THE ADSORPTION OF ADSORBABLE ORGANIC HALIDE ONTO BIOLOGICAL SOLIDS

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DANIEL JAMES GAPES

Department of Process and Environmental Technology
Massey University

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ABSTRACT

Chlorinated organic molecules may be removed from wastewaters by adsorption onto the biomass present in biological treatment systems. This study assessed the adsorption onto biological solids of Adsorbable Organic Halide (AOX) from two New Zealand kraft pulp and paper mill bleach plant wastewaters.

Batch adsorption studies were carried out to determine the characteristics of this adsorption process, with activated sludge as an adsorbent. Different molecular weight AOX fractions from two bleach plants' wastewaters were studied. The first wastewater was a combined C and E stage effluent from the CEH bleach sequence previously used at the Tasman Pulp and Paper Co. Ltd, Kawerau. The second was a combined D and E_0 stage effluent from the $OODE_0D$ bleach sequence used at New Zealand Forest Products Kinleith Mill, Tokoroa.

For each mill's wastewater, the adsorption isotherms were characterised for four different molecular weight fractions, and the unfractionated wastewater. Adsorption isotherm models used to fit the data for each of the fractions were the Freundlich, Langmuir and Irreversible isotherms. No single model was able to successfully describe the adsorption characteristics for all of the fractions analysed, indicating significant differences in the adsorption processes occurring in the various fractions.

Analysis of the adsorption of the different molecular weight fractions demonstrated that the adsorption affinity of the AOX increased with increasing molecular weight. It appeared that molecules with higher chlorination levels were more effectively adsorbed onto the biomass. Competition for adsorption sites on the biomass by the different molecular weight fractions was a significant factor in the adsorption of the unfractionated wastewater.

Analysis of the adsorption of AOX from the wastewaters at concentrations typical of those expected in different biological treatment systems showed that:

- treatment systems with low biomass concentrations, such as aerated lagoons, would not be expected to remove significant amounts of AOX by adsorption.

- treatment systems utilising higher biomass levels have the potential to remove significant amounts of AOX by adsorption. Conventional activated sludge systems could remove 15-20%, and oxygen activated sludge systems 25-50% of the AOX entering these systems.

The impact of the modernisation of bleach sequences on the adsorption of AOX, by the introduction of oxygen delignification and chlorine dioxide substitution, was assessed. This was carried out by comparison of the adsorption characteristics of the two mills' wastewaters. The Tasman mill's bleach sequence was used as an example of older, conventional bleaching, and the Kinleith mill's sequence an example of modernised bleaching. Significant differences were found in the adsorptive behaviour of the molecular weight fractions, and that of the unfractionated wastewaters, between the two.

From the analysis, adsorption onto biomass in a biological treatment system is predicted to alter the molecular weight distribution of the AOX in wastewaters. The conventional sequence's wastewater should show a decrease in the proportion of high molecular weight AOX due to this adsorptive removal, an effect not as significant in the adsorption of AOX from a modern bleach plant wastewater. Modern bleach sequence wastewaters are expected to reveal a decrease in the proportion of the low molecular weight material, an effect not as notable for the conventional sequence's AOX.

Modernisation was found to decrease the adsorptive affinity of the wastewater, suggested to be due to the lower chlorination levels and average molecular weights of the molecules in the wastewater. It was concluded that the modernisation of bleach sequences has reduced the significance of adsorption onto biological solids as an AOX removal mechanism.

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1. INTRODUCTION

1.1. THE NEW ZEALAND PULP AND PAPER INDUSTRY

In 1992 pulp and paper exports contributed $785 million to the New Zealand economy, 40% of all forest products export earnings (Department of Statistics, 1993), indicating the importance of this industry to the nation. There are presently eight pulp and/or paper mills in New Zealand. The location, type and capacity of each are given in Table I.

Table I: Pulp and Paper Mills in New Zealand (PPI, 1992)

Mill	Mill Type	Processes	Production (Air dried tonnes/year)
Oji Kokusaku Pan Pacific Napier	pulp	TMP	215 000
Caxton Paper Mills Kawerau	pulp	SCTMP	75 000
NZFP Pulp and Paper Ltd Kinleith	pulp and paper	kraft, NSSC	470 000
NZFP Pulp and Paper Ltd Mataura	paper	-	24 000
NZFP Pulp and Paper Ltd Te Papapa	paper	-	66 000
NZFP Pulp and Paper Ltd Whakatane	pulp and paperboard	SGW, NSSC	65 000
Tasman Pulp and Paper Co. Ltd Kawerau	pulp and paper	SGW, RMP, kraft	630 000
Winstone Pulp International Karioi	pulp	CTMP	120 000

NZFP = New Zealand Forest Products

TMP = Thermomechanical pulp; CTMP = Chemithermomechanical pulp; SCTMP = Sulphonated Chemithermomechanical pulp; NSSC = Neutral Sulphite Semichemical; SGW = Stone Groundwood; RMP = Refiner Mechanical pulp.

There are two mills in New Zealand that produce kraft pulp. These are described in more detail below.

1.1.1. Tasman Pulp and Paper Company Ltd.

This mill has undergone many modernisations and expansions since it was commissioned in 1955. There are 4 pulp mills currently operated at this site:

- stone groundwood 225,000 tonnes/year
- refiner mechanical pulp 125,000 tonnes/year
- kraft (2 mills) 280,000 tonnes/year

The kraft pulp produced is bleached in one of two bleach plants. The number one plant is semi bleached and operates with an HH sequence at a nominal capacity of 80,000 tonnes/year. This bleach plant was recently converted from a CEH sequence to reduce effluent colour. The number two plant uses an $OD/CE_{O}DED$ sequence, and has a nominal capacity of 135,000 tonnes/year. The nomenclature used for defining these and other bleaching stages is discussed in Section 2.3.3. The work discussed here utilised bleach effluent from the old CEH sequence.

Two paper machines produce 355,000 tonnes/year of paper, printing mainly newsprint and directory paper (PPI, 1992).

1.1.2. NZFP Pulp and Paper Ltd, Kinleith Industries

The NZFP Kinleith mill has also undergone numerous expansions and modernisations since commissioning in the mid 1950's. At present this mill operates a neutral sulphite semichemical mill with a capacity of 20,000 tonnes/year, and two kraft mills with a combined capacity of 450,000 tonnes/year. One bleach plant is operated, comprising of an $OODE_{O}D$ sequence, processing approximately one third of the kraft pulp.

The mill has two paper machines that produce 210,000 tonnes/year of kraft linerboard and 20,000 tonnes/year of packaging and industrial grade papers. Approximately 190,000 tonnes/year of market bleached pulp is also produced (PPI, 1992).

1.2. ADSORBABLE ORGANIC HALIDE

The chlorine bleaching of pulp is carried out to remove any residual lignin that remains after the pulping process has been completed, so that a whiter, brighter product may be obtained. Chlorine reacts with the lignin polymer structure, causing it to fragment and become alkali soluble. Many of the organic compounds thus formed in the bleaching stages are chlorinated, with the molecules present covering a wide molecular weight range. These move from the pulp fibre structure into the liquid

phase of the bleaching liquors, which is removed as wastewater to be treated externally.

The fate of these chlorinated organics in the biological systems used for the treatment of pulp and paper wastewater is of importance, many of these compounds may contribute to the oxygen demand, colour and toxicity of effluent entering a receiving body of water.

One of the earliest measures used in the regulation of the discharge of chlorinated organic compounds was that of Adsorbable Organic Halide (AOX).

AOX is defined in the test method SCAN-W 9:89 (SPPBTC, 1989) as the amounts of the elements chlorine, bromine and iodine that in a sample of water is bound in dissolved or suspended organic matter. The element of concern for the pulp and paper industry is chlorine. The AOX parameter measures the amount of chlorine bound to organic matter that is capable of being adsorbed onto activated carbon.

AOX is not a single compound. It is made up of a wide range of molecules of differing molecular weights, degrees of chlorination, biodegradability and toxicity. Because it is impracticable to measure each of the individual chlorinated compounds in a wastewater, a bulk parameter of all the compounds provides a simple measure. It is this simplicity of measurement of the chlorinated organic material by the AOX test that it has been accepted for use in regulatory requirements in countries such as Finland, Germany, Denmark, Sweden and Australia. In New Zealand, AOX is not used as a regulatory tool but is used as an indicator of the environmental performance of the pulp and paper mills, in conjunction with other environmental parameters such as Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

Berry (1992) states that the problem with AOX as an environmental parameter is that only a small fraction of the total AOX has the chemical characteristics that could cause it to be toxic, bioaccumulable and persistent in the environment. It has been found that changes in AOX levels due to alterations in the technology in the pulping and bleaching processes do not adequately mirror the changes in toxicity of the effluent. Focus on reduction of the total AOX load in a pulp mill effluent will not necessarily produce the desire result of reduced toxicity unless emphasis is placed to reducing that fraction of the AOX that causes the toxicity. AOX, therefore, is of little use as an indicator of toxic effect. It is, however, the parameter that is in wide use

and acceptance in New Zealand and around the world for regulation and comparison of a mill's environmental performance and for this reason is of importance.

1.3. OBJECTIVES OF THE WORK

It has been observed that chlorinated organic molecules undergo adsorption onto biological solids (Amy *et al.*, 1988; Bell and Tsezos, 1987, Stuthridge and McFarlane, 1993). The significance of this adsorption as a removal mechanism of these compounds is not well understood. Many of the low molecular weight chloroorganics are capable of being biologically degraded by the microorganisms in the treatment systems. In order for this to occur, they first must be adsorbed onto the cell wall, from which they can be transported into the cell for consumption by the microorganism. Higher molecular weight material that is too large for transport through the cell membrane may still adsorb onto the biological material, thus removing it from the wastewater. Once adsorbed, it could remain adsorbed to the biomass and thus become a problem on removal of the biomass sludge from the system, or the potential exists for this material to be fragmented by extracellular enzymes, and the fragments consumed by the microorganisms or released back into the wastewater. It is for these reasons that knowledge of the adsorption characteristics of chlorinated organic compounds onto biomass is important.

The objectives of the work undertaken were to:

1. assess the potential significance of the adsorption onto biological solids as a source of removal of AOX from pulp and paper effluent.

2. assess whether changes in the initial stages of pulp bleaching sequences by the introduction of oxygen delignification and chlorine dioxide substitution could have altered the adsorption characteristics of the resultant AOX produced by the bleaching process and therefore changed the significance of adsorption onto biomass as a removal mechanism of the AOX in the wastewater treatment systems.

To achieve these objectives a preliminary kinetics study was carried out and the equilibrium adsorption characteristics of batch systems were determined on different molecular weight fractions of the two wastewaters. The wastewaters from two different bleaching systems were used in the work; one from the C and E stages of a conventional CEH bleach sequence (Tasman Pulp and Paper Company Ltd, Kawerau, New Zealand), and the other from the D_1 and E_1 stages of a modern $OODE_OD$ bleach

sequence (New Zealand Forest Products Kinleith Mill, Tokoroa, New Zealand). This work was carried out on the two types of wastewater in order to assess the difference in adsorption characteristics that the use of oxygen delignification (O stage) and chlorine dioxide (D stage) in the bleaching of pulp makes to the adsorptive fate of the chloroorganic material (AOX) produced by the bleaching process.

2. LITERATURE REVIEW

2.1. GENERAL INTRODUCTION

The pulp and paper industry provides a substantial contribution to the New Zealand economy, converting wood as a primary product into secondary processed goods. As a result of this processing, wastes are inevitably created. Concerns have been increasing as to the effects that many of these wastes may be having on the environment.

Sections 2.2 and 2.3 give a broad overview of the features of chemical pulping and pulp bleaching operations. The nature of bleaching effluents is discussed in Section 2.4, including the environmental impact of pulp bleaching operations. Literature on the standard methods of reducing the discharge of chloroorganic compounds to the environment is reviewed in Sections 2.5 and 2.6. Adsorption as a physical/chemical process is discussed in Section 2.7, as is the available literature on the adsorption of organic compounds onto biological solids.

2.2. OVERVIEW OF CHEMICAL PULPING

Chemical pulping of wood is predominantly carried out by either of two methods:

i) kraft pulping
ii) sulfite pulping.

Clayton *et al.*, (1989) give an outline of the processes involved in chemical pulping, on which the following discussion is based.

Both methods are used to remove lignin, a highly branched aromatic polymer that binds the wood fibres and imparts rigidity to the fibre walls. Pulping thus separates the wood fibres and improves the properties of the fibres for papermaking. Kraft pulping involves cooking wood chips at 160-180°C with a liquor comprising sodium hydroxide and sodium sulfide. This liquor induces cleavage of ether bonds in the lignin structure and the products formed from the degradation are dissolved in the liquor. In addition to lignin products, various organic extractives and some portions of the wood polysaccharides are dissolved into the pulping liquor. Pulping can be carried out as either a batch or a continuous process. In both processes, the cooked

chips are discharged from the cooking vessel under pressure so as to break up the chips into individual fibres. The pulp from the cooking process contains wood fibres and the used cooking liquor called black liquor due to its dark colour, is removed from the pulp in a washing stage and it is processed to recover the cooking chemicals. The washed pulp is screened to remove material such as knots and uncooked wood, and sent on for further processing, such as bleaching, or directly to a papermaking machine.

The sulfite process degrades lignin by a sulfonation process. The pulping liquor for this process contains sulphur dioxide and an alkaline oxide such as sodium, magnesium or calcium. Sulfite pulping is not considered in this review as the kraft method is by far the most dominant process used in the New Zealand pulping industry.

2.3. OVERVIEW OF PULP BLEACHING

2.3.1. Introduction

The pulping process removes about 90-95% of the total amount of lignin. The remainder cannot be removed by extending the pulping process as too much damage to the cellulose fraction would result.

The aim of pulp bleaching is to give pulp high brightness and good brightness stability. For chemical pulps, this can be achieved by removal of much of the residual lignin that remains in the pulp after the cooking procedure, and subsequent oxidation of any coloured chromophore structures in the pulp.

2.3.2. Lignin Structure

Although the exact structure of lignin in its native form is unknown, much is known about isolated lignin. An aromatic polymer, it is built up from a mixture of three different 4-hydroxyarylpropenyl alcohol monomers (Figure 1). Different wood species contain lignin made up from different proportions of these monomeric units. Figure 2 shows the prominent structure of a softwood lignin as suggested by Adler (1977). This reveals the branched nature of the molecule and the types of bonds that link the monomer units.

Figure 1: Lignin Precursors (Adler, 1977)

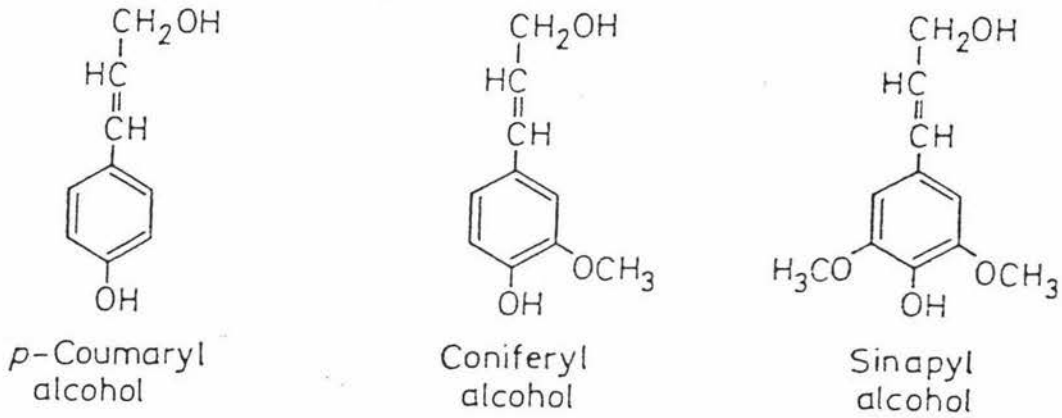
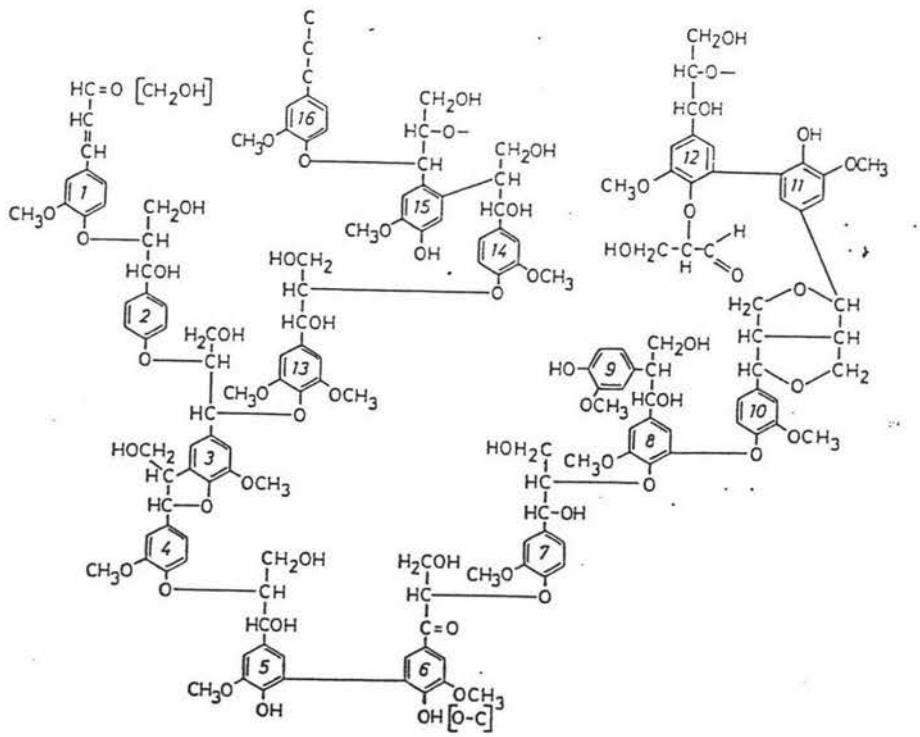


Figure 2: Prominent Structures in Softwood Lignin (Adler, 1977)



Bleaching of chemical pulps is a multistage process that can be defined by two types of operation: a) delignification and b) selective oxidation of the coloured chromophore structures of the pulp.

Delignification is carried out through the bleaching of pulp by oxidation of the lignin and subsequent alkaline extraction of the soluble fragments. Oxidation fragments the lignin structure and also creates new functional groups in the lignin, such as carboxylic acids and phenols, which increase the ionic character of the structure. The soluble lignin fragments are able to be extracted from the pulp in the following alkali extraction stage.

The following is an overview, much of which is summarised from work by Gierer (1982), of some of the important stages used in bleaching technology. Each stage can be identified by a symbol that is used for quick reference to the stage. In this discussion, these symbols are given in brackets after the title of the stage.

2.3.3. Bleaching Stages used in the Pulp and Paper Industry

2.3.3.1. Chlorine (C)

In chlorine bleaching, the reacting species is the chloronium ion, Cl^+, formed by heterolytic cleavage of the Cl-Cl bond in elemental chlorine, or the Cl-O bond in the conjugate acid of hypochlorous acid, $ClOH_2^+$. This reacts with residual lignin in electrophilic substitution or addition type reactions. Typical sites of attack include the ortho and para positions on free and etherified phenolic structures (Figure 3), addition to C=C double bonds conjugate to the benzene ring (Figure 4), as well as addition to other olefinic structures in the lignin structure (Figure 5). Apart from adding chlorine to the lignin some of these reactions cleave the lignin structure, increasing its solubility in alkali.

2.3.3.2. Alkali Extraction (E)

The chlorination stage is usually followed by an extraction with alkali. In this stage, the chlorinated (and unchlorinated) quinonoid structures generated as shown in Figure 3, are attacked by nucleophilic hydroxide ions, and are converted into resonance stabilised, hydroxy substituted quinonoid structures (Figure 6a). These are readily soluble in alkali.

