses worn at all times.

b. 'Kimguard' chemically resistant gloves used.

c. Where prolonged contact with the vapour was involved, a face mask was used.

d. A plentiful supply of water was maintained close at hand, for spillages.

e. The chemicals, when not in use, were stored in a strong, metal, safety cabinet.

f. During all experiments, an extractor fan, over the equipment was operated.