Figure 3: Substitution and Dealkylation Reactions of Chloronium Ion (Gierer, 1982)

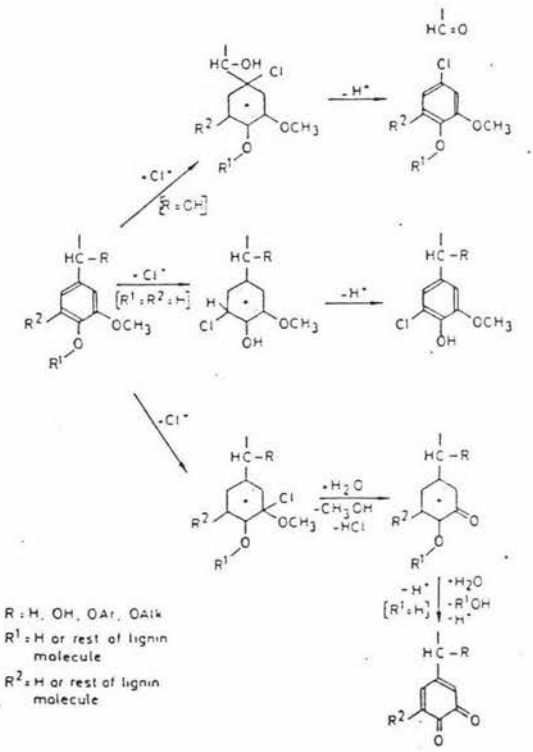


Figure 4: Addition Reactions of Chloronium Ion to C=C Bond (Gierer, 1982)

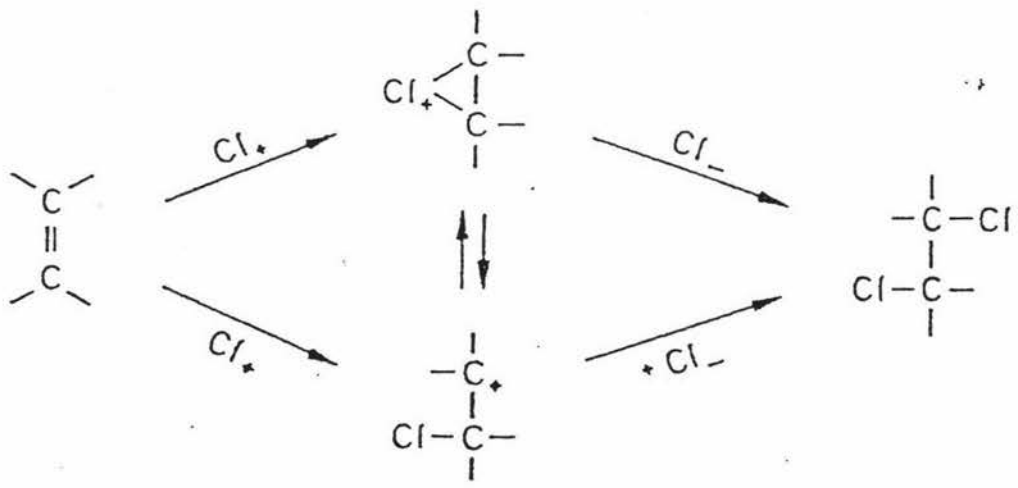


Figure 5: Addition Reactions of Chloronium Ion to other Ring Conjugated Structures (Gierer, 1982)

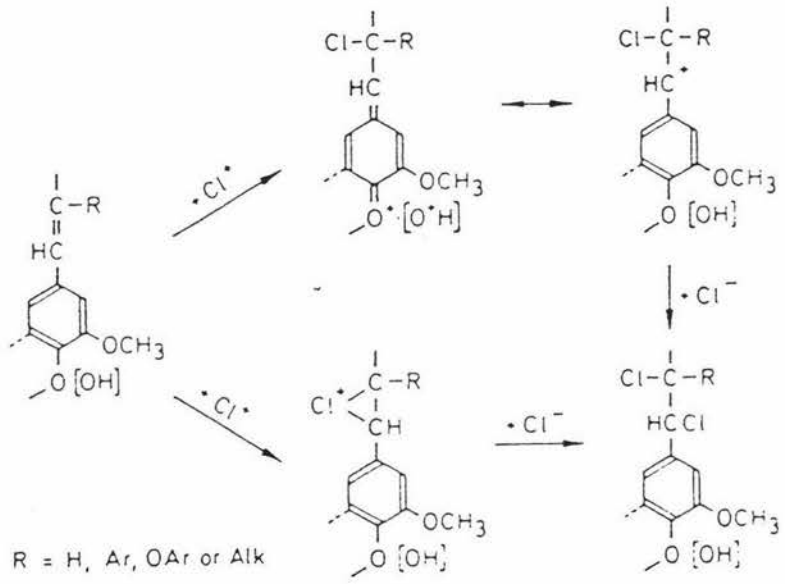
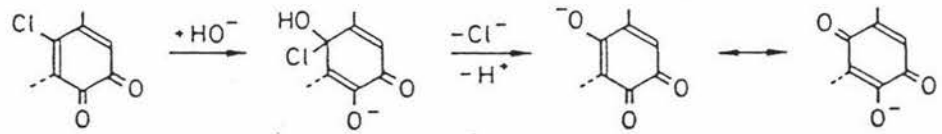
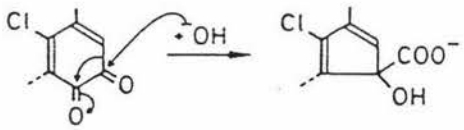


Figure 6: Displacement of Chlorine By OH^- Ions, and Alkali Promoted Rearrangements (Gierer, 1982)

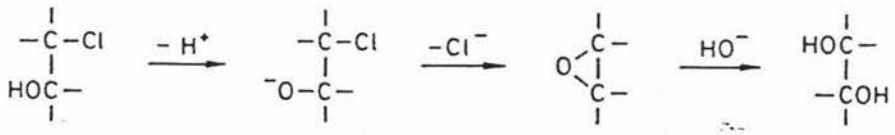
a. Formation of hydroxy substituted quinonoid structures.



b. Benzilic acid type rearrangement.



c. Conversion of lipophilic lignin structures to lyophilic lignin structures.



The hydroxide ions may also attack carbonyl carbons in ortho-quinonoid structures and promote benzilic acid type rearrangements (Figure 6b). This type of conversion may contribute to the solubilisation of lignin in this stage. A further reaction that occurs in this stage is the conversion of lipophilic lignin structures, arising during the chlorination stage, into hydrophilic structures. This type of reaction can be exemplified by the exchange of aliphatically bound chlorine atoms for hydroxyl groups (Figure 6c).

The first alkali extraction stage is often reinforced by the addition of oxygen, forming an E_O stage, in order to increase delignification and reduce the chlorine requirement in the first chlorination stage (Wartiovaara 1991).

2.3.3.3. Chlorine Dioxide (D)

Chlorine dioxide is used in both the delignification and the final oxidative stages of pulp bleaching. According to Gierer (1982), chlorine dioxide acts only to oxidise the phenolic groups of the lignin structure in the delignification process, without the formation of final substitution products. Chlorine substituted products that are observed from this reaction should be attributed to the action of elemental chlorine arising from the partial decomposition of the chlorine dioxide molecule. Wartiovaara (1991) indicates that because of the specificity of the chlorine dioxide reaction, it is not as effective as chlorine in oxidising the lignin structure. However, addition of chlorine with the chlorine dioxide, creating a C/D stage bleaching operation, achieves good delignification results.

Wartiovaara (1991) states that chlorine dioxide is very effective in oxidising chromophores in the final bleaching stages, as it does not react to any significant extent with carbohydrates.

2.3.3.4. Oxygen (O)

Oxygen has gained much attention as a partial substitute for chlorine based chemicals in the bleaching of pulp. Wartiovaara (1991) provides a review of the process of oxygen bleaching. At high temperatures and under alkaline conditions, oxygen is reduced to anions and radicals. These are strong oxidants that can be used in the delignification of pulp to break down the lignin into smaller fragments capable of extraction from the fibre structure. Used in pulp bleaching, oxygen is rather

unselective and its use must be controlled to minimise pulp strength loss caused by oxidation of carbohydrates. Because of this lack of selectivity, oxygen cannot completely replace chlorine chemicals for delignification in bleaching sequences. If an oxygen bleaching stage is used prior to any chlorine stages, the effluent produced can be circulated for use as washing liquor in the mill's recovery system. Oxygen can also be added at the first alkaline extraction stage, resulting in a reduced requirement of chlorine chemicals for delignification.

2.3.3.5. Hydrogen Peroxide (P)

In reviewing hydrogen peroxide bleaching, Wartiovaara (1991) explained that this chemical performs similar reactions to oxygen, with the advantage that it can be used under less severe conditions, thus reducing the extent of reaction with pulp carbohydrates. Peroxide is both more expensive and less effective than oxygen for pulp delignification, making it rarely used for this purpose. Oxygen and peroxide are sometimes used together for reinforcement of the alkaline extraction stage. Unlike oxygen, hydrogen peroxide can oxidise chromophores and so is used in the final bleaching stages. Although more expensive and less effective than chlorine dioxide, it is the only chlorine-free chemical available for final bleaching.

2.3.3.6. Ozone (Z)

Wartiovaara (1991) asserts that ozone has characteristics that make it a very promising bleaching chemical. It is a non-chlorine compound with high reactivity towards lignin, even under mild conditions. The high reactivity of ozone is also a disadvantage in that its reactions are unselective, resulting in oxidation of carbohydrate material as well as lignin. In bleaching, ozone is used for delignification of the pulp, often after an oxygen bleaching stage.

2.4. NATURE OF BLEACHING EFFLUENTS

2.4.1. Introduction

Most of the residual lignin remaining in the unbleached pulp is removed in the first two stages of bleaching; chlorination and the first alkaline extraction. Therefore most of the material dissolved during bleaching originates from the effluents of these stages. Table II gives the approximate composition of bleaching filtrates as estimated

from the constituents dissolved from unbleached pulps in the bleaching stages, using Scots pine as the softwood and birch as the hardwood. For softwoods, it can be seen that lignin degradation products make up a large proportion of the dissolved substances in the bleach effluents, while for hardwoods carbohydrate material is present in comparable weight to the degraded lignin.

Table II: Substances dissolved during bleaching of kraft pulps (Valtilla, 1991)

	Softwood		Hardwood
Kappa Number	35	18	20
Lignin (kg/tonne of pulp)	50	28	20
Carbohydrates (kg/t)	19	11	22
Extractives (kg/t)	1	0.5	3
Total (kg/t)	70	39.5	45

For the purposes of discussion the constituents of typical bleaching liquors may be separated into two categories: those compounds of high molecular weight (relative molecular mass, M_r>1000) and those of low molecular weight (relative molecular mass, M_r<1000).

2.4.2. High Molecular Weight Compounds

The structures of the high molecular weight compounds present in bleach plant effluents are poorly defined. Elemental compositions for these compounds in spent liquors have been reported by Kringstad and Lindstrom (1984) as being $C_9H_9O_4Cl$, $C_{10}H_{14}O_7Cl$ and $C_9H_{10}O_8Cl$ for the chlorination stage, with $C_{14}H_{15}O_8Cl$ and $C_{14}H_{10}O_9Cl$ the compositions representative of spent alkali extraction liquor compounds. Work carried out by Van Buren and Dence (1970) and Erickson and Dence (1976) suggests that a significant amount of the organically bound chlorine is attached to non aromatic molecules, and UV studies by Hardell and de Sousa (1977a, 1977b) appear to indicate that much of the structure of the high molecular weight material consists of cross-linked, probably unsaturated aliphatic compounds. Of the aromatic groups that are present in the structure, it has been shown that these are demethylated to a considerable degree compared to the original lignin structure, and the nuclei carries 0-3 chlorine substituents.

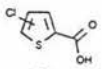
2.4.3. Low Molecular Weight Compounds

McKague *et al.*, (1989) provide an extensive list of 313 low molecular weight compounds identified in bleach effluents.

Bryant and Amy (1988) suggest that about 50% of the organically bound chlorine in C stage effluents and 20% in E stage effluents is of low molecular mass (Molecular weight (M_R) < 1000). Jokela and Salkinoja-Salonen (1992) suggest that these proportions may be too low, as from their work, using size exclusion chromatography for fractionation of bleach plant effluents, it was found that 85-95% of the organic halogen compounds in the effluents studied had molecular weight of less than 1000.

Table III gives the structure of some of the compounds that have been identified in spent pulping liquors.

Table III: Some Compounds Identified in C and E Stage Wastewaters (Kringstad and Lindstrom, 1984)

Formula	Compound	Chlorination (g/tonne)	Extraction (g/tonne)
HOOC-COOH	Oxalic acid	130	590
	Trichloropropenoic acid	-	+
	Chloro-2-thiophenic acid	-	+
	2,4-Dichlorophenol	0.7	2
	Tetrachloroguaiacol	0.1	9
	Dichlorovanillin	0.5	1.5
$CHCl_3$	Chloroform	10	30
	Trichloroethene	0.5	-
	Pentachlorobenzene	0.05	-

The compounds can be placed into three groups: acidic, phenolic and neutral compounds (Kringstad and Lindstrom, 1984).

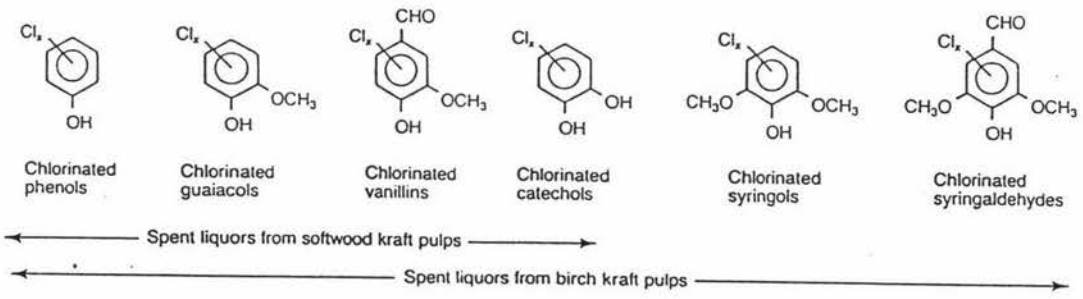
2.4.3.1. Acidic Compounds

This group can be subdivided into fatty, hydroxy, dibasic, aromatic and resin acids. The higher fatty acids and resin acids originate from extractives. Formic and acetic acids are the most abundant of the fatty acids present, while amongst the hydroxy acids, glyceric acid tends to predominate. It is likely that most of the hydroxy acids present in bleach effluents, apart from glyceric and 3-hydroxypropanoic acids, are formed as a result of oxidation of carbohydrate material. Of the dibasic acids, oxalic, malonic, succinic and malic acids are present in significant quantities in both chlorination and alkali extraction spent liquors. Aromatic acids, formed by oxidation of the alpha-carbon in the phenylpropane unit of residual lignin compounds, are probably present in low levels. Three types of aromatic acids are formed: those with one hydroxyl group (phenolic), two hydroxyl groups (catecholic) and those with one hydroxyl and one methoxyl group (guiacolic).

2.4.3.2. Phenolic compounds

Figure 7 gives a summary of the important phenolic compounds found in bleaching liquors. It has been observed that chlorinated catechols occur as the main chlorophenolics discharged from chlorination stages, with chlorinated guaiacols being predominant in the alkali extraction stage effluent (Stuthridge *et al.*, 1991, Kringstad and Lindstrom, 1984). The phenolics present in the spent liquors are all formed from residual lignin.

Figure 7: Phenolic Compounds Most Frequently Identified in Spent Bleaching Liquors (Kringstad and Lindstrom, 1984)



2.4.3.3. Neutral Compounds

Methanol and hemicelluloses make up the largest proportion of the total neutral compounds present in bleach effluents. Methanol is formed as a result of cleavage of

the methoxyl groups that are present in large amounts in lignin. Present in varying degrees are a large number of other compounds, including chlorinated saturated and unsaturated hydrocarbons, aldehydes, ketones, and esters, various chlorinated benzene derivatives and chlorinated sulphur containing materials. Of these, the chlorinated acetones, chloroform, dichloromethane and 1,1-dichloromethylsulfone tend to predominate (Kringstad and Lindstrom, 1984).

Many of the neutral compounds may be formed as degradation products of residual lignin, but some may result from impurities in the pulp. Much attention has been directed toward the presence of chlorinated dioxins and furans in bleach effluents. According to Valtilla (1991), research work has revealed procedures for avoiding their formation. Therefore, these compounds should not be a problem for the pulp and paper industry in the near future.

2.4.4. Environmental Effects of Bleach Effluents

There are several main areas of concern that are raised by the liquid effluents produced by a pulp and paper mill. Suspended solids, typically grit and wood fibre, may cause blanketing of bottom dwelling organisms. Colour reduces photosynthetic activity and is aesthetically unpleasant. Dissolved solids, consisting of salts, some metal compounds and a wide range of organic materials, pose potential toxicity to aquatic flora and fauna.

The organic load of the effluent acts as a food source for heterotrophic microbiological activity, causing reduction in the dissolved oxygen levels of the receiving water.

Bleaching effluent contributes specifically to the effluent load of a pulp mill in the way of dissolved organic material, much of which is chlorinated. High molecular weight AOX contributes significantly to the highly coloured nature of the effluent, making it unaesthetic and reducing the photosynthetic activity in the receiving water.

Crooks and Sikes (1990) provide a good overview of the toxic constituents of traditional bleached kraft mill effluents, and much of the following discussion in this section is derived from this paper.

2.4.5. Toxic Constituents of Bleach Plant Effluents

Berry (1992) states that the fraction of AOX that is extractable by a non polar solvent is of greatest environmental significance as it is this fraction that contains the relatively lipophilic (fat soluble) neutral organic compounds, primarily of low molecular weight. The low molecular weight compounds are potentially biologically active if they are small enough to penetrate the cell walls of living organisms. Some of these low weight chlorinated compounds have been shown to exhibit toxic effects on fish and other aquatic organisms.

Chlorination stage effluent toxins are mainly chlorophenols, with catechols and quinones also contributing. Extraction stage effluent toxicity is largely due to trichloroguaiacol, tetrachloroguaicol and several fatty acids (for example mono and dichlorinahydroabietic acid and epoxystearic acid). There are several compounds in bleach plant liquors that have been proven to be mutagenic to bacteria; particularly chloroacetones, a chlorinated furanone and 2-chlorophenol. It is worth noting, however, that most of these mutagens are extremely unstable in seawater or at high pH values, and mutagenicity is effectively eliminated by biological treatment.

Chlorinated dioxins and furans are formed in the chlorination stage of bleaching. Studies on their toxicity on fish have shown significant effects on health and survival. It is considered likely that the formation of dioxins and furans can be virtually eliminated by carefully controlling pulp bleaching conditions.

Chlorate is a herbicide that is formed when using chlorine dioxide in the bleaching process. Chlorate emission has been shown to have devastating effects on *Fucus vesiculosis*, a brown alga. The levels of emission of chlorate can also be greatly diminished by careful control of the bleaching process.

Bleach plant effluents contain amounts of chloroform and carbon tetrachloride, which have been identified as carcinogens on the basis of standard methods of animal testing.

Crooks and Sikes (1990) report on several studies carried out on the toxicity of whole effluent, rather than on individual components. Most of the laboratory studies carried out give evidence that traditional bleach kraft mill effluent can be defined in toxicological terminology as being mildly acutely toxic, and that once the effluent is

treated and adequately diluted, the toxic effects are greatly reduced and often disappear. Of the studies carried out in the field, the results show that significant toxic effects do occur to fish and other aquatic life, but that dilution of the effluent causes a rapid decrease in any observable effects.

The significance of the chronic effects that bleached mill effluent has on the environment is much more difficult to define and is the subject of much debate.

2.5. REDUCTION OF CHLOROORGANICS IN BLEACH EFFLUENTS

2.5.1. Introduction

Kringstad and Lindstrom (1984) estimate the yield of organically bound chlorine produced from the bleaching process to be around 4 kilograms per tonne of pulp, but this clearly varies with pulp type, specific pulping process and bleaching sequence. This is shown by the fact that Stuthridge *et al.*, (1991) report discharge of 5.7 kg/tonne as the average during their studies, while Wilson *et al.*, (1991) report values of between 0.6 and 2.2 kg/tonne in their work. Reduction in the levels of waste material discharged to the environment is a prime objective of those involved in the treatment of the effluent from a pulp and paper mill. As can be seen from the previous section, chlorine containing chemicals are a major source of the environmental pollution produced by the pulp and paper industry, and is therefore beneficial to focus attention on reducing the discharges of these materials.

There are two main means of reducing the load of chloroorganic material discharged to the environment:

- alteration of the pulping and bleaching processes (in-process reduction)
- use of effluent treatment systems.

2.5.2. In-Process Reduction

In reviews by LaFleur (1991) and Crooks and Sikes (1990), a number of methods are described for minimising the formation of various chlorinated organic compounds. The production of chlorinated dioxins and furans can be greatly reduced by control of the type of defoaming agents, added to the brownstock prior to bleaching, to ensure that they do not contain dibenzo-p dioxin and dibenzofuran.

It has been found that addition of small amounts of oxygen gas to caustic soda in the first alkali extraction stage (E_1) can reduce the total organic chlorine discharge by up to 15%. Chloroform formation is greatly reduced by elimination of the hypochlorite stage in the bleaching process, and further reductions are possible by chlorine dioxide substitution in the first bleaching stage.

Decreasing the chlorine requirement in the first chlorination stage has many beneficial effects. This can be achieved by the use of extended pulp cooking technology and by including oxygen and/or ozone delignification as pre-bleaching stages. These methods reduce the lignin content of the pulp prior to the addition of elemental chlorine, thus reducing the amount of precursors available for degradation to chloroorganic compounds. Increasing chlorine dioxide substitution into the first bleaching stage reduces the formation of chloroorganic compounds, including chlorinated phenolics, dioxins and furans. One unit of chlorine dioxide (measured as the dose of chlorine dioxide equivalent to one unit of chlorine/tonne of pulp) will generate roughly one fifth the amount of organic chlorine than one unit of molecular chlorine. Wilson *et al.*, (1991) report that increasing chlorine dioxide substitution from 60 to 100% resulted in a 60-70% reduction of chlorinated organic formation. This increase appeared to have no impact on the proportion of low molecular weight (<1000 daltons) to high molecular weight chloroorganic formed in the bleaching. The formation of chlorinated phenolic compounds, many of which are regarded as being deleterious to the environment, was shown to decrease with this increase in chlorine dioxide substitution.

2.5.3. Effluent Treatment

Activated sludge (A.S) systems and aerated lagoons (A.L) are the predominant biological processes used by pulp and paper mills for the treatment of their effluents. These were designed to treat conventional pollutants, such as suspended solids and biological oxygen demand (BOD). According to McFarlane *et al.*, (1991), activated sludge systems typically remove 80-95% of the wastewater's BOD with aerated removing lagoons 40-90% They report that the removal of total suspended solids (TSS) is quite variable but can be approximated to 85% for activated sludge and 70% for aerated lagoons.

With increasing interest in more unconventional parameters such as Adsorbable

Organic Halide (AOX), chlorinated dioxins and furans, colour and toxicity, effort is being put into assessing the ability of these biological systems to treat these parameters.

AOX is defined as the amount of the elements chlorine, bromine and iodine that, in a sample of water, is bound in dissolved or suspended organic matter and that is determined under specified conditions (SCAN-W 9:89 (SPPBTC, 1989)). It is this parameter that is widely used in evaluating the organochlorine content of a sample and is used as such in this discussion. AOX removal will be the main focus of this review of treatment of bleach plant effluents.

The removal mechanisms for chlorinated organics are similar for both activated sludge and aerated lagoons. They are described by McFarlane *et al.*, (1991) as follows:

Abiotic processes:

- gas stripping of volatile compounds
- adsorption onto biomass
- precipitation
- abiotic mineralisation under aerobic conditions
- abiotic mineralisation under anaerobic conditions (aerated lagoons only)

Biological processes:

- aerobic biological mineralisation and transformation
- incorporation into cell material
- anaerobic biological mineralisation and transformation (aerated lagoons only)

2.5.3.1. Gas Stripping

The organic halide that can be removed by volatilisation into the atmosphere, either by the action of aeration or merely at the liquid/gas interface, is termed purgeable organic halide (POX). Bryant *et al.*, (1987) report that of the total organic halide in the bleached kraft mill effluent (BKME) under study, less than 10% was in the form of POX, and nearly 90% of this was made up of chloroform. Complete removal of this purgeable fraction was observed across the lagoon studied. Valtilla (1991) and Lindstrom and Mohamed (1988) present data to show that at least 85% of the

chloroform entering a treatment system is removed. Due to the high volatility of chloroform, it is likely that the primary mechanism of this removal is gas stripping.

2.5.3.2. Precipitation

Precipitation of organic material occurs when chlorination stage and extraction stage wastewaters are mixed (Hynninen and Gullichsen, 1985). Hynninen (1989) found that organic compounds with molecular weights greater than 1500 daltons were removed most effectively. This mechanism of removal may be of considerable importance, but Stuthridge and McFarlane (1993) found no significant decrease in AOX due to precipitation apon simple mixing of acid and alkali pulp and paper mill effluents.

2.5.3.3. Adsorption onto Biomass

The adsorption onto the biological solids generated in the conventional treatment systems is a potential source of removal of AOX. Amy *et al.*, (1988) and Stuthridge and McFarlane (1993) show from their work with adsorption isotherms that significant removals can potentially occur. The work by Amy *et al.*, (1988) also suggests that low molecular weight AOX is more effectively adsorbed than high molecular weight material. That biosorption does not dominate AOX removals in activated sludge treatment has been pointed out by Saunamaki *et al.*, (1991), whose study of two activated sludge plants revealed that less than 10% of the total AOX reduction was attributable to removal in the excess sludge biomass. Randle *et al.*, (1991), found similar results when working on laboratory scale activated sludge and aerated lagoons.

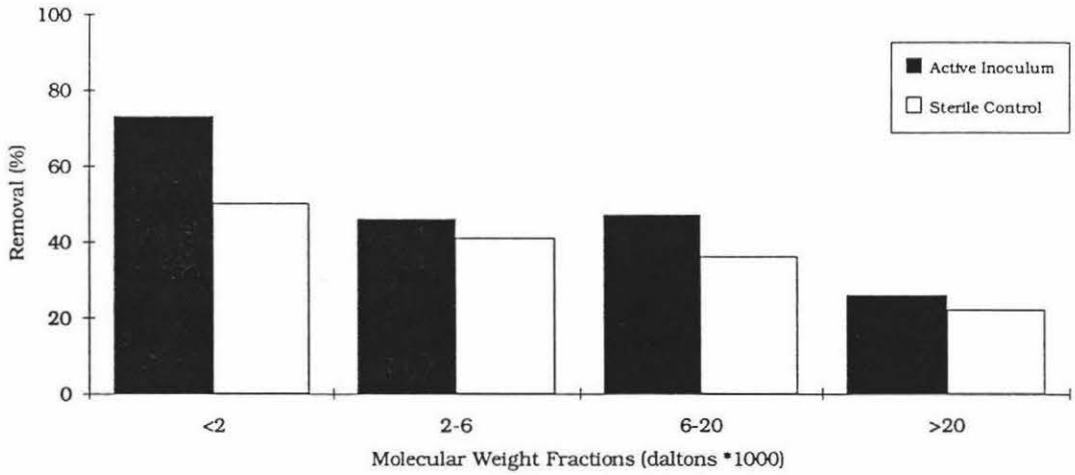
2.5.3.4. Abiotic and Biological Mineralisation

A review by Kringstad and Lindstrom (1984) states that chlorinated phenols are biodegradable, but that their rate of removal depends heavily on the treatment conditions. Haggblom and Salkinoja-Salonen (1991) have shown significant degradation of polychlorinated phenols, guaiacols and syringols by two *Rhodococcus* strains. Neilson *et al.*, (1983) found that transformation of chlorophenols and chloroguaiacols occurred using bacteria isolated from sediments exposed to chloroorganic discharges. The metabolites produced appeared to be more resistant to further transformation than the original substrate. Eriksson *et al.*, (1985) also found

significant transformation of chlorinated guaiacols and catechols when using mixed bacterial cultures from an aerated lagoon.

Analysis of whether much of the degradation that occurs is as a result of microbiological processes or abiotic processes has proved difficult. Bryant *et al.*, (1987) postulate that a large part of the AOX removal in aerobic lagoons takes place due to adsorption onto biomass which settles to the bottom and subsequently the AOX undergoes anaerobic dehalogenation in the anoxic benthal layer of the lagoon. Fitzsimons *et al.*, (1990) have shown that a large proportion of this dehalogenation may be abiotic, with biological degradation being most significant for the lower molecular weight fractions (Figure 8).

Figure 8: Anaerobic Removal of AOX during the Batch Digestion of Different Molecular Weight Fractions of Bleach Plant Effluent (Fitzsimons et al., 1990)



2.6. AOX REMOVALS IN ACTIVATED SLUDGE PLANTS AND AERATED LAGOONS

Table IV provides an overview of the AOX removals obtained in the full scale biological treatment of pulp and paper wastewaters, from activated sludge plants and aerated lagoons.

Table IV: Removal of AOX From Biological Treatment Systems.

TYPE OF TREATMENT PLANT	PULPING CONDITIONS	BLEACHING CONDITIONS		AOX REMOVAL (%) of different molecular wt. fractions (daltons)			SOURCE
				TOTAL	<1000 Fraction	>1000 Fraction	
A.S	-	-		56	-	-	Gergov *et al.*, (1988)
A.S	-	-		65			Gergov *et al.*, (1988)
		X(CD)(EO)DED*	86 kg Cl/t	52			
A.S	Pine	X(OP)DED	78 kg Cl/t	55			Jokela *et al.*, (1993)
		(CD)(EO)DED	84 kg Cl/t	49			
Anaerobic/Aerobic Lagoon	Pine, spruce, birch	O(CD)(EO)DED	70 kg Cl/t	63			
			56-70 kg Cl/t	66			Jokela *et al.*, (1993)
			56 kg Cl/t	65			
A.S	Pine, birch	(CD)(EP)D(EP)D					
		(CD)EDDED		30-50			Jokela *et al.*, (1993)
		(CD)(EP)H(EP)D					
		(CD)EP)HD					
A.L	52-100% s.w Summer			33-38	27-41	29-42	Bryant *et al.*, (1987)
	0-100% s.w Spring			-	49-58	2-42	
A.L	s.w**	CEHDED		23	25	23	Lindstrom and
		O(C+D)EDD		29	38	26	Mohamed (1988)
A.S	s.w/h.w*** kraft			38	65	3	Bryant *et al.*, (1992)
	s.w h.w sulfite			53	62	47	
A.L	s.w/h.w			34	55	18	Bryant *et al.*, (1992)
Extended- Aeration A.S		D/CED(EP)D + C/DEDED		53			Saunamaki *et al.*, (1991)
High Load A.S	h.w/s.w	D/C(EO)D(EP)D		23			
A.L	s.w/h.w	C_DE_OHDED		28-34			Tomar and Allen (1991)
A.L****	s.w/h.w	A		65			Stuthridge *et al.*, (1991)
		B		7			
A.S	kraft and TMP		60% ClO_2 substitution	16	35	7	Strang (1992)
			100% ClO_2 substitution	0.9	44	0	

*X stage involves use of enzyme bleaching (hemicellulase). **s.w = softwood. ***h.w = hardwood.

****This treatment system consists of two separate aerated lagoons. The bleaching sequences used at the mill are CEDHP and (D+C)E_ODED. Treatment system A receives effluents from C and D and (C+D) and general mill wastewaters. System B receives the alkali extraction bleach effluents and foul condensates.

Table IV reveals that neither system appears to be significantly more effective than the other at removing AOX. Activated sludge plants remove low molecular weight compounds slightly more effectively than aerated lagoons. From the literature reviewed, there is no clear trend for the relative effectiveness of removal of high molecular weight compounds between the two types of treatment system.

For both systems, low molecular weight compounds are removed more effectively than high molecular weight compounds. Stuthridge *et al.*, (1991), in observations on two lagoons that treated bleach effluents of differing molecular weight fractions, found that the lagoon treating effluent containing 57% of low molecular weight compounds (less than 3000 daltons) achieved a 65% reduction in the level of AOX, while the lagoon treating effluent with high levels of high molecular weight compounds (43% greater than 30,000 daltons) achieved negligible AOX reductions. However, Jokela *et al.*, (1993) suggest that molecular size is not the main factor limiting removal in wastewater treatment. They found that the fraction of the AOX in bleach effluent that was insoluble in tetrahydrofuran (THF) was most resistant to removal during biological treatment, and previous work had shown that this fraction did not have significantly higher molecular weight than the THF-soluble fraction (Jokela and Salkinoja-Salonen, 1992).

Some of the variations in AOX removals for different systems may be accounted for by the differing in-mill processes and environmental parameters observed at the various sites, but results are far from conclusive. Bryant and Amy (1989) observed that the removal of the low molecular weight fraction in an aerated lagoon occurred at two distinct levels dependant on the season of the year: in the summer, removals averaged 35% of the total; while in the spring, average removals increased to 55%. This trend of increased removal with lower temperature was perceived as being consistent with the response of biosorption to temperature changes. In contrast to these observations, Bryant and Barkley (1990), in their study of three activated sludge systems and six aerated lagoons, did not notice any significant seasonal changes in removal of low molecular weight compounds in the activated sludge plants and observed slight decreases in removal of these compounds in the winter months for the aerated lagoon systems. Bryant and Amy (1989) observed that removal of the molecular weight fraction greater than 1000 daltons appeared to be strongly correlated with the proportion of softwood material present in the pulp, and unrelated to any seasonal effects. In another study Bryant *et al.*, (1987) found that the removal efficiency of the total fraction of organic halide from an aerated lagoon was not

seriously affected by the proportion of softwood bleached in the mill.

Increasing the substitution of chlorine with chlorine dioxide from 60% to 100% substitution has been observed by Strang (1992) to decrease the overall removal efficiency of AOX, although removal of low molecular weight compounds was observed to have increased. Removal of high molecular weight material was reduced to zero. In analysing this result, it must be taken into account that the increased chlorine dioxide substitution reduced the overall production of AOX from 29 to 12 mg/L, therefore reducing the overall AOX load on the environment, even without any reductions due to effluent treatment.

2.7. ADSORPTION OF ORGANIC POLLUTANTS

Weber *et al.*, (1991) and Weber (1972) provide an overview of the adsorption process, and it is from these works that which Sections 2.7.1 to 2.7.6 is largely based.

2.7.1. Adsorption Phenomena

Adsorption involves the concentration of substances at the interface between two phases. This process can occur between any two phases, for example, solid-liquid, liquid-liquid, solid-gas. The material that is being concentrated at the interface is called the adsorbate or solute, the adsorbing phase the adsorbent, and the phase from which the adsorbate is removed the solvent or solution.

Adsorption arises as a result of a variety of different forces between adsorbate molecules, solvent molecules and surface molecules of the sorbent. The primary driving force for adsorption may be a result of the lyophobic behaviour of the solute relative to the solvent, or it may be due to the attraction of the solute to the sorbent. Adsorption is usually a combination of these driving forces.

Three different categories of adsorption are traditionally distinguished: physical, chemical and electrostatic.

Physical adsorption processes are characterised by the forces associated with the dipole moments of sorbate and sorbent molecules causing interactions. Dipole moments arise due to charge separation within a molecule. These can be either permanent or induced. Physical adsorption can occur between polar molecules

(molecules containing permanent dipoles) or polar and non-polar molecules, where the dipole moments are induced. Another class of physical adsorption occurs due to rapidly fluctuating or instantaneous dipole moments, set up by motion of electrons around their orbitals. Physical adsorption forces are relatively weak and short range, with their influence typically decreasing inversely proportionally with the third to sixth power of the distance between molecules. These forces are amplified when the solute is solvophobic as repulsion of the molecule from the solvent enhances the adsorption. As the distance between adsorbent and adsorbate molecule decreases, repulsive forces will eventually become significant. These forces become negligible beyond an extremely small and characteristic intermolecular distance, called the van der Waals radius. The distance at which the force of attraction equals the force of repulsion will be the equilibrium intermolecular distance of the adsorbed molecule to the sorbent molecule.

Electrostatic adsorption forces are much stronger and extend over a greater range than those responsible for physical adsorption. These forces arise as a result of specific electrostatic interactions between discretely charged entities. The forces vary inversely with the square of the distance between the molecules and directly with the product of the charges. The forces can be attractive, in the case of oppositely charged species, or repulsive, in the case of like charges.

Chemical adsorption, or chemisorption, involves formation of bonds between sorbent and sorbate molecules that have the characteristics of true chemical bonds. The interaction range of these bonds is short, the bonds are strong and the intermolecular distance between sorbent and sorbate is small.

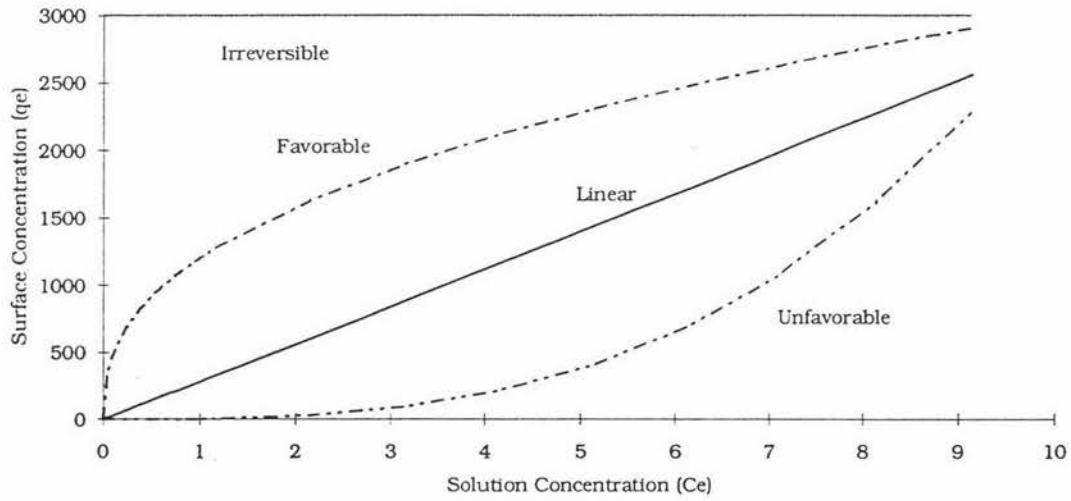
In reality the above adsorption mechanisms do not act independently. Rather, their collective action in a particular system results in the overall adsorptive behaviour observed in a particular system.

2.7.2. Adsorption Equilibria

Adsorption results in the removal of solute from solution onto the surface of the adsorbent until the concentration of the solute remaining in solution is in dynamic equilibrium with that at the surface. At this equilibrium, there is a defined distribution of solute between solvent and adsorbent phases.

Models used for characterising this equilibrium distribution commonly relate q_e, the amount of solute adsorbed per unit of adsorbing phase, to C_e, the amount of solute remaining in the solvent, at the equilibrium position. An expression of this type, defined at a fixed temperature, is termed an adsorption isotherm. Examples of different isotherm patterns are given in Figure 9.

Figure 9: Generalised Equilibrium Adsorption Isotherms.



2.7.2.1. Linear Isotherm

The most simple isotherm is the linear model, where accumulation of solute by the sorbent is directly proportional to the solution phase concentration:

$$q_e = K_D C_e$$

K_D is referred to as the partition coefficient. The linear isotherm is useful for describing adsorption where the energetics of adsorption are uniform with increasing concentration and the loading of the sorbent is low ("Henry's region" adsorption). It has been found to adequately describe adsorption where very low solute concentrations exist and for adsorbents of low adsorption potential.

2.7.2.2. Langmuir Isotherm

The Langmuir model was developed for systems in which adhere to the following limiting assumptions: adsorption leads to deposition of a single layer of solute

molecules on the surface of the sorbent, the energy of adsorption for each molecule is constant and independent of surface coverage, and sorption occurs at localised sites and involves no interactions between adsorbed molecules. From these assumptions, the Langmuir model can be derived by the use of kinetic or thermodynamic methods.

The resultant expression is:

$$q_e = \frac{abC_e}{1+bC_e}$$

where a represents the adsorbed solute concentration on the adsorbent corresponding to complete monolayer coverage, and b is an adsorption coefficient related to the enthalpy of adsorption.

In reality, the assumptions required by the Langmuir isotherm rarely apply, with significant heterogeneity of adsorption site energies and interaction between adsorbed molecules usually occurring. This does not prevent it from being a useful model in many applications. Determination of this model's suitability in a specific situation can be determined by a simple regression of a linearised form of the above equation:

$$\frac{1}{q_e} = \frac{1}{a} + \frac{1}{abC_e}$$

2.7.2.3. Freundlich Isotherm

The Freundlich isotherm is widely used for describing adsorption. It is largely an empirical model but can be shown to be thermodynamically rigorous for special cases of adsorption on heterogeneous surfaces. The model has the form:

$$q_e = K_f C_e^{1/n}$$

K_f is a constant relating to the adsorptive capacity of the system, while n is related to adsorption intensity.

The linear, Langmuir and Freundlich isotherms are among the most commonly used for single adsorbate isotherms. For a specific case, the Langmuir and Freundlich

isotherms may often be equally useful over a moderate range of solution concentrations, but significant differences will occur over larger ranges.

2.7.2.4. Irreversible Isotherm

Weber and Smith (1987) mention the existence of an irreversible isotherm. This can be described by a horizontal line on standard isotherm axes (Figure 9). Systems following an irreversible isotherm display no changes in the extent of uptake of the adsorbate by the adsorbent. with any variation in adsorbent or initial solute concentrations. The irreversible isotherm can be described by the equation:

$$q_e = K_i$$

Irreversible adsorption could be expected to be exhibited when the adsorbent remains in a saturated condition with respect to adsorption of the adsorbate, over the entire range of adsorbate/adsorbent concentration combinations used in the determination of the adsorption isotherm. Thus increasing the amount of adsorbent in the adsorption system, say, results in adsorptive uptake with the final equilibrium concentration of the adsorbate being reached as a result of saturation of the adsorbent surface with the adsorbate molecules.

2.7.3. Mechanistic Models

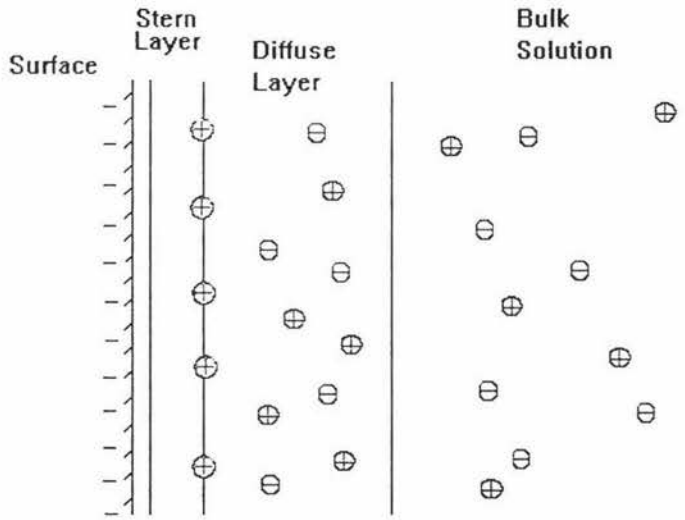
Models have been developed that describe the energetics of intermolecular reactions underlying adsorption. These aid in giving an understanding of the mechanisms that control adsorption, thus enabling analysis of anticipated responses of specific systems to changing conditions.

2.7.3.1. Ion Exchange and Surface Complexation

Adsorbents with surfaces containing charged species exert a large influence on the adsorption of ionic and polar species. In order to maintain electroneutrality, an electrical double layer exists at the interface of solvent and adsorbent. This double layer consists of the charged surface sites and equivalent aqueous phase excess of counter ions that accumulate near the surface of the particle. This gives rise to a concentration gradient in the fluid near the adsorbent, which in turn sets up a potential for random diffusion of ions away from the surface. The actions of electrostatic attraction and counter-diffusion spread the charge over a diffuse layer

where the counter-ion concentration is highest nearest to the surface and decreases with distance. The phenomena is illustrated in Figure 10.

Figure 10: Schematic Representation of an Electrical double Layer (Weber et al., 1991)



2.7.3.2. Solvophobic Adsorption

This mechanism for adsorption arises from the greater affinity of the adsorbate for the adsorbent than the solvent. In the case where water is the solvent, hydrophobic adsorption occurs when the molecules are neutral and relatively non-polar. The association of organic molecules with soils and sediments often results in linear type adsorption patterns. It has been suggested that the sorption reaction that occurs in these cases may be a result of partitioning of the organic molecules into an organic phase on the surface of the particles, due to the observation that the extent of sorption is significantly influenced by the organic carbon content of the sorbent. The importance of adsorbate solvophobicity in influencing adsorption reactions has been illustrated, for the case of water as the solvent, by the observations that K_D values for a large number of solutes acting on soils and sediments can be correlated quite well with the octanol/water partition coefficients of the solutes. Predictions of adsorption based on partitioning of solute into organic phases on adsorbents may however fail to take into account the role of macromolecular organic molecules dissolved in the

solvent phase. These have been shown to increase the effective solubility of hydrophobic compounds, reducing the effect of this mechanism on adsorption.

2.7.4. Sorption Rate Processes

The equilibrium relationships for adsorption only apply if sufficient time is given for equilibrium to be reached. The processes that govern the rate at which equilibrium is obtained include mass transfer of the solute through the stationary surface film surrounding the adsorbent particle, transfer of adsorbate within the pores of the adsorbent (if the adsorbent is porous), and finally the adsorption of the solute molecule onto the adsorbent surface.

The step of adsorption onto the particle surface, whether it be a physical, electrostatic or chemical mechanism, is usually very fast and is often not the rate limiting step for adsorption, although this may not always be the case. The transport of the adsorbate through the stationary surface film occurs largely due to random (Fickian) diffusion and is often the rate controlling step. For porous adsorbents under conditions of sufficient turbulence, the rate may be controlled by the transport of the adsorbate within the pore structure, also a diffusion mechanism. For Fickian motion, the rate of diffusion can be defined by:

$$F = -D \frac{dC}{dx}$$

where F is the flux through a unit cross section in unit time, C is the mass concentration of diffusing substance, and x is the space coordinate in the direction of diffusion, dC/dx being the local concentration gradient of the diffusing substance. D is the diffusion coefficient and is affected by factors such as the size, configuration and chemical structure of the adsorbate and the physical and chemical properties of the liquid.

In defining a system of adsorption it is important to note that just because a particular model used to describe an adsorption process fits well with the available experimental data, this does not verify the mechanism apon which the model is based. Similarly, care must be taken when applying data from one situation to another, as there are a large number of variables that affect the adsorption process

and differences in these between any two systems may cause significant differences in the observed adsorption phenomenon.

2.7.5. Factors Affecting Adsorption

2.7.5.1. Nature of the Adsorbate

As discussed previously, the solubility of the solute is often a controlling factor in the adsorption process, with an inverse relationship existing between the extent of adsorption of a solute from solvent and its solubility in the particular solvent.

The molecular size and shape of the adsorbate molecules may also affect the adsorption process if the rate of adsorption is dependant on transport of the solute within the porous structure of the adsorbent.

The ionic character of the adsorbate may have a significant effect on the adsorption process. Many molecules, such as acids, phenolic species and amines, have the property of undergoing ionisation given the right conditions and pH. Depending in the net charge of the adsorbent, surface charges on the adsorbate molecule may cause attractive or repulsive interactions, thus affecting the adsorption process. It has been found that, for structurally simple compounds, it is possible to make a general rule that adsorption is at a minimum for the charged species of a molecule, and at a maximum for the uncharged species.

2.7.5.2. Nature of the Adsorbent

The physical and chemical nature of the adsorbent has a profound effect on the rate and extent of the adsorption process. Two of the important factors are the available surface area and the presence of surface functional groups that interact with the solute molecules and with the solvent. This latter factor includes the overall surface charge carried by the adsorbent as well as the presence of chemical groups which may undergo chemical reactions.

2.7.5.3. Surface Area

The extent of adsorption is governed by the portion of the total surface area that the adsorbent has available for the solute to adsorb onto. This is termed the specific

surface area. The amount of adsorption per unit weight of adsorbent increases with decreasing particle size, as this increases the surface area available for adsorption.

Similarly, particle shape and porosity affects the available surface area, therefore affecting adsorption.

2.7.5.4. Temperature

Adsorption reactions are generally exothermic, and so the extent of adsorption generally increases with decreasing temperature. However, small variations in temperature generally have only minor effects and tend not to alter the adsorption processes to any great extent.

2.7.6. Adsorption of Mixed Solutes

Adsorption systems commonly occur where there exists more than one solute undergoing adsorption. The different solutes may enhance adsorption, act independently, or they may exert competitive effects on each other. Mutual inhibition of adsorption can be predicted to occur when adsorption is confined to a single or a few molecular layers, the adsorption affinities of the solutes are within similar orders of magnitude, and there is no specific interaction between the solute molecules to enhance adsorption. The rates of adsorption of each species in a multi-component system can be expected to be decreased relative to the single solute rates, due to the adsorption of one solute decreasing the number of sites available for adsorption, thus decreasing the adsorption driving force for the other solutes.

The degree of competition between solute molecules is dependant on the relative sizes of the molecules, the relative affinities for adsorption and the relative concentrations of the solutes.

2.7.7. Sorption of Organics onto Wastewater Solids

Wang *et al.*, (1993) provide a description of the mechanism of uptake of organic pollutants by biological solids. They suggest that the compounds are taken up by two mechanisms:

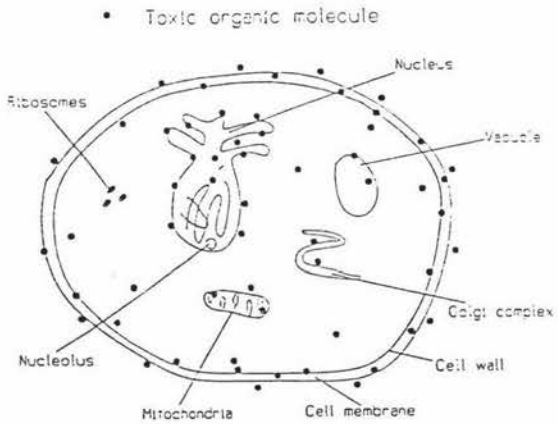
i. adsorption of the compound from the bulk liquid onto the surface of the sludge.

ii. partitioning of the compound between the aqueous phase and the organic matter in sludge. The authors suggest that the biomass present in wastewater treatment systems can be satisfactorily represented by a simple cell (Figure 11).

The cell wall, nucleus, ribosomes etc. are basically made up of fats, proteins and carbohydrates, which resemble organic solvents. Organic molecules adsorbed onto the walls of the cell can then partition into the cell material and distribute into the interior. This can be viewed as a partitioning process where the solute is distributed between the aqueous and organic phases.

Figure 11 Representation of Sorption Process into Biological Cell

(Wang *et al.*, 1993)



The authors find support for their theory by comparing the calculated surface coverage of various organic molecules onto activated carbon to that on activated sludge. The surface coverage was defined as the ratio of experimental uptake of the adsorbate to the calculated theoretical monolayer uptake. Their analysis revealed that the calculated surface coverage on activated sludge is very high compared to activated carbon and is in fact so large for two of the compounds that for adsorption to account for this, multilayer coverage so high as to be unstable would have to occur. Bell and Tsezos (1988) completed a similar analysis and suggested that, for multicomponent solutions, if simple adsorption was the main mechanism of removal, significant competitive effects should have occurred at high solute concentrations. They found that competition effects between the organic pesticides studied were in fact minimal and suggest that absorption of the molecules by the biomass could be occurring. The authors find some evidence for this suggestion in their subsequent work (Tsezos and Bell, 1989). In experiments carried out examining the uptake of the

organic pesticides lindane and diazonon by activated sludge and the fungus *Rhizopus arrhizus*, they found that adsorptive uptake by cell wall preparations of these biological systems accounted for less than half of the uptake observed in whole cell sorption experiments, indicating significant effects on adsorbate removal by cell components other than the cell walls.

Amy *et al.*, (1988) give a similar description of sorption mechanism in their discussion on the adsorptive behaviour of chloroorganics onto biomass.

Weber *et al.*, (1992) provide a conceptually different model for adsorption of compounds by soils and sediments. They propose that different surface regions of an adsorbent may contain different physical and chemical properties. The various surfaces can therefore be expected to display different reactivities toward the adsorption of a particular solute. The overall isotherm behaviour of the bulk adsorbent can thus be thought of as the additive effects of several different isotherms. Wang *et al.*, (1993) point out the significant difference between the amount of organic matter in soils and sediments (usually less than 5%) and the amount found in activated sludge biomass (50-85%). This could mean that this latter model may not be as appropriate for modelling biomass adsorption.

2.7.8. Adsorption of AOX onto Biological Solids

Weber *et al.*, (1991) state that chlorinated hydrocarbons in aqueous solutions tend to adsorb to organic rich soils due to hydrophobic bonding, that is, the hydrocarbon-natural organic interactions are energetically preferred to hydrocarbon-water interactions. This may be a significant factor in the adsorption of chloroorganic molecules onto biomass, as the organic content of biological solids is high.

Attempts have been made at defining the adsorptive behaviour of chloroorganic material onto biological solids. Most have made use of the Freundlich models in defining the isotherms generated. Table V presents the results of several workers attempts to define Freundlich adsorption isotherms for chlorinated compounds and various molecular weight fractions of bleach mill effluents.

Table V: Freundlich Parameters for Adsorption of Chloroorganics onto Biological Solids

SOLUTE	SORBENT		K_f	1/n	SOURCE
Lindane*	Dead A.S	34.5°C	0.7	1.1	
		20°C	1.5	1.0	
Lindane	Dead *R.arrhizus*	5°C	1.8	1.0	
		20°C	2.3	1.0	Bell and Tsezos (1987)
Pentachlorophenol	Dead A.S	20°C	10.1	0.8	
Pentachlorophenol	Dead *R.arrhizus*	20°C	28.8	0.9	
2-Chlorobiphenyl	Dead A.S	20°C	20.5	0.8	
2-Chlorobiphenyl	Dead *R.arrhizus*	20°C	62.6	1.1	
Pentachlorophenol	A.S (dried, crushed)		7.08	-**	Bell and Tsezos (1988)
Lindane	A.S (dried, crushed)		1.56	-**	
Pentachlorophenol (PCP)***	Live A.S		85.06	0.6	Tsezos and Bell (1989)
Pentachlorophenol	*Live R.arrhizus*		32.13	0.56	
2-Chlorobiphenyl	Live A.S		261.5	0.69	
2-Chlorobiphenyl	*Live R.arrhizus*		798.5	1.26	
Lindane	Live A.S	20°C	.56	1.04	
Lindane	*Live R.arrhizus*	20°C	1.37	0.93	
Lindane	Live A.S	5°C	0.49	1.16	
Lindane	*Live R.arrhizus*	5°C	1.17	1.01	
1,1,2-Trichloroethane	Dead A.S		3.378	0.580	Tsezos and Seto (1986)
1,1,2,2-Tetrachloroethane	Dead A.S****		8.427	0.496	
1,1,2-Trichloroethane	Dead *R.arrhizus*		1.922	0.641	
1,1,2,2-Tetrachloroethane	Dead *R.arrhizus*		5.522	0.5468	
	Live A.S pH3	22°C	0.089	1.20	
	Live A.S pH7	22°C	$3.89 \cdot 10^{-4}$	1.67	
	Live A.S pH3	35°C	$1.18 \cdot 10^{-7}$	2.69	Amy *et al.*, (1988)
TOX from kraft Mill Bleach effluent.	Live A.S pH7	35°C	$3.16 \cdot 10^{-8}$	2.21	
	Hg inhibited A.S pH3	22°C	$5.25 \cdot 10^{-7}$	2.50	
	Autoclaved A.S pH3	22°C	$9.55 \cdot 10^{-8}$	2.67	
<1000 MWt fraction from Bleach Effluent	Live A.S pH7	35°C*****	$6 \cdot 10^{-57}$	17	Amy *et al.*, (1988)
Total AOX Fraction kraft Mill B.E.	2° solids from aerated lagoon. pH7.		$3.98 \cdot 10^{-5}$	5	Stuthridge and McFarlane (1993)

* gamma hexachlorocyclohexane. ** Linear isotherm model used. *** Biodegradation may have been a factor influencing result for PCP.

**** Tsezos and Seto (1986) used modified Freundlich parameters $q_e = K_f(C_e - C_r)^{1/n}$, with C_r being a residual concentration term used to account for an apparently non-adsorbable fraction present. ***** approximate Freundlich parameters obtained from graphical data

The results from Bell and Tsezos (1987) reveal that the low molecular weight chloroorganics studied are characterised by nearly linear isotherms, that is 1/n values are close to unity. Tsezos and Seto (1986) found that 1/n values for tri- and tetra- chloroethane were indicative of nonlinear, favourable isotherms.

Comparison of the experiments carried out with temperature being the only variable, it can be seen that K_f, the capacity term in the Freundlich equation, increases with decreasing temperature while 1/n remains relatively constant, indicating an exothermic reaction. Bell and Tsezos (1987) carried out an analysis of the heats of adsorption for lindane and found that the values obtained were negative and of the magnitude that indicated physical adsorption processes dominating.

Amy *et al.*, (1988) carried out adsorption studies on Total Organic Halide (TOX) contained in a kraft mill bleach effluent. They found that adsorption equilibrium was reached in 4 hours. Fitting the Freundlich isotherm to their results revealed that the isotherms were unfavourable (1/n values greater than 1). Their results indicate that adsorption occurs to a greater extent at low pH and low temperatures. Bacteria exhibit a net negative charge at neutral pH. Chlorolignin molecules contain ionisable functional groups such as hydroxyl and phenolic groups and the authors suggest that reduction in the pH at which the adsorption is carried out may result in the reduction of charge barriers between the solute and the biomass. Greater sorption at low temperatures may have been due to reduced solubility of the solute leading to greater affinity for the cell lipids.

Amy *et al.*, (1988) also state that little difference exists between the adsorption of live and of mercury inhibited biomass. However, comparison of the Freundlich constants does reveal some differences in the parameters between the two. Autoclaved and mercury inhibited biomass gave a lower adsorption capacity (K_f) and lower intensity (n) than live biomass.

Desorption experiments were also carried out. The results showed that very little desorption of the TOX occurred unless the desorption pH was significantly higher than the adsorption pH, suggesting a certain irreversibility in the nature of the adsorption.

Adsorption isotherms were compared between the total effluent and the low molecular weight (less than 1000 daltons) organic halide fractions by Amy *et al.*,

(1988). It was determined that the low molecular weight material gave higher biomass loadings (q_e) at a given water phase solute concentration (C_e), than did the unfractionated effluent. These results suggest that lower molecular weight material is sorbed more effectively by the microbial solids than high molecular weight material. In discussing the possible reasons for different adsorption of the fractions, two distinct removal mechanisms are suggested to be at work. First, higher molecular weight molecules would be expected to be more hydrophobic in character, and therefore have greater affinity for the hydrophobic cell material. However, the low molecular weight compounds should be more effective in partitioning into the cell lipids, and small enough to passively diffuse through a cell membrane, facilitating their removal. It must be noted that the parameter measured in this analysis was the amount of organic halide present in each sample, and comparison of different molecular weight fractions is not necessarily a measure of the difference in molecular adsorption between the two, due to possible differences in the number of chlorine atoms per molecule.

3. MATERIALS AND METHODS

3.1. ULTRAFILTRATION OF BLEACH PLANT SAMPLES

Bleach plant effluent, from the C and E effluent drains of a conventional CEH bleach sequence, was collected from the number 1 bleach plant of the Tasman Pulp and Paper Company Ltd mill in Kawerau, New Zealand, on the 3rd April 1992. The samples were taken before the number 1 bleach plant was converted to an HH sequence.

A 2L sample of C and 1L of E effluent were mixed in a large beaker and the pH adjusted to 7 with concentrated sulphuric acid (Analar, BDH Ltd, Poole, England). The mixture was then filtered through a 9.0 cm diameter Whatman #1 filter paper, under a slight vacuum, to remove any suspended solid material. This sample was defined as the unfractionated wastewater. The 2:1 mixing ratio of C:E was considered to be similar to the proportions of the flow of the two drains into the wastewater system.

From this unfractionated wastewater, 200 mL was placed into an Amicon Model 402 stirred cell ultrafiltration unit, fitted with an Amicon UM2 membrane, nominal molecular weight cut-off (MWCO) of 2000 daltons. A further 1800 mL was placed in the reservoir of the ultrafiltration unit. The unit was operated in concentration mode using nitrogen gas (NZIG, New Zealand) to supply the pressure for the system (345 kPa), with the contents of the cell being stirred at 500 rpm.

After the contents of the reservoir had been concentrated into the 200 mL in the cell, the permeate obtained was stored and the sample retentate diafiltered (system pressure 345 kPa) with pH7 distilled water to obtain a further permeate volume of approximately 4L, thus giving a 20 times washout of the 200mL retentate in the cell (Eriksson *et al.*, 1985).

The permeates collected from the concentration and diafiltration stages were mixed together, the pH of this mixture adjusted to 7, and stored at $4^{o}C$ in high density polyethylene (HDPE) containers.

The retentate was removed and its pH adjusted to 7. The membrane was replaced with an Amicon PM30 membrane (nominal MWCO of 30,000 daltons). The retentate

was recharged into the cell and diafiltered with 15 volumes of water as for the previous membrane.

This diafiltration procedure was followed using an Amicon XM100 membrane (nominal MWCO 100,000 daltons), using a system pressure of 70 kPa.

For each membrane the permeates were pH adjusted and stored as for the UM2 permeates. The unfractionated wastewater was also stored in this way. The final retentate was diluted to 2L with distilled water, its pH adjusted to 7, and was stored as for the other permeates.

A sample of each of the stored samples was taken for an initial analysis of their AOX concentrations.

3.2. SAMPLE DEFINITION

The ultrafiltration procedure produced the following samples, and they are identified in the remainder of the work as defined in Table VI.

Table VI: Samples From Ultrafiltration Procedure

Membrane	Nominal MWCO of sample produced (kilo daltons, kD)	Sample definition
UM2	2	<2kD
PM30	30	2-30kD
XM100	100	30-100kD
XM100	>100 (retentate)	>100kD

After two weeks of storage of the samples at $4^{o}C$ it was decided to freeze them at $-30^{o}C$ until they were used, in order to prevent degradation reactions that might occur to the AOX.

Prior to experimental work being carried out using a particular fraction, it was removed from the freezer, thawed and stored at $4^{o}C$ until required.

3.3. PH ADJUSTMENT

Throughout the course of this work, adjustment of samples to neutral pH was routinely carried out. Unless specified, all procedures that refer to pH adjustment used nitric acid (Rhone Poulenc Chemicals Ltd, United Kingdom) or 0.2M sodium hydroxide (A.R grade, Scientific Supplies Ltd, New Zealand) to make these adjustments. pH measurements were made using a PHM 61 Laboratory pH meter.

3.4. DETERMINATION OF AOX CONCENTRATION

The apparatus required for conducting the AOX analysis, consisting of furnace, control unit, coulometer cell and microcoulometer (EUROGLAS, Delft, Holland) and integrator (model 3392A, Hewlett Packard) were located at the New Zealand Forest Research Institute Ltd. in Rotorua so all samples were acidified to a pH between 1 and 2 and then frozen prior to transport from Palmerston North, the location of all other experimental work. The samples were thawed to room temperature prior to use in the AOX analysis procedure. The measuring range of the AOX apparatus is listed as being 25-250µg/L (SCAN-W 9:89 (SPPBTC, 1989)), but for the purposes of this work, attempts were made to measure AOX concentrations for all samples in the range of 50-90µg/L, and so appropriate dilutions were made of each of the individual samples.

The method used for determining the AOX concentration of the individual samples was that given in the test method SCAN-W 9:89 (SPPBTC, 1989).

3.5. REJECTION COEFFICIENT DETERMINATION

The rejection coefficients of each of the permeate fractions, across each of the membranes through which they originally permeated, was estimated in the following manner.

A 200 mL sample of the appropriate fraction was placed in the Amicon ultrafiltration cell fitted with the relevant membrane. The sample was concentrated by 100 mL and the final 5 mL of permeate collected in a beaker. A sample of the final retentate was

also collected and the absorbance at 280nm of these samples measured on a Philips PU8625 UV/Vis spectrophotometer.

The rejection coefficient for the sample was calculated from the equation:

$$R = \frac{A_{ret} - A_{perm}}{A_{ret}}$$

where

R = apparent rejection coefficient

A_{ret} = absorbance of final retentate (280nm)

A_{perm} = absorbance of final 5mL of permeate (280nm).

3.6. DETERMINATION OF CONDUCTIVITY

Because of the influence of ionic strength on the adsorption process (Sections 2.7.3.1 and 2.7.5.1), it was desirable to conduct all experiments at a consistent ionic strength, in order to allow meaningful comparison of the adsorption characteristics from different samples. It was decided that the ionic strength of a typical biological system treating pulp and paper effluents could be simulated by carrying out the experiments in solutions that gave the same conductivity as a 0.2g/L aqueous sodium chloride solution (P.N McFarlane, pers. comm.).

A Philips PW 9501/01 Laboratory Conductivity meter with a PW9510 conductivity cell was used for all conductivity measurements.

The meter was calibrated using the following settings:

- Cell constant 0.3-1 cm^{-1}
- Measuring frequency 2000 Hz
- Temperature compensation ; none
- Calibration to conductivity reading of 7 on 0-10 scale

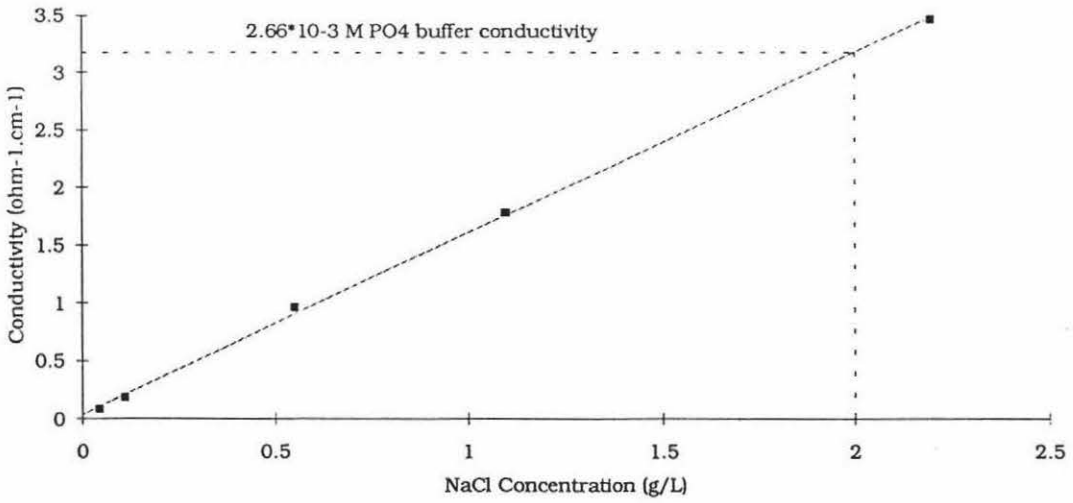
Standard solutions were prepared from sodium chloride (A.R grade, Scientific Supplies, New Zealand) and standard curves for the conductivity of sodium chloride

constructed from these. These were used to determine the Equivalent Sodium Chloride Concentration (ESCC) of sample solutions. The ESCC is defined as the concentration of a sodium chloride solution that is required to give the same conductivity as the sample solution being tested.

In the adsorption studies, phosphate buffers were used to maintain neutral pH and adjust the ionic strength of samples. Conductivity experiments were conducted on pH 7 phosphate buffers with differing phosphate concentrations to determine the relationship between the buffer concentration and the ESCC.

From the standard curves (Figure 12) the response of conductivity to changes in sodium chloride concentration was determined to be linear over the desired range. Similarly, the response of the conductivity to changing phosphate buffer concentrations was also linear, allowing for a direct proportionality between the conductivity given by one mol/L phosphate buffer and that given by 1g/L NaCl. The phosphate buffer strength that gave an equivalent conductivity as that of a 0.2g/L NaCl solution (an ESCC of 0.2g/L) was then determined to be a solution $2.66*10^{-3}$ molar in PO_4 (Figure 12).

Figure 12: Standard Curve for Conductivity of Sodium Chloride Solution



The ESCC of subsequent samples was determined by measurement of the conductivity of the sample and comparing it to that of a reference solution of either 0.2 g/L sodium chloride or $2.66*10^{-3}$M phosphate buffer. The ESCC of the sample was calculated from the equation

$$ESCC_{(sample)} = \frac{K_{(sample)}}{K_{(reference)}} \times ESCC_{(reference)}$$

where K is the conductivity ($ohm^{-1}cm^{-1}$).

Care was taken to ensure that measurements were obtained with all solutions at a constant temperature, in order to allow meaningful comparison of the conductivity measurements without errors occurring due to temperature effects.

3.7. COLLECTION AND STORAGE OF BIOMASS

Mixed Liquor Suspended Solids (MLSS) from the return sludge sump of the activated sludge system at the Kapiti District Council Sewage Treatment Plant was chosen as the source for the biomass. Samples were collected and stored at $4^{o}C$. The samples were held for a maximum of 48 hours prior to use, with most experiments carried out after a 24 hour storage period.

The microbiology of an activated sludge plant is dominated by bacteria, with protozoa and rotifers also playing an important role (Metcalf and Eddy, 1979). It is important to acknowledge that the microbiological makeup and characteristics of the particular biomass used in this work has a significant impact on the adsorption characteristics observed.

3.8. MEASUREMENT OF ADSORPTION ISOTHERMS

This procedure is based on that used by Bell and Tsezos (1987) and Amy *et al.*, (1988).

3.8.1. Tasman Effluents

A 20L sample of MLSS was collected from the sewage treatment plant. The MLSS concentration was determined by filtration of 50 mL of the thoroughly mixed sample through dried, pre-weighed Whatman #1 filter paper. The filter paper, with the retained solids, was dried overnight at 103-105^{o}C (Contherm series 5 oven). The dried sample was removed and placed in a desiccator until ambient temperature was reached, and weighed on a Mettler balance.

$$\text{MLSS concentration(mg/L)} = \frac{\text{Net weight on filter (mg)}}{\text{Sample Volume used (L)}}$$

Two 500mL 0.05 M phosphate stock solutions were prepared for use in the adsorption experiments, one (stock A) from di-sodium hydrogen orthophosphate (Analar, BDH Ltd. Poole, England), and the other (stock B) from sodium dihydrogen orthophosphate (Riedal-de Haen).

Additions of 65 mL stock A solution and 41.5 mL stock B were made to a 2L volumetric flask and this was made up to the mark with distilled water to give a phosphate solution with an ESCC of 0.2g/L. For the purposes of the experimental work, this was termed the phosphate wash solution.

By determining amount of sodium chloride that a sample required in order to give a particular ESCC, it was possible to obtain a solution of the desired conductivity by addition of phosphate stock solutions, the appropriate amounts of which were calculated from the above equivalence of sodium chloride to phosphate buffer. An example of the type of calculation used in this procedure is given in Appendix A1.

A sample of MLSS was taken that would provide sufficient solids for the adsorption studies to be carried out, with an extra 10% added to compensate for losses during the solids preparation. This sample was allowed to stand for 1 hour. The supernatant was then decanted and discarded to give a MLSS concentration of 6640 mg/L for the solids containing fraction (excluding the extra solids added for losses).

After thorough mixing, 350mL aliquots of this MLSS were transferred into 500mL centrifuge tubes. These were centrifuged at 1000 rpm (relative centrifugal force 106 G) for 10 minutes (Sorvall model RC5C, GS-3 rotor, DuPont).

From each tube, 250mL supernatant was removed. Phosphate wash solution (200mL) was added back into each and the tubes thoroughly mixed by shaking. The tubes were centrifuged at 1000 rpm (106 G) for 10 minutes.

From each tube, 200 mL of supernatant was removed, 200mL wash solution added, and the contents mixed. The tubes were then re-centrifuged under the same conditions.

This process of supernatant removal, wash solution addition, shaking and centrifugation was repeated twice more, ensuring thorough washing of the MLSS so that the starting pH of the mixture was 7, and its ionic strength as close as possible to that of a solution with an ESCC of 0.2g/L. The washing also attempted to effect removal, to low levels, of any AOX associated with the MLSS sample.

After the final centrifugation, supernatant was removed from each to give a MLSS concentration of 25000 mg/L, and the contents of the tubes were added together.

The appropriate ultrafiltered fraction was removed from the $4^{o}C$ cold room and allowed to equilibrate to ambient temperature for 1 hour. The sample was thoroughly mixed and a volume removed that was sufficient for use in the adsorption experiment. Phosphate buffer was added to the AOX sample and the sample diluted with distilled water. The fraction was diluted so as to give a six-fold dilution of the AOX concentration that the fraction would have had in the unfractionated wastewater sample (a 1:6 dilution, this being defined as equivalent to 1mL diluted to 6mL).

For the AOX fractions used, the dilutions and phosphate buffer additions required to give the desired AOX concentrations and a 0.2 g/L ESCC are given in Table VII.

Table VII: Dilution and Phosphate Buffer Addition of Tasman AOX Samples

Sample	Dilution of UF'ed Sample from original	Dilution required for UF'ed sample to give 1:6 dilution	ESCC of UF'ed sample(g/L).	Phosphate buffer addition required to give ESCC of 0.2g/L to 1:6 diluted sample (mL/L diluted sample).	
				0.05M HPO4 (Stock A)	0.05M H2PO4 (Stock B)
<2kD	3.14	1.91	0.365	1.45 *	0.92*
2-30kD	2.11	2.84	0	32.5	20.8
30-100kD	2.13	2.82	0	32.5	20.8
>100kD	1.02	5.88	0	32.5	20.8
Unfractionated	1.17	5.12	0.991	1.05	0.67

* Used 0.025 M phosphate stock solutions for this experiment. Therefore used a volume of twice that recorded in Table VII.

Aliquots of the prepared MLSS sample were diluted to 60mL with the phosphate wash solution to give a range of solids concentrations. Each of these 60 mL portions were added to 500mL Erlenmeyer flasks, along with 90 mL of the prepared AOX solution. For each experiment, five different MLSS concentrations were used, ranging between 1000 and 10000 mg/L. The resulting AOX concentrations of each of the flasks was one tenth of that present in the unfractionated wastewater.

Sample controls were prepared by substituting the MLSS with 60mL of phosphate wash solution. Sample blanks were prepared by substituting the AOX solution with 90 mL phosphate wash solution and using the undiluted MLSS for the 60 mL solids addition.

The samples were stoppered with cotton wool bungs and placed on an orbital shaker (Lab-Line incubator/shaker) at 250 rpm and 25^{o}C. The Tasman <2kD fraction samples were shaken for 15 hours, all other samples for 24 hours.

The adsorption experiments were carried out in duplicate for each MLSS concentration, blanks and control samples. The Tasman fractions of 30-100kD fraction, >100kD fraction, and the unfractionated wastewater had the duplicate runs carried out as separate experiments on consecutive days, while for all other samples, the duplicates were carried out as part of the same experiment.

After the required contact time, each flask was removed from the shaker and the contents centrifuged at 3000 rpm (958 G) for 5 minutes in HDPE centrifuge tubes and the supernatant was removed for filtration. The filtration apparatus consisted of a Buchner funnel and flask with the filter paper used being a preweighed Whatman GF/C filter paper (9 cm diameter). Prior to filtration of the supernatant, two 100 mL aliquots of distilled water were washed through the apparatus to remove any leachable material from the filter paper. A 70 mL portion of supernatant was then filtered through in order to bring the filter paper to adsorption equilibrium with the AOX in the supernatant. The filtrate from this was discarded. The remaining supernatant was filtered and the filtrate from this transferred to HDPE storage containers, acidified to pH 2 with three drops of concentrated nitric acid, and stored at -30^{o}C prior to AOX analysis.

The residual solids from the centrifugation step and from the walls of the adsorption shake flask were transferred to a pre-weighed moisture dish for drying to a constant weight at 103-105^{o}C. This typically took 4-6 days, due to the large amount of water to be removed from the moisture dishes, a result of the washings required to obtain quantitative transferral of the solids from the tube and flask to the dish. The filter paper used for the filtration of the supernatant was dried and weighed in a similar manner, with constant weight typically being attained after 24 to 36 hours.

The solids concentration was determined from the dry weight of material in the moisture dish and on the filter paper pertaining to each individual flask. This weight represented the MLSS concentration, and was considered to be the weight of sorbent in the flask.

3.8.2. Kinleith Effluents

Bleach plant effluent, from the D_1 and E_1 effluent drains of the number two bleach plant (bleach sequence $OODE_OD$) was collected from the New Zealand Forest Products Kinleith pulp and paper mill in Tokoroa, New Zealand, on the 15th February 1993. For the purposes of this work the E_O stage was defined as E_1.

Ultrafiltration, to obtain the various molecular weight fractions, was carried out as for the Tasman effluent, using 2L of a 2 D_1: 1 E_1 mixture adjusted to neutral pH with concentrated nitric acid. This 2D :1E mixture was defined as the Kinleith unfractionated wastewater.

Due to the short time span over which these fractions were used in experimentation, freezing of the samples was not required. All samples were stored at 4^{o}C until used.

A sample of each of the stored samples was taken for an initial analysis of their AOX concentrations.

In carrying out the adsorption isotherm experiments, each fraction was diluted so as to give a similar initial concentration of AOX in the adsorption flasks as that used in the studies using the Tasman fractions. The dilutions required to give these equivalent AOX concentrations are given in Table VIII.

Table VIII: Dilution and Phosphate Buffer Addition of Kinleith AOX Samples

Sample	Dilution of UF'ed Sample from original	Dilution of UF'ed sample required to make AOX concentration. equal to Tasman 1:6 diluted fraction	ESCC of UF'ed sample (g/L).	Phosphate buffer addition required to give ESCC of 0.2g/L to 1:6 diluted sample (mL/L).	
				0.05M HPO4 (Stock A)	0.05 H2PO4 (Stock B)
<2kD fraction	2.95	1.22	0.53	-	-
2-30kD fraction	2.04	2.25	0	32.5	20.8
30-100kD fraction	2.08	-	$1.2*10^{-4}$	32.5	20.8
>100kD fraction	0.53	1.83	0	32.5	20.8
Unfractionated	1	3.21	1.48	-	-

The conductivities of the <2kD fraction and the unfractionated wastewater were such that following the standard procedure produced adsorption systems with ESCC values of approximately 0.35 g/L.

For these fractions, methods were devised to reduce the ESCC of the washed MLSS slurry in order to obtain an adsorption system with ionic strength close to an ESCC of 0.2g/L. For the <2kD fraction experiment, liquid was removed from the solids by spreading the slurry onto sheets of chromatography paper (46 x 57cm Whatman 3mm Chr), allowing the liquid move into the paper, and scraping the more concentrated solid onto a further sheet for continued blotting. After three sheets had been used in this manner, the solids were scraped into a beaker and diluted back to their original volume (MLSS concentration, 25000mg/L) with pH 7 distilled water. Instead of using phosphate wash solution as diluent to give the correct solids concentration in the various adsorption flasks, the MLSS sample aliquots were diluted to 60 mL using pH 7 distilled water. This method resulted in a reduction of the ESCC of the adsorption mixtures to within a range of 0.26-0.3 g/L.

For the unfractionated wastewater experiment, it was decided to dilute the AOX sample to an overall dilution of 1:3.57 (that is, 1mL made up to 3.57mL) prior to addition to the MLSS sample, instead of 1:3.21. A further washing stage was incorporated after the four phosphate washes, following the same procedure as the previous washes but using pH7 distilled water as the wash solution. The supernatant of the centrifuged MLSS sample was removed to give an approximate concentration of 30000 mg/L.

To each adsorption flask, 100mL of AOX solution was added, along with 50 mL of diluted MLSS slurry. The dilutions of the MLSS aliquots for use in the individual shake flasks were completed using pH7 distilled water instead of phosphate wash solution. This method produced adsorption mixtures with an ESCC of approximately 0.28g/L, similar to the reduction achieved in the UM2 experiment, but without the messy procedure.

For both of the AOX samples, the procedure for the remainder of the experiment remained the same.

The Kinleith 30-100kD fraction had an AOX concentration so low that it was not possible to obtain an initial AOX concentration in the adsorption flasks equal to that

of the Tasman 30-100kD fraction. The permeate was adjusted to an ESCC of 0.2g/L using the stock solutions, and 100mL of this was added to 50 mL aliquots of the biomass, in an attempt to give an initial concentration as close as possible to that of the Tasman effluent.

3.9. MODIFICATION TO MLSS PREPARATION PROCEDURE

During the course of the experiments, the Kapiti sewage treatment plant encountered a problem in the microbiota of the activated sludge system. Filamentous organisms were found to be more dominant than usual, causing settling problems for the sludge produced by the system. The presence of this filamentous element precluded the use of quiescent settling of the MLSS sample as the method for removal of supernatant prior to the washing stage.

An alternative procedure was therefore developed where 350 mL portions of the sample were centrifuged (1000rpm, 106 G, 5 minutes) and the supernatant from these removed to obtain the required reduction in the total MLSS sample volume. The sample solids were subsequently mixed together before continuation of the standard washing procedure. The adsorption experiments that were affected by this filamentous element were those carried out on the Tasman 2-30kD fraction and all Kinleith samples.

3.10. ADSORPTION RATE EXPERIMENTS

Adsorption rate experiments were carried out in order to determine the time required to reach adsorption equilibrium for the various fractions.

The Tasman <2kD fraction and >100kD fraction were chosen for use in the experiments as it was considered that these fractions would encompass the extremes of the times required to reach equilibrium for all fractions, one being the lowest, and the other the highest molecular weight fraction.

The rate experiments were carried out prior to the isotherm experiments, but are recorded here because a full description of the method of adsorption isotherm determination was considered necessary.

The procedure followed for the rate experiments was similar to that used for adsorption isotherm determination, with the only differences being that, instead of adsorption flasks with differing solids concentrations, nine flasks with 10000 mg/L MLSS in each were prepared. A flask was removed from the orbital shaker and processed as for the isotherm experiments after times of 15, 45, 75, 120, 180, 240, 360, 600, and 1440 minutes. Duplicate samples were not obtained for these flasks. Sample controls and blanks were carried out in duplicate, and these were removed from the shaker after the maximum time (24 hours).

The liquid phase AOX concentration, and the MLSS concentration, of each of the samples removed at the set times, was determined as for the adsorption isotherm experiments.

3.11. BLEACH PLANT DEFINITION

In this work, a bleach sequence involving no oxygen delignification and an initial C stage with no chlorine dioxide substitution, such as the Tasman sequence sampled from, is termed a conventional bleach plant.

A bleach sequence that utilises oxygen delignification and chlorine dioxide substitution in the first chlorination stage, such as the Kinleith sequence, is termed a modern bleach sequence.

3.12. DETERMINATION OF ADSORPTION ISOTHERM MODELS

3.12.1. Introduction

The results of the adsorption tests, namely the MLSS concentration and AOX concentration of the liquid phase of each flask after adsorption, were used to calculate adsorption isotherms for the samples.

Bell and Tsezos (1987), in conducting adsorption experiments involving a constant initial solute concentration and varying the adsorbent concentrations, pointed out that the true independent variable is in fact the adsorbent concentration and the true dependant variable is the equilibrium effluent concentration C_e. Therefore, in calculation of the adsorption isotherms, they used a nonlinear least squares routine on the true dependant and independent variables. This was the approach adopted in

the present work. The non linear routines were carried out using the statistical software package SAS (SAS System for Windows 3.1, Copyright SAS Institute Inc. Cary N.C. USA), and the routines used are recorded in Appendix A2.

q_e, the amount of solute adsorbed per unit of adsorbing phase is calculated by the following expression:

$$q_e = \frac{(C_o - C_e)}{MLSS}$$

MLSS = Concentration of solids in adsorption flask.
C_o = initial concentration of solute in the liquid phase. This was the concentration of the AOX in the flask with MLSS = 0.

C_e = equilibrium solute concentration. This was the AOX concentration of the liquid phase after adsorption.

Section 2.7.2 defines the remainder of the variables used in each of the isotherm models.

3.12.2. Langmuir Isotherm

The Langmuir isotherm can be defined as

$$q_e = \frac{(C_o - C_e)}{MLSS} = \frac{abC_e}{(1+bC_e)}$$

This can be rearranged to give

$$MLSS = \frac{C_o - C_e}{abC_e} + \frac{C_o - C_e}{a}$$

and rearrangement of this equation results in

$$-bC_e^2 + C_eC_ob - C_e - MLSS \times abC_e + C_o = 0$$

which is a quadratic equation able to be solved for C_e from the following equation

$$C_e = \frac{-B \pm (B^2 - 4AC)^{0.5}}{2A}$$

where $A = -b$

$B = C_o b - 1 - MLSS \times ab$

$C = C_o$

This equation was used in the nonlinear least squares routine to determine the adequacy of the Langmuir isotherm model.

3.12.3. Freundlich Isotherm

The Freundlich isotherm can be defined as

$$q_e = \frac{(C_o - C_e)}{MLSS} = K_f C_e^{1/n}$$

The best rearrangement of the above equation for fitting of the isotherm was found to be

$$MLSS = \frac{(C_o - C_e)}{K_f C_e^{1/n}}$$

Although this defines MLSS as the dependant variable, this was the equation used to determine the fit of the Freundlich isotherm to the data.

3.12.4. Irreversible Isotherm

The irreversible isotherm

$$q_e = \frac{(C_o - C_e)}{MLSS} = K_i$$

was rearranged to give

$$C_e = C_o - K_i \times MLSS$$

from which the constant K_i could be determined using a linear regression analysis.

4. RESULTS AND DISCUSSION

4.1. AOX DETERMINATION

The chloroorganic compounds present in bleach plant wastewaters consist of a large number of compounds that cover a wide molecular weight range. These compounds vary with differing feedstocks and bleaching processes. Many of the higher molecular weight compounds are currently poorly defined. It is excessively expensive and impractical to identify all compounds present in such a wastewater for use in routine monitoring. Also, many of the high molecular weight compounds cannot be analysed by conventional techniques. Therefore, for purposes of analysis, methods have been developed that quantify the amount of chlorine that is bound to organic compounds present in a sample. It is this non-specific parameter that is usually used to define the chloroorganic content of the sample.

The parameter used in this experimental work for the determination of chloroorganic content was Adsorbable Organic Halide (AOX), defined in the SCAN-W 9:89 (SPPBTC, 1989) test method as the amount of the elements chlorine, bromine and iodine that, in a sample of water, is bound in dissolved or suspended organic matter and that is determined under the specific conditions described in the standard. For the purposes of this work AOX was defined as the mass of organically bound chlorine present in the volume of sample analysed, as determined by the method specified in SCAN-W 9:89 (SPPBTC, 1989).

The total amount of organically bound chlorine (TOX) in a sample can be divided into two parts, namely that which is adsorbable and that which is non-adsorbable onto activated carbon. AOX provides an easy measure of the fraction that will adsorb onto activated carbon. Poorly adsorbable compounds will not be accurately measured using this method. Also, volatile compounds such as chloroform are likely to escape quantitative determination. For these reasons, AOX can only be treated as synonymous with TOX if the non-adsorbable fraction is known to be negligible. Jokela *et al.*, (1993) state that the presence of a non-adsorbable fraction does not necessarily diminish the value of AOX for monitoring of bleach mill discharges because they found that the non-adsorbable halogenated matter was efficiently removed from wastewater during biotreatment, and is therefore unlikely to enter the aqueous ecosystem.

Analysis of the experimental errors present in the measurement of AOX revealed that a 90% confidence interval on the duplicate measurements taken for each sample was within 16% of the mean for a 50µg/L AOX measurement, and 9% of the mean for a 90µg/L AOX measurement, these representing the AOX measurement range of the large majority of the samples (Appendix A3). The SCAN-W 9:89 (SPPBTC, 1989) standard reports a coefficient of variation of 4.5% for the repeatability of the AOX measurement. The results of the statistical analysis from the present work reveal a value of 2.5-3% for this parameter, indicating good repeatability.

4.2. ULTRAFILTRATION OF SAMPLES

4.2.1. Introduction

The separation of the bleach plant effluent into different molecular weight fractions was effected by ultrafiltration. The membranes used have nominal molecular weight cut-off (MWCO) values assigned to them that are defined by the molecular weight of a globular solute that is 90% rejected by the membrane (rejection coefficient of 0.9). Rejection of a solute occurs as a result of molecular size and shape, solute concentration, solvent type, interactions between the solute molecules, and the extent of concentration polarisation occurring on the membrane surface. Highly branched molecules will tend to be rejected to a greater extent and thin, unbranched molecules to a lesser extent than a globular molecule of similar molecular size. Interactions such as aggregation between the solute molecules may occur to increase the effective size of the molecule in the system, thus increasing its rejection. The degree of hydration, the presence of counter ions, and steric effects all have the potential to influence the behaviour of molecules in ultrafiltration systems.

Concentration polarisation is defined as the accumulation of rejected solute on the membrane surface. This eventually leads to the formation of a gel layer, or secondary membrane, which influences the rejection properties of the membrane. The build-up of this secondary layer is dependent on interactions of pressure, viscosity, cross-flow velocity (liquid velocity across the membrane surface), bulk fluid flow conditions, flow channel conditions, temperatures, and concentration of the solute.

All of the above-mentioned influences on the rejection of solute molecules determine that the molecular weight cut off of a particular membrane is not sharp, and the true cut-off value may be significantly lower than the nominal. For this reason

ultrafiltration for solute fractionation is therefore best achieved when the molecular weights of the solutes differ in size by at least an order of magnitude. Because the bleach plant effluent contained organic molecules with such a wide range of molecular weights, the ultrafiltration procedure obtained fractions with considerably blurred MWCO values.

4.2.2. Ultrafiltration of the Wastewaters

The AOX concentrations and the molecular weight distributions in the bleach effluents from the Tasman and Kinleith mills are given in Figures 13-15. Concentration polarisation was evident from the build-up of a brown gel layer on each membrane, most likely to be polymeric high molecular weight material, causing an increase in the rejection of molecules that would have otherwise passed through. This gel layer was more significant for the Tasman effluent than for the Kinleith, in agreement with the observation of lower amounts of high molecular weight AOX material in the latter (Figures 14 and 15).

An AOX balance for the Tasman effluent reveals that the fractions account for 81% of the total AOX as determined from the unfractionated wastewater. The build-up of the gel layer on the membrane can account for some of these losses. An AOX balance for the Kinleith effluent showed that 99% of the total AOX was accounted for by the four fractions, indicating that of the AOX originally present in the unfractionated wastewater, minimal losses had occurred during the fractionation procedure. This observation was consistent with the observed molecular weight distribution in the Kinleith mill's effluent, as losses due to formation of a gel layer on the ultrafiltration membranes were insignificant due to the low levels of high molecular weight material.

4.2.3. Rejection Coefficient Analysis

The rejection coefficients, shown in Table IX, reveal that the two wastewaters behaved in a similar manner in the ultrafiltration procedure.

Table IX: Apparent Rejection Coefficients (R) for Wastewater Fractions

Sample	R (Tasman)	R (Kinleith)
>2kD	0.86	0.85
2-30kD	0.36	0.47
30-100kD	0.74	0.87

Figure 13: AOX Distribution of Unfractionated Samples

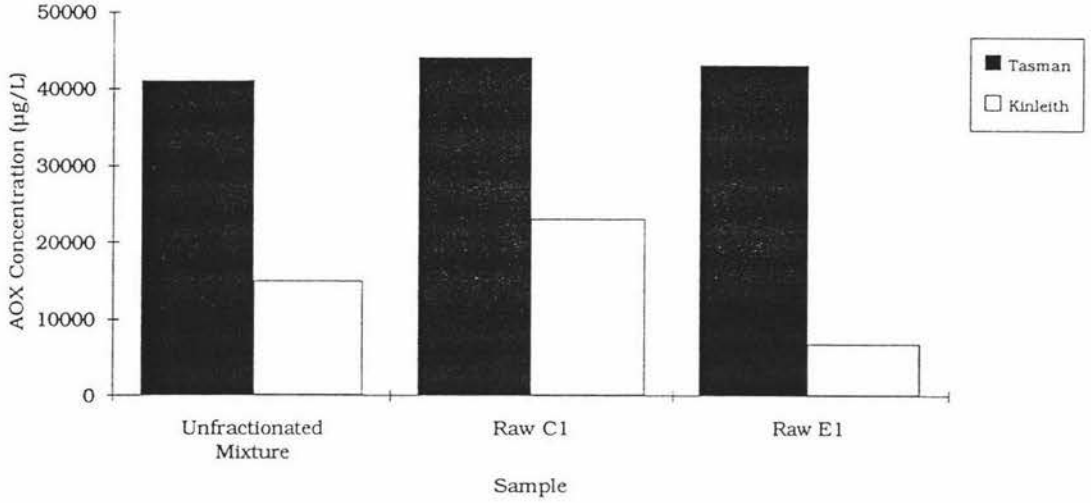


Figure 14: Molecular Weight Distribution of Wastewater Samples

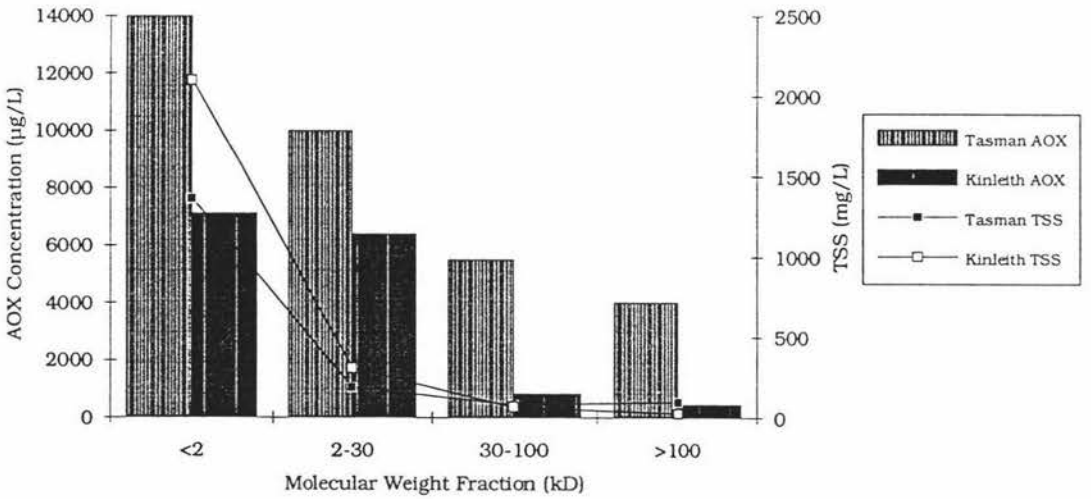
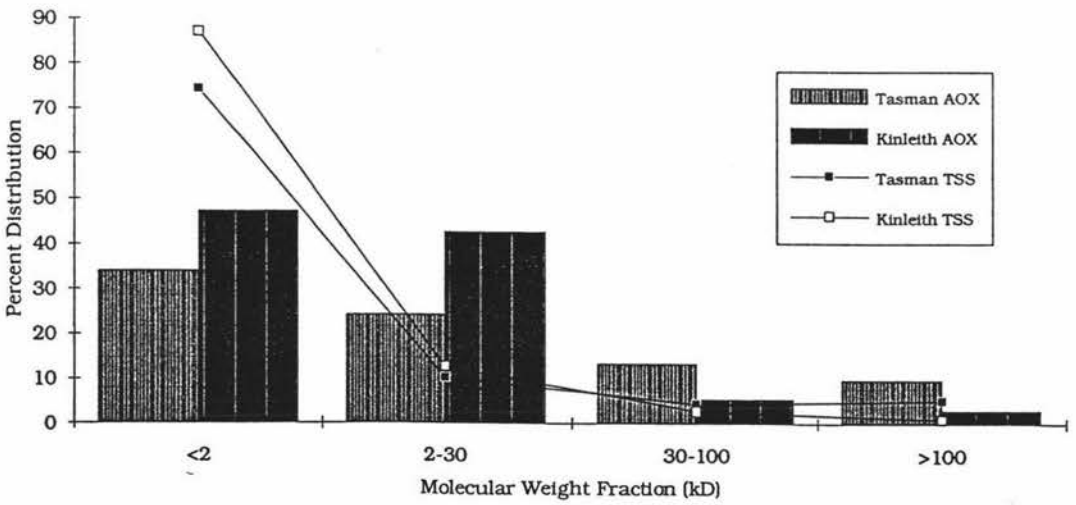


Figure 15: Proportional Distribution of Total AOX and TSS Present in Each Fraction



The <2kD fraction and 30-100kD fractions exhibited very high rejection values, while the lower rejection of the 2-30kD fractions was also consistent between effluents. The high rejection of the high molecular weight fraction may be attributable to the formation of aggregates amongst the polymeric material. Jokela and Salkinoja-Salonen (1992) suggest that the ultrafiltration of bleached kraft mill effluents is subject to interference from intermolecular associations that occur when the concentration of the solvent increases above a certain level. They suggest that the behaviour of the effluent in ultrafiltration may be a reflection of micelle formation in the aqueous system. For the UM2 and PM30 membranes, rejection coefficient analysis was carried out without the presence of the higher molecular weight material, and so the high rejection of the lower molecular weight fraction indicates that concentration polarisation or aggregation by polymeric material is not the only mechanism inhibiting the free passage of solute. Jokela and Salkinoja-Salonen (1992), analysing bleach plant effluents from four mills by size exclusion chromatography, clearly showed that significant proportions of AOX compounds exist at all molecular weights between 50 and 3,000 daltons. If this observation was consistent for the effluents under study, it would be expected that the rejection of the molecules in the less than 2,000 dalton fraction would be high, due to a significant proportion having sizes close to that of the molecular weight cut off of the membrane, and the lack of a sharply defined cutoff of ultrafiltration membranes, as discussed above.

In a study involving analysis of bleach plant wastewaters, Stuthridge *et al.*, (1991) indicated that, of the AOX less than 30 000 Daltons, 85-90% was of molecular weight less than 10 000 Daltons. If a similar distribution holds for the wastewaters under study, this could account for the rejection coefficient of the 2-30kD fraction being significantly lower than that of the <2kD fraction, as the nominal cut-off value of the PM30 membrane would be three times the size of almost 90% of the material able to be passed through the membrane.

4.3. COMPARISONS BETWEEN TASMAN AND KINLEITH FRACTIONS

4.3.1. AOX Distribution

The reduction in the overall AOX concentration upon mixing of 2L C with 1L E effluent, subsequent pH adjustment to 7.0 and filtration through Whatman #1 filter paper, was 6% for the Tasman effluents. Mixing of 2L D_1 with 1L E_1 Kinleith bleach

effluent, with similar pH adjustment and filtration, resulted in an AOX reduction of 15% for the Kinleith samples. Mixing of the acidic C (or D_1) effluent with the alkali E liquor was expected to result in AOX reduction, due to precipitation of higher molecular weight compounds or alkaline dehalogenation (Stuthridge and McFarlane, 1993). Filtration of the mixture would remove precipitation products as well as any AOX that was already associated with non-filterable suspended solids prior to the mixing stage. Stuthridge and McFarlane (1993) found that, on mixing and filtration of alkali mill effluents with acid effluent samples, reductions in AOX did occur which were attributable to both precipitation and removal of previously non-filterable AOX. In conducting experiments on the effect that the pH at which the chlorination and extraction stage effluents was mixed had on AOX reduction, the authors found that AOX losses were greater at higher mixing pH. In the present work, the pH on mixing of the Tasman effluent samples was 9.3, whereas that for the Kinleith samples was 11. Although no quantitative work was carried out to differentiate losses due to mixing effects, alkaline dehalogenation, and those attributable to removal of previously non-filterable AOX, this higher mixing pH could explain the greater reduction in AOX by the Kinleith effluent samples.

The Tasman mill consists of a CEH sequence, whereas the Kinleith bleaching sequence involves modified oxygen delignification and 100% chlorine dioxide substitution. These modifications to the conventional bleaching sequence eliminate elemental chlorine as an input to the bleaching process, resulting in reductions in the AOX load from the bleach plant (Crooks and Sikes, 1990, Carlberg, 1991), reduced effluent colour and chlorophenolic formation (Wilson *et al.*, 1991), and reduced toxicity (Crooks and Sikes, 1990). The results obtained from the present work concur with these observations, with the total effluent AOX concentration from the Kinleith bleach stage effluent drains being significantly lower than that from the Tasman drains (Figure 13).

Yin *et al.*, (1990) found that wastewaters from bleach sequences that utilised oxygen delignification and chlorine dioxide substitution in the first bleaching stage contained lower molecular mass chlorinated organic material than wastewaters from bleach sequences without these modifications. Figure 15 reveals that the proportion of lower molecular weight material is significantly higher for the Kinleith wastewater, with 90% of the total being less than 30 000 Daltons, as opposed to the Tasman effluent's 58%. The higher molecular weight material (greater than 30kD) present in the Tasman effluent is much more significant than that present at Kinleith, making up 23% of the total as opposed to 8% for the latter mill.

The results of the AOX distribution are consistent with those found by Stuthridge *et al.*, (1991), who analysed the AOX levels present in the wastewaters from the Kinleith pulp and paper mill prior to bleach plant modernisation, where oxygen delignification and 100% chlorine dioxide substitution was introduced to the process. Table X gives a comparison the results of the published analysis with the molecular weight distribution found in this present work.

Table X: AOX Distribution in Kinleith Mill Wastewaters

Stuthridge *et al.*, (1991)		Present work	
Molecular size	Distribution (%)	Molecular Size	Distribution (%)
<3kD	55	<2kD	47
3-30kD	29	2-30kD	43
30-100kD	8	30-100kD	6
>100kD	8	>100kD	3

Table X indicates that the modernisation program appears to have increased the proportion of AOX material in the 3-30kD fraction and decreased the amount of material in the lowest molecular weight fraction, but it must be noted that the MWCO of the lowest fractions differs between the pre-modernisation analysis and that carried out in the present work. The material in the >100kD fraction appears to have decreased since the modernisation of the bleaching process. Comparison of the two sets of data must take into consideration that the Stuthridge *et al.*, (1991) data was based on total pulping and bleaching effluent wastewaters, whereas that from the present work analysed only effluent from D_1 and E_1 drains of the bleach plant.

4.3.2. Suspended Solids

Figures 14 and 15 also show the total suspended solids (TSS) of the various fractions.

Most of the material in the wastewaters is present in the <2kD fraction. (75-90%). Comparing the distributions of the two wastewaters, the Kinleith sample had a higher proportion of material in the <2kD and 2-30kD fractions, while the Tasman sample displayed a higher proportion of material in the 30-100kD and >100kD fractions (Figure 15). This concurs with the discussion in Section 4.3.1 that oxygen

delignification and chlorine dioxide substitution in bleaching operations produces a lower molecular weight material than does conventional plants without these modifications.

Although the Kinleith sample AOX concentration is lower for all fractions, the TSS distribution reveals that for both the <2kD and 2-30kD fractions, the suspended solids concentration is higher for the Kinleith wastewater. This observation is indicative of lower chlorination levels of the material in these fractions, for the effluent from bleach sequences using oxygen delignification and chlorine dioxide substitution. It is recommended that this be confirmed by conducting, in addition to AOX determination, total organic carbon analyses on the different molecular weight fractions of two mills of similar bleach sequences to those studied in this work, an analysis not undertaken in this study.

4.4. ADSORPTION RATE EXPERIMENTS

The results of the rate experiment carried out for the Tasman <2kD fraction and >100kD fractions are shown in Figures 16-18. From these it was determined that the time to reach equilibrium was approximately fifteen hours for the <2kD and twenty hours for the 30-100kD fraction. The fractions used were the two molecular weight extremes of the Tasman effluent sample and it was inferred that the AOX fractions with molecular weights intermediate between these two would display behaviour intermediate between these two time extremes. Therefore, the Tasman <2kD fraction adsorption isotherm experiments were carried out using a contact time of fifteen hours while the remaining Tasman fractions, and unfractionated effluent sample, utilised a twenty four hour contact time. It was also assumed that the Kinleith samples would display similar rate behaviour, and so for all fractions from this mill a twenty four hour contact time for the adsorption isotherm experiments was used.

Figure16: Adsorption - Time Plots for Tasman <2kD and >100kD Fractions.

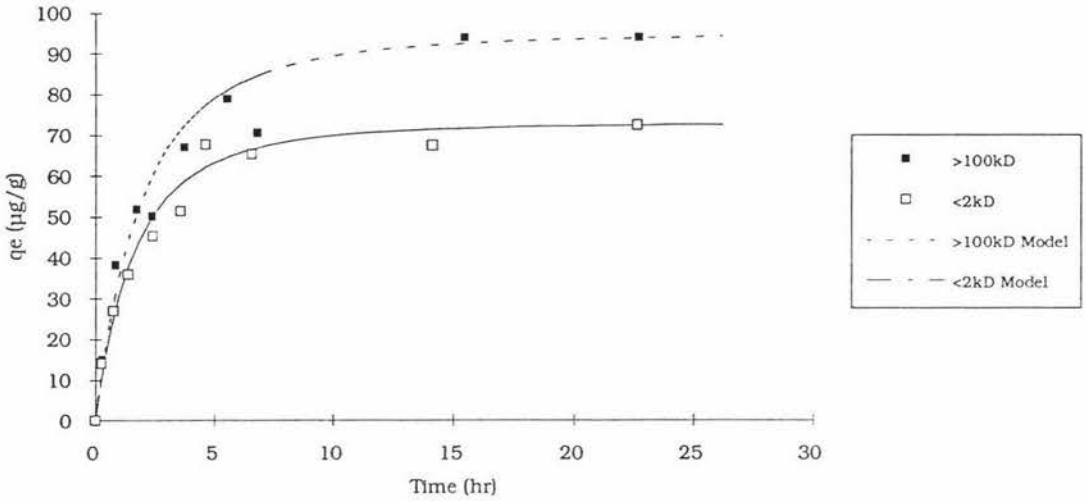


Figure17: Modelled Adsorption Rates for Tasman <2 and >100kD Fractions.

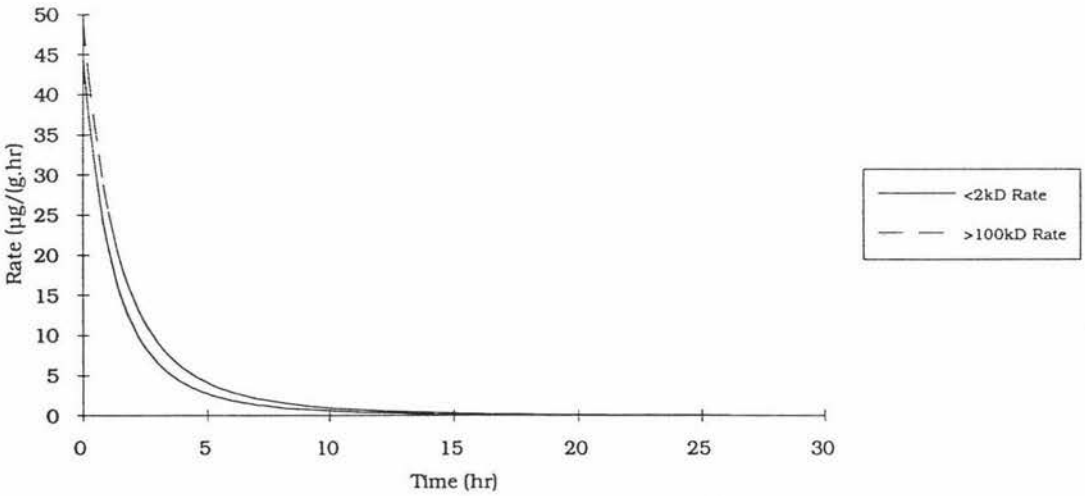
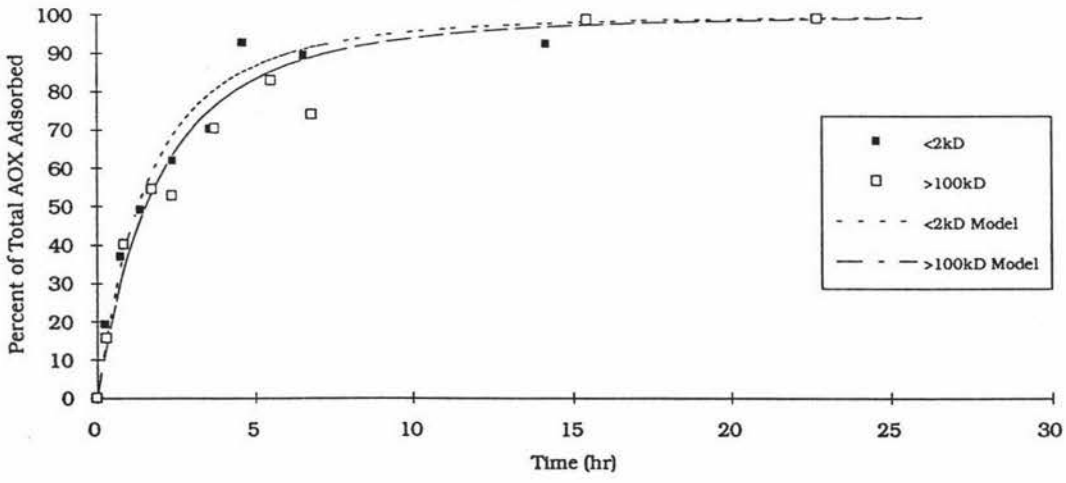


Figure18: Percentage Adsorption-Time Plots forTasman <2kD and >100kD Fractions.



The rate of adsorption was modelled using an equation of the form:

$$\frac{-dq(t)}{dt} = m(q_e - q(t))^j$$

where

t = mixing time (hr)

q(t) = calculated sorbate uptake at a given time (µg AOX/g MLSS).

$$= \frac{C_o - C(t)}{MLSS}$$

C(t) = liquid phase AOX concentration after adsorption of time t.

q_e = equilibrium concentration of AOX adsorbed onto biomass, (µg/g sorbent)

m and j = empirical rate constants.

q_e was estimated by visual analysis of the plots of the q(t) vs t data.

Hendricks and Kuratti (1982), in their assessment of different equations used for modelling adsorptive uptake, described a model of the same form as the one used in this work, differing in that the rate constant j was set at a value of 1.

The parameters m and j for each sample were determined by a least squares analysis (described in Appendix A4).

Analysis of the data for the two fractions obtained the parameters shown in Table XI.

Table XI: Calculated Rate Parameters for Tasman Wastewater Fractions

SAMPLE	m	j	q_e (µg/g)	R^2
<2kD fraction	0.11	1.4	73	0.97
>100kD fraction	0.086	1.4	95	0.94

Figure 16, and the regression parameter (R^2) in Table XI, indicates a good fit of the data and so the model was deemed useful for describing the adsorption rate process.

From the form of the model, the rate of adsorption is dependent on the equilibrium adsorption concentration, q_e. This parameter is dependent on a number of factors, some of which include; the nature of the adsorbate molecules, the initial concentrations of the adsorbate and adsorbent, and any interactions that exist in the system, including adsorbate-adsorbent, adsorbate-adsorbate, adsorbate-solvent and adsorbent-solvent interactions. These factors make q_e a system specific parameter that must be evaluated for each set of conditions used. Therefore, in any use of the derived empirical model to make observations on the rate behaviour of a particular system, this limitation must be acknowledged.

Although empirical, some useful information can be inferred from the model form and parameters. The form of the equation reveals that the driving force for the adsorption reaction rate is dependent on the difference between equilibrium adsorption and the adsorption that occurs at time t. Assuming that the amount of AOX adsorbed at time t is directly proportional to the number of sites on the biomass that have been filled in the adsorption process, the driving force for the adsorption rate is therefore dependent on the difference between the number of sites available at equilibrium and that at time t.

Figure 17 shows the modelled adsorption rates for both fractions. The plots reveal that the rate of adsorption is greatest for the high molecular weight fraction, over the entire time recorded. This implies that the high molecular weight material has a higher affinity for adsorption onto biomass than the low molecular weight material. Because their initial AOX concentrations were widely different, it is difficult to generalise this result.

The extent to which the adsorption had been carried to completion over the recorded times is shown in Figure 18. From this it can be observed that very little difference exists between the <2kD fraction's and the >100kD fraction's relative rate to equilibrium. Using the derived model, comparison of the times for the systems to reach 98% of the equilibrium adsorption gave 15.1 hours for the <2kD fraction and 18.1 hrs for the >100kD fraction. It may therefore be inferred from the model that the <2kD fraction does in fact reach equilibrium more quickly than the >100kD fraction, even though the rate of adsorption is greater for the high molecular weight fraction. This comparison of models relies on perfect fit of the experimental data, and given the scatter of the results, this analysis must be considered speculation until repeated consistently.

Because the rate experiments were carried out merely to determine the time required for the AOX to reach adsorptive equilibrium with the biomass, the experimental work was not exhaustive. The fit of the model to the experimental data of two very different molecular weights is interesting as it predicts that the rate parameters are similar between both the low and the high molecular weight fractions. It is recommended that further work be carried out to examine the usefulness of this model in describing adsorptive behaviour of AOX onto biomass.

4.5. DETERMINATION OF ISOTHERMS

4.5.1. Introduction

The equilibrium AOX concentrations at the various biomass solids concentrations for each molecular weight fraction are shown in Figures 19-28. The usual method of representing the adsorption of a particular system is that of an adsorption isotherm (Weber *et al.*, 1991). The adsorption isotherms of the samples are shown in Figures 29-38. The line associated with the legend term model in each of the plots is the modelled adsorption line calculated for each of the data sets. These will be discussed in this Section.

Figure 19: Adsorption of Tasman <2kD Fraction

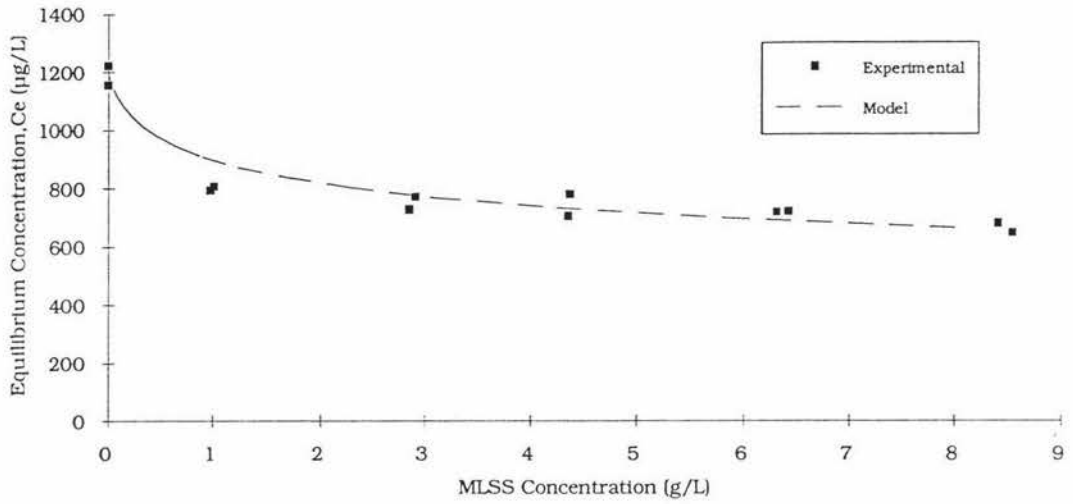


Figure 20: Adsorption of Tasman 2-30kD Fraction

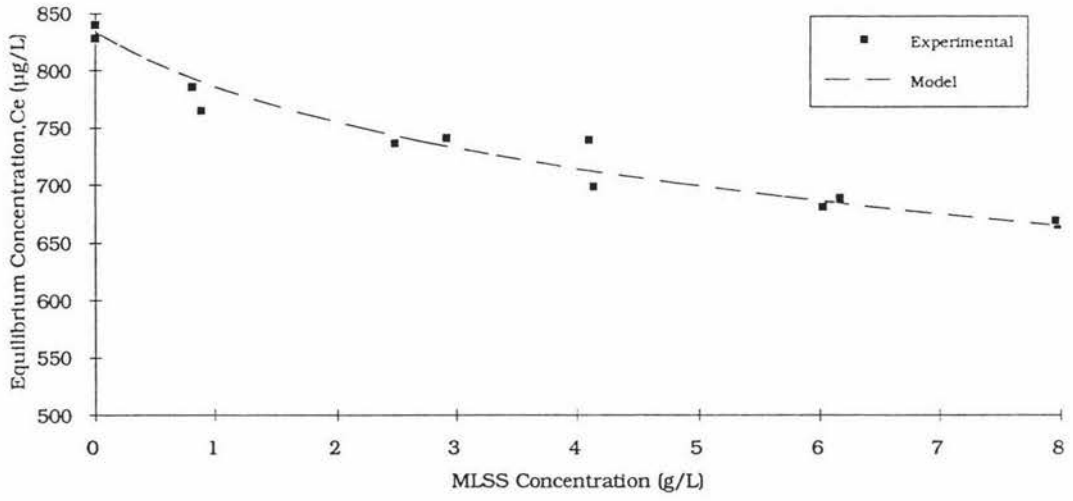


Figure 21: Adsorption of Tasman 30-100kD Fraction

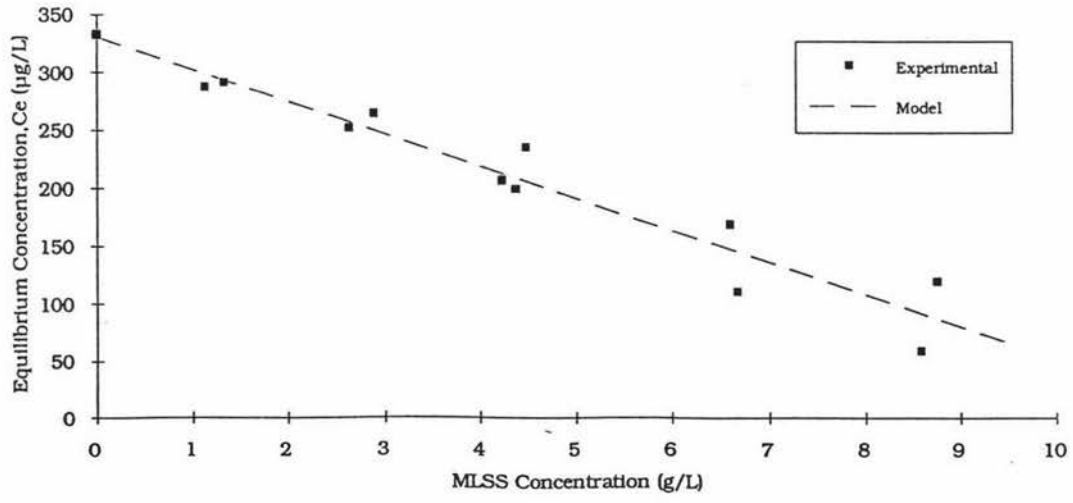


Figure 22: Adsorption of Tasman >100kD Fraction

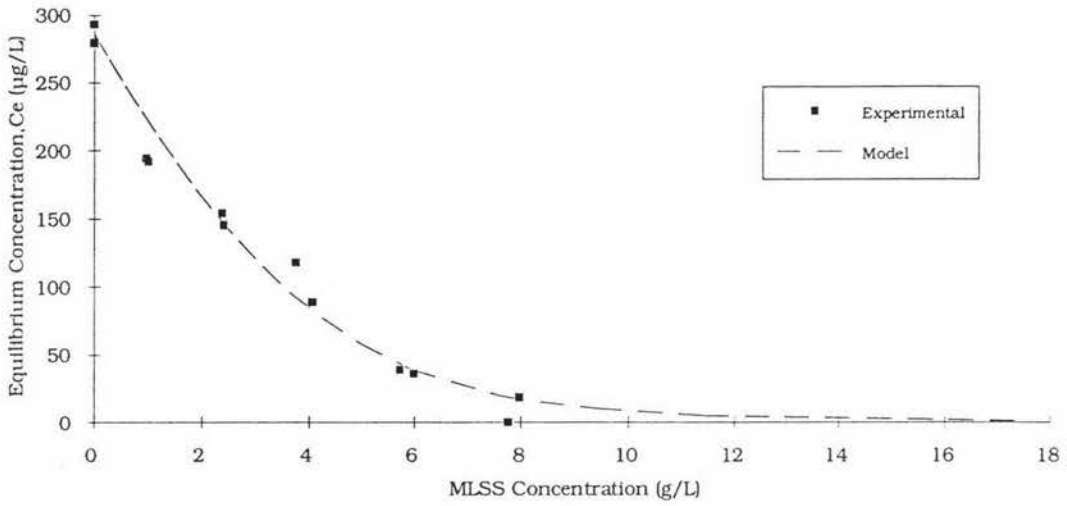


Figure 23: Adsorption of Tasman Unfractionated Sample

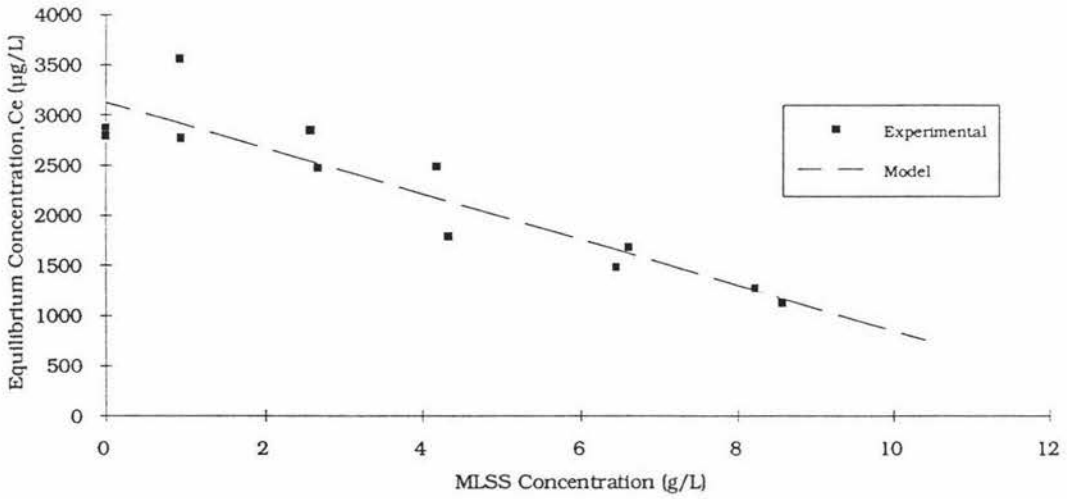


Figure 24: Adsorption of Kinleith <2kD Fraction

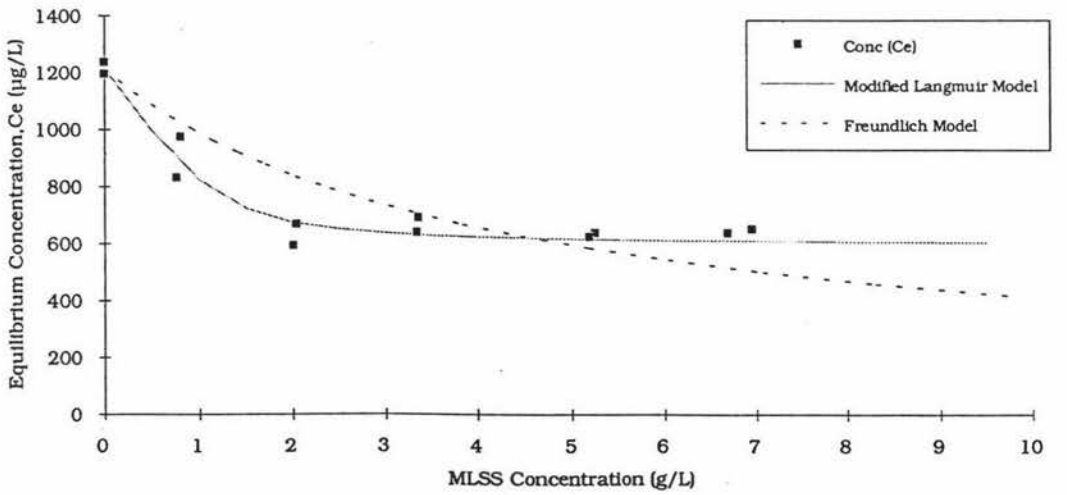


Figure 25: Adsorption of Kinleith 2-30kD Fraction

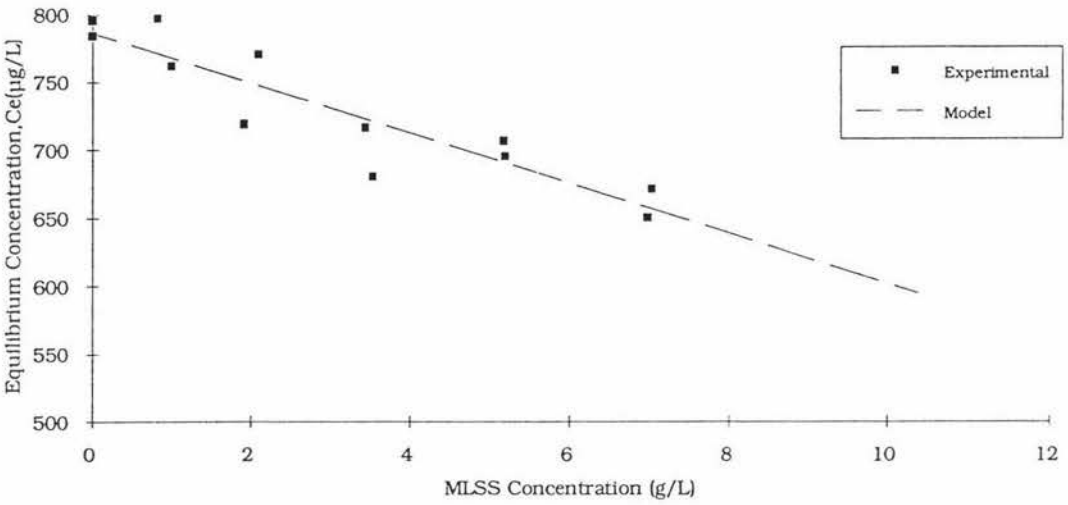


Figure 26: Adsorption of Kinleith 30-100kD Fraction

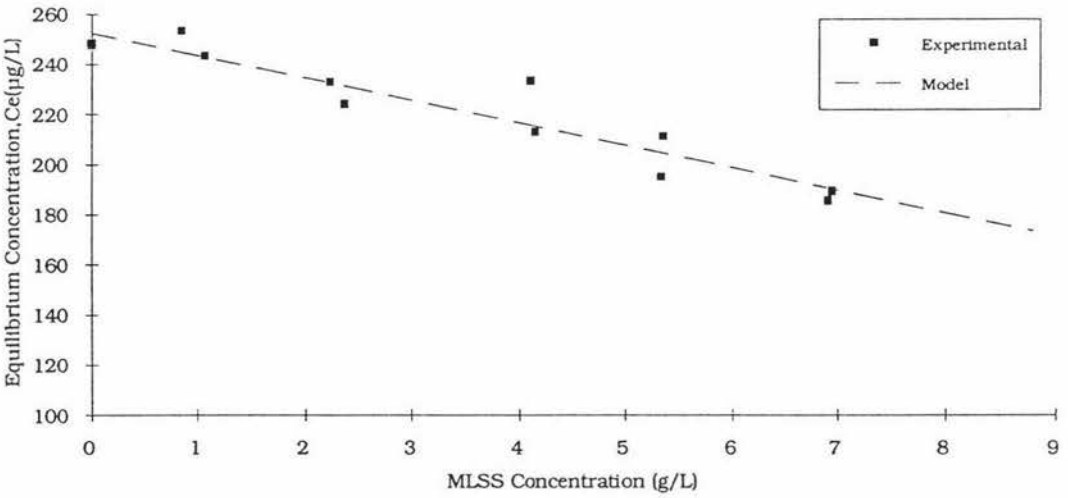


Figure 27: Adsorption of Kinleith >100kD Fraction

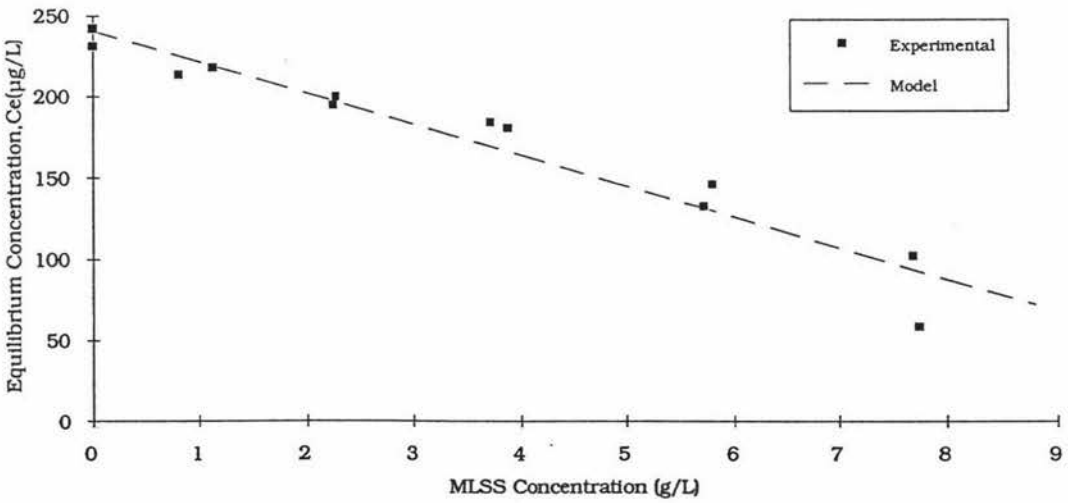


Figure 28: Adsorption of Kinleith Unfractionated Sample.

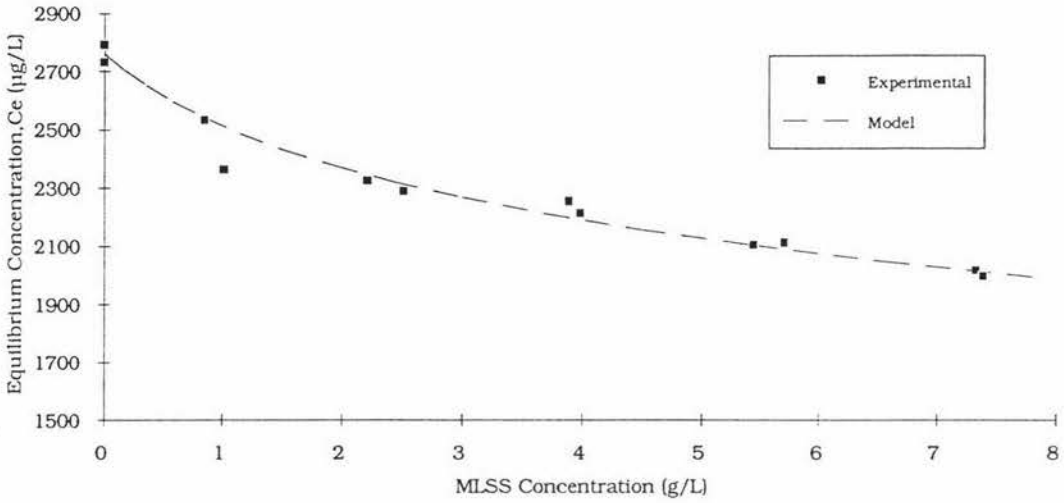


Figure 29: Adsorption Isotherm, Tasman <2kD Fraction

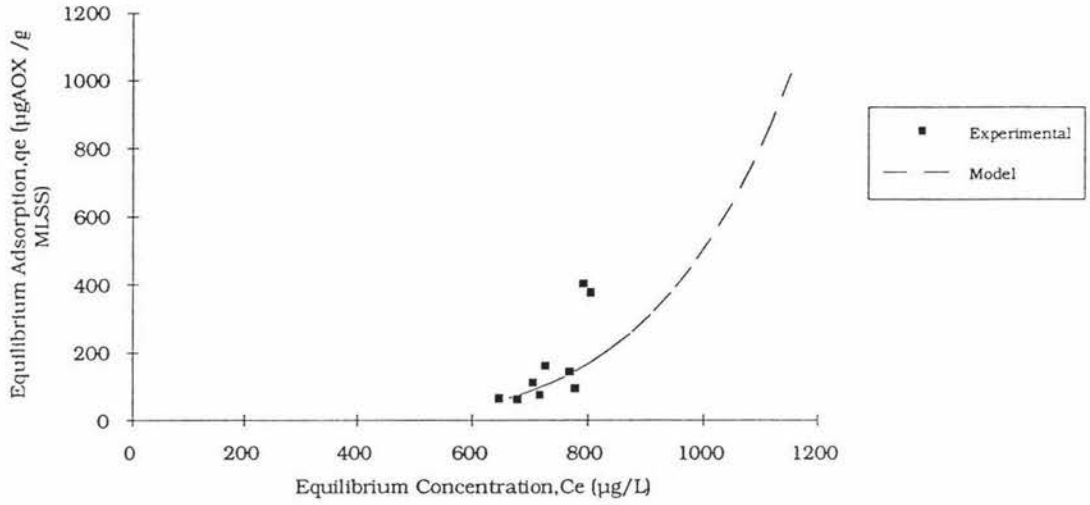


Figure 30: Adsorption Isotherm, Tasman 2-30kD Fraction

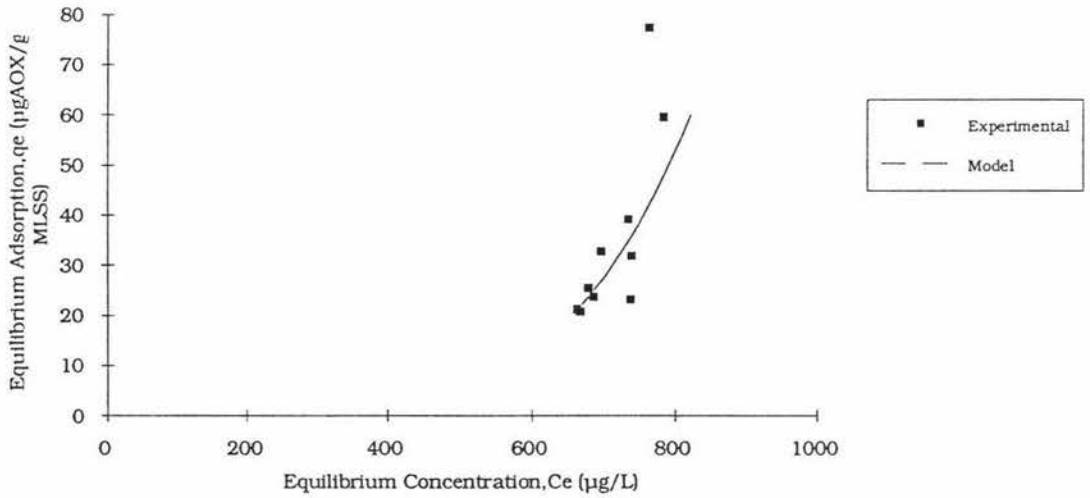


Figure 31: Adsorption Isotherm, Tasman 30-100kD Fraction

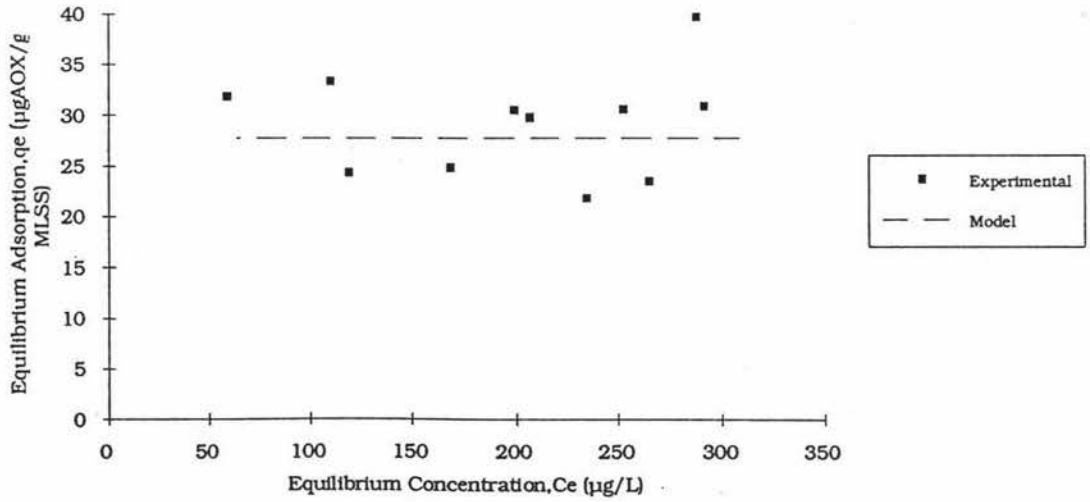


Figure 32: Adsorption Isotherm, Tasman >100kD Fraction

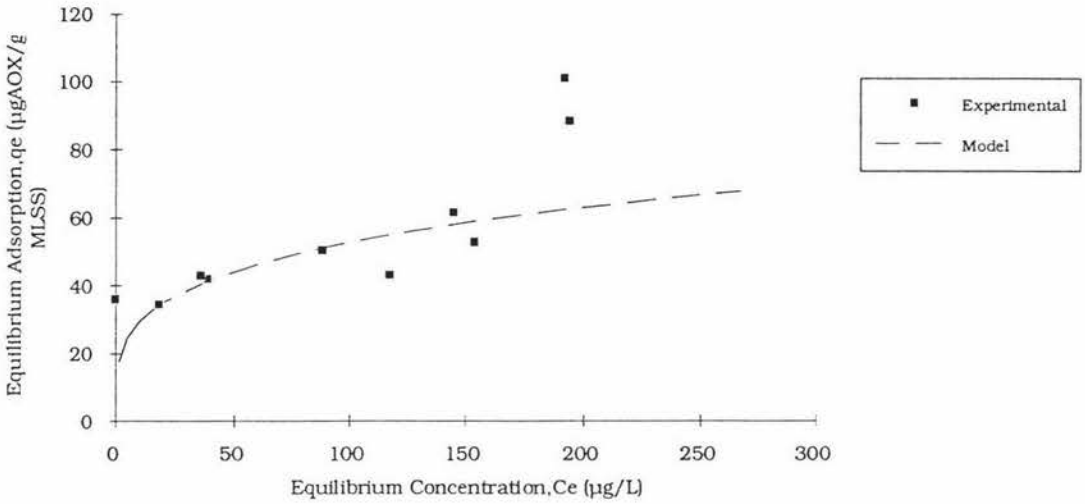


Figure 33: Adsorption Isotherm, Tasman Unfractionated Sample.

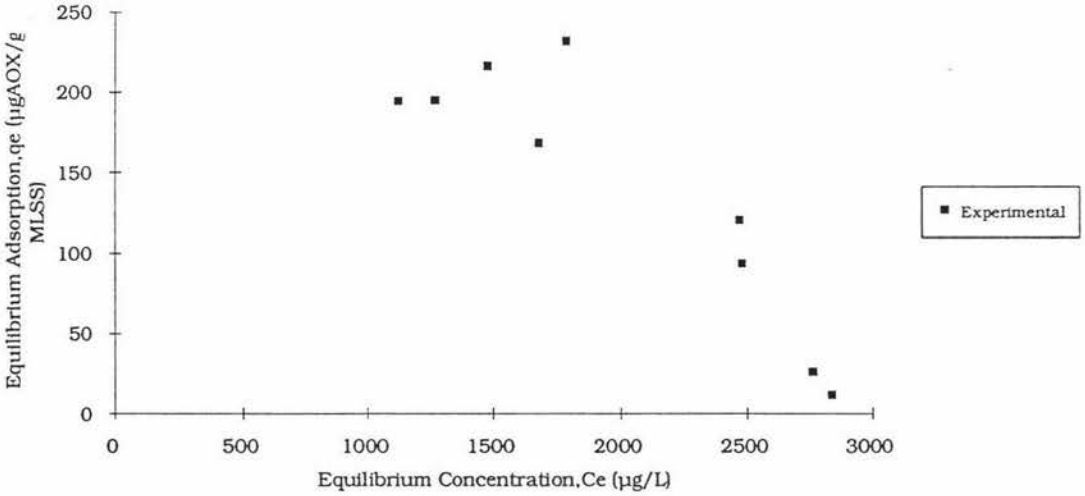


Figure 33b: Adsorption Isotherm, Tasman Unfractionated Sample using Model Co value

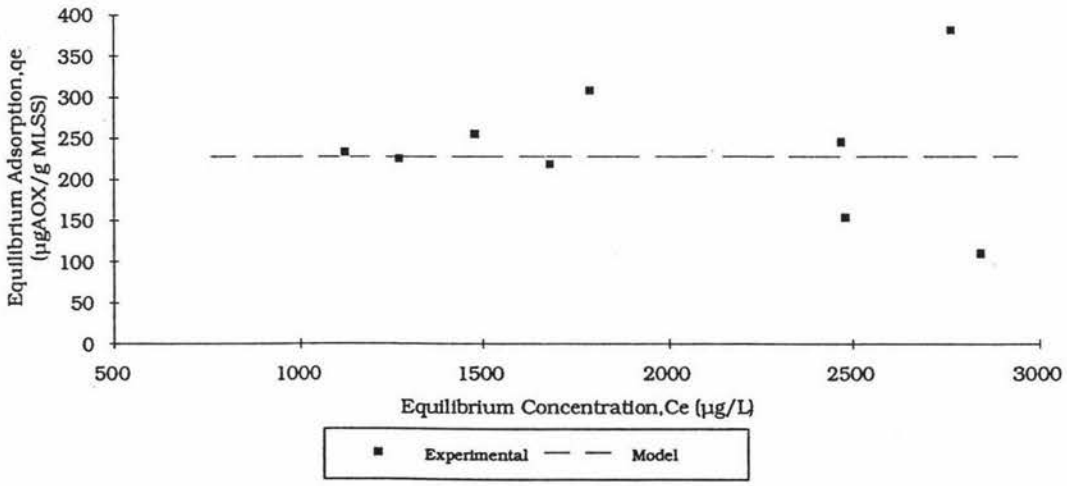


Figure 34: Adsorption Isotherm, Kinleith <2kD Fraction

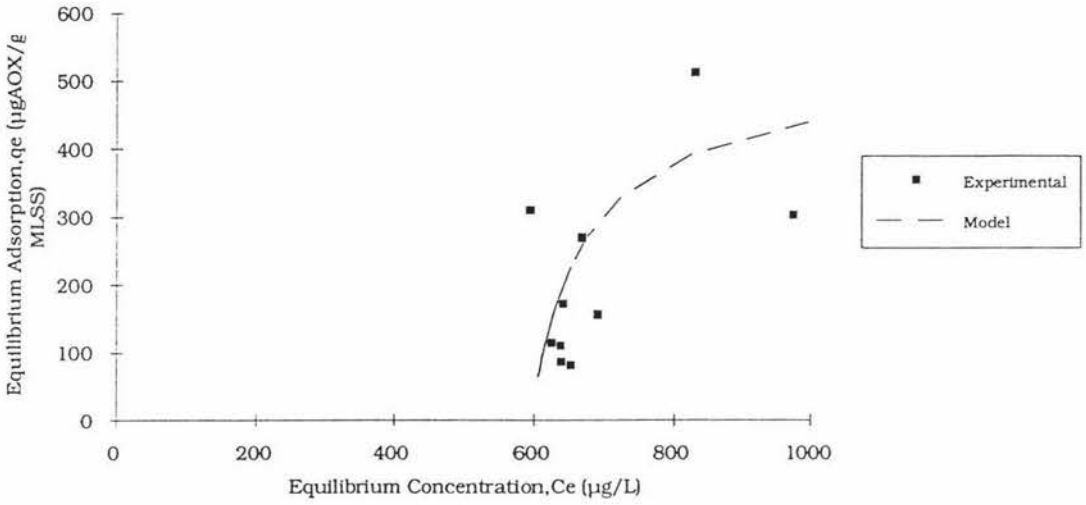


Figure 35: Adsorption Isotherm, Kinleith 2-30kD Fraction

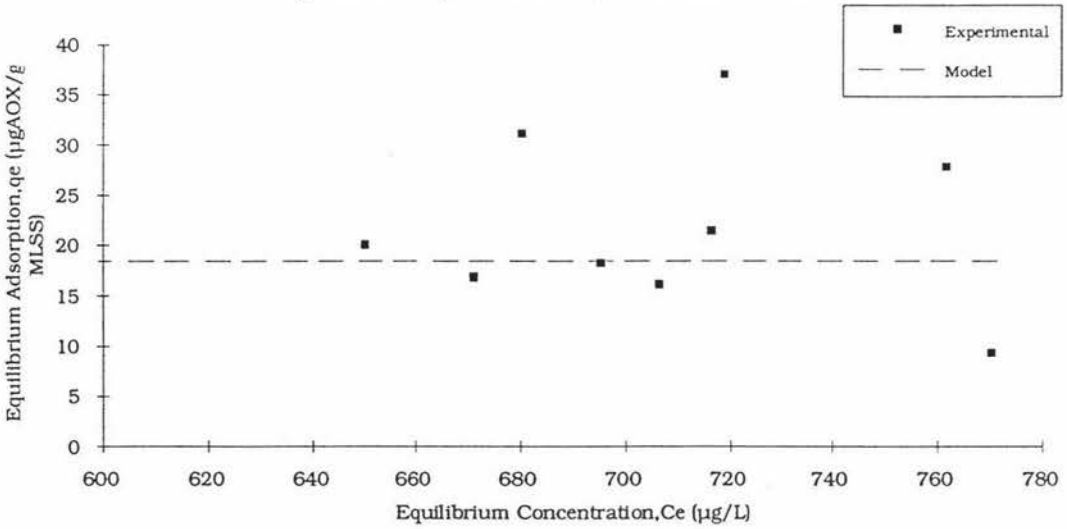


Figure 36: Adsorption Isotherm, Kinleith 30-100kD Fraction.

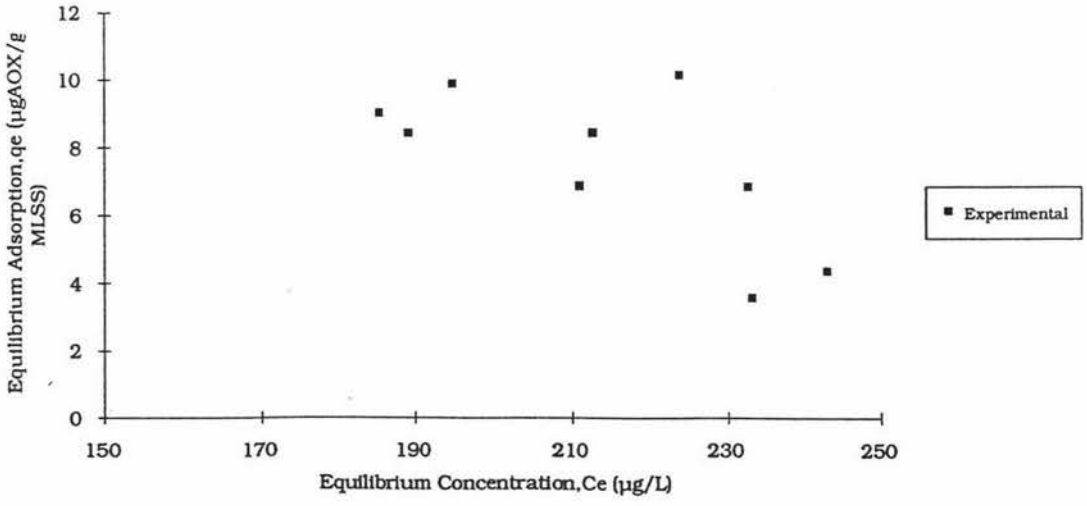


Figure 36b: Adsorption Isotherm, Kinleith 30-100kD Fraction using model Co.

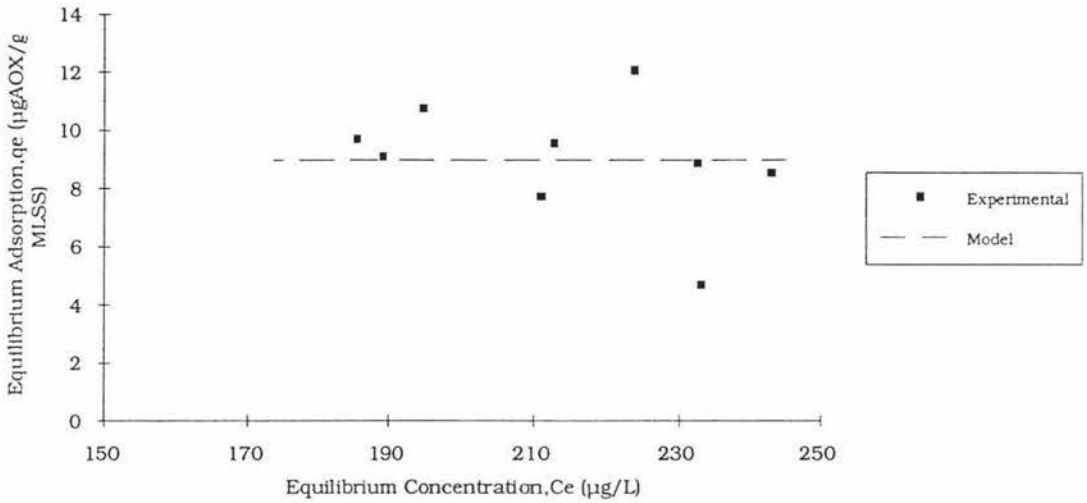


Figure 37: Adsorption Isotherm, Kinleith >100kD Fraction

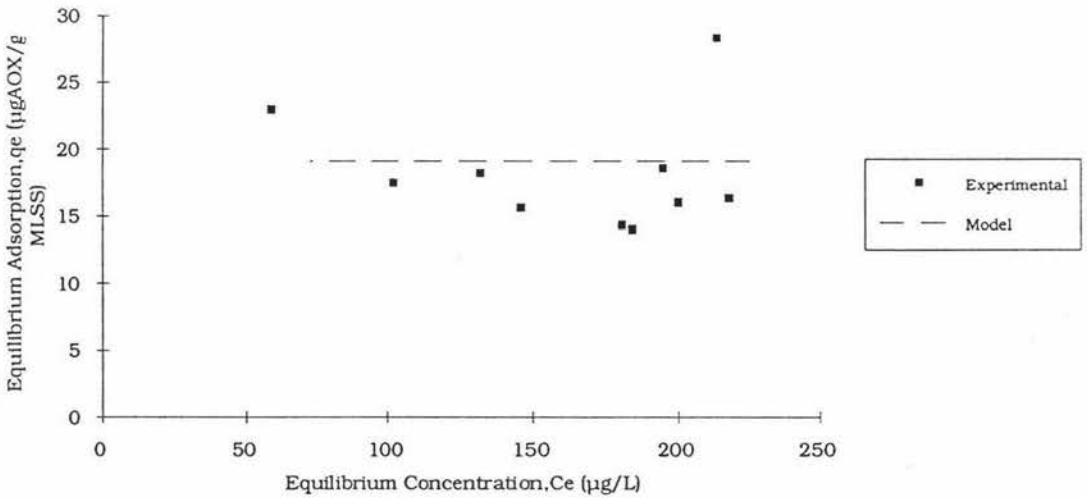
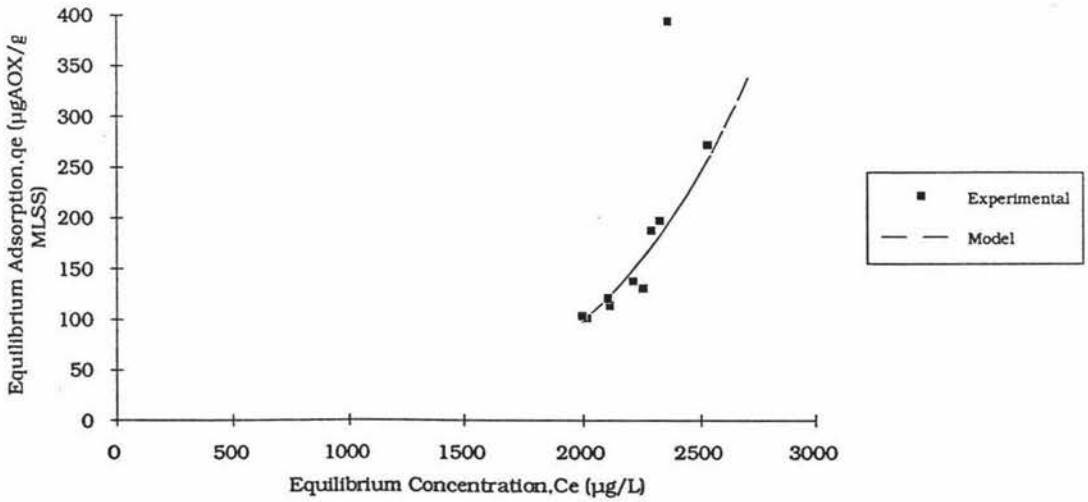


Figure 38: Adsorption Isotherm, Kinleith Unfractionated Sample.



4.5.2. Langmuir Isotherm

The adsorption isotherms were initially fitted to the Langmuir adsorption isotherm. The results of the nonlinear analysis are shown in Table XII.

Table XII: Results of Langmuir Adsorption Isotherm Analysis

	a	b	R^2
Tasman Samples			
<2kD	large	approaching 0	-
2-30kD	large	approaching 0	-
30-100kD	29	0.50	0.93
>100kD	86	0.018	0.96
Unfractionated	180	large	-
Kinleith Samples			
<2kD	large	approaching 0	-
2-30kD	19	large	-
30-100kD	8.0	large	-
>100kD	18	large	-
Unfractionated	large	approaching 0	-

The Langmuir equation

$$q_e = \frac{abC_e}{1+bC_e}$$

indicates that for values of b for which the product b x C_e is small compared with one, the isotherm reduces to

$$q_e = abC_e$$

which is the same form as the linear adsorption isotherm. Therefore for the samples that gave results for the Langmuir parameters a = large, b approaching 0, the Langmuir adsorption isotherm form was rejected.

For cases where the value of b for which the product of b x C_e is large compared with 1, the isotherm reduces to

$$q_e = a$$

which is the same form as the irreversible adsorption isotherm. For samples that gave a large value for b, the irreversible adsorption isotherm was considered as a more appropriate model for the data.

The only samples that appeared to be modelled by the Langmuir isotherm were the Tasman 30-100kD and >100kD samples.

4.5.3. Irreversible Isotherm

Figures 21, 23, 25, 26, and 27 indicate a linear decrease in C_e with increasing solids concentration. This should result in a horizontal line on q_e vs C_e axes when the data are transformed and plotted as an adsorption isotherm (Figures 31, 33, 35, 36, and 37). Such an isotherm is defined as irreversible adsorption (Weber and Smith, 1987), because a constant amount of adsorbate is removed from solution per unit mass of the adsorbent, irrespective of the final equilibrium value of C_e. An irreversible isotherm can be determined by simple linear regression of C_e vs MLSS (mass concentration of biomass in adsorption flask) data. The results of the regression for the Tasman 30-100kD fraction and unfractionated sample, and the Kinleith 2-30kD, 30-100kD and >100kD fractions are summarised in Table XIII.

Table XIII: Results of Irreversible Adsorption Isotherm Analysis

	K_i(µg/g)	R^2
Tasman Samples		
30-100kD	27.8	0.93
Unfractionated	227.9	0.85
Kinleith Samples		
2-30kD	18.4	0.84
30-100kD	8.96	0.90
>100kD	19.1	0.94

From the R^2 values it can be observed that in all cases the fit of the data is adequate. The fit of the Tasman 30-100kD fraction indicates that either the Langmuir or the irreversible isotherm could be used to characterise the adsorption. Because it is the simpler of the two, and can be considered as a reduced form of the Langmuir isotherm (as discussed in Section 4.5.2) the irreversible model was considered to best explain the shape of the isotherm for this fraction.

As discussed in Section 2.7.2.4, an irreversible isotherm may indicate that the biomass surface is saturated with respect to AOX, at all biomass levels used in the experimental work. If this is correct, then the implication for treatment systems with similar concentrations of AOX and comparable MLSS concentrations is that the adsorption capacity of the biomass in the system may become exhausted at low AOX levels, and further addition of AOX via the influent to the treatment system would go through the system without adsorption being a significant removal mechanism.

The values given for K_i in Table XIII are comparable to the values found from the Langmuir analysis (Table XII), indicating good agreement between the two models for the form of the adsorption isotherm for these samples.

Although the Tasman unfractionated and Kinleith 30-100kD samples fitted irreversible type isotherms, Figures 33 and 36 reveal that the loading of AOX onto the biomass appeared to decrease as the equilibrium concentration in the liquid increased. The adsorption isotherm results show marked deviation from those predicted by the irreversible isotherm. This deviation may be accounted for by consideration of the nature of the variable q_e. For a particular adsorbate, q_e is proportional to the difference between the initial and the equilibrium effluent concentration of a shake flask. In this experimental work, the level of AOX adsorbed at the low solids concentrations is small relative to the total amount of AOX present in the system. Because of this, the q_e values obtained are subject to large relative errors, and small variations in the measured AOX levels result in widely different q_e values. In an attempt to overcome this difficulty, the adsorption models for all samples were determined using the true dependent and independent variables, C_e and MLSS respectively, rather than using q_e as the dependent variable. In defining the adsorption isotherms for the Tasman unfractionated sample and the Kinleith 30-100kD fraction, the predicted models gave a result for the initial AOX level, C_o, that was larger than the average value of C_o found by experimental measurement. This discrepancy was assumed to be the result of experimental errors in the measurement of the AOX concentrations. As discussed above, the effect of such errors on the q_e

values was to give an erroneous indication of the isothermal behaviour of the two samples. Replacing the experimental C_0 with the predicted value made the adsorption isotherm plots for these two samples fit much better with the predicted isothermal behaviour. Therefore, in the description of the adsorption isotherm of these samples, C_0 was altered from the experimental value to that which was predicted by the irreversible type model. Because the isotherm models themselves were determined using only the experimental data, this replacement did not affect the model parameter estimation, merely the form of any experimental plots using parameters that involved C_0. Comparison of the experimental data with the modelled adsorption isotherms for the Tasman unfractionated and Kinleith 30-100kD samples is given in Figures 33b and 36b, respectively.

4.5.4. Freundlich Isotherm

For the samples that did not display a linear decrease in C_e with increasing solids concentration (Figures 19, 20, 22, 24, 28), the Freundlich adsorption isotherm was fitted to the data, and the resulting constants K_f and 1/n are shown in Table XIV.

Table XIV: Results of Freundlich Adsorption Isotherm Analysis

	K_f	1/n	Units of K_f	R^2
Tasman Samples				
<2kD	6.18*10-13	4.97	$L^{4.97}\mu g^{-3.97} g^{-1}$	0.93
2-30kD	2.56*10-13	4.93	$L^{4.93}\mu g^{-3.93} g^{-1}$	0.96
>100kD	16.3	0.255	$L^{0.255}\mu g^{0.745} g^{-1}$	0.97
Kinleith Samples				
<2kD	0.0623	1.19	$L^{1.19}\mu g^{-0.19} g^{-1}$	0.81
Unfractionated	4.25*10-12	4.05	$L^{4.05}\mu g^{-3.05} g^{-1}$	0.96

From the fit of the model to the C_e vs MLSS data, it was considered that the fractions that underwent adsorption that was adequately described by a typical Freundlich isotherm were the Tasman <2kD and 2-30kD fractions, the Tasman >100kD fraction, and the Kinleith unfractionated wastewater. The Freundlich isotherm described slightly more of the variation than the Langmuir isotherm for the Tasman >100kD fraction, and was thus used to define the adsorptive behaviour of this fraction. The Kinleith <2kD fraction gave a poor fit to the Freundlich isotherm (Figure 24) and its adsorptive behaviour is discussed in Section 4.5.5.

The modelled adsorption isotherms for the fractions fitted to the Freundlich adsorption isotherm are shown in Figures 29, 30, 32, and 38.

4.5.5. Kinleith <2kD Fraction

Figure 24 shows that the Kinleith <2kD fraction did not yield a very good fit to the Freundlich isotherm. As is apparent from this Figure, the isotherm does not follow the linear decrease in C_e with increasing solids concentration that is indicative of an irreversible isotherm. One feature of the data represented in Figure 24 is that the AOX concentration in the liquid decreases to a minimum value at a solids concentration of approximately 2g/L, beyond which there is no significant reduction in AOX concentration despite the increasing number of sites available for adsorption due to higher biomass loadings. This indicates that a significant portion of the Kinleith <2kD fraction AOX may be non-adsorbable. Upon observing an apparently non-adsorbable residual organic concentration in the adsorption of chloroethanes onto microbial biomass, Tsezos and Seto (1986) modified the Freundlich and Langmuir isotherms to account for this residual. The equations used were of the form:

$$q_e = K_f(C_e - C_{emin})^{1/n}$$

for the modified Freundlich isotherm, and

$$q_e = \frac{ab(C_e - C_{emin})}{1+(C_e - C_{emin})}$$

for the modified Langmuir isotherm.

C_{emin} was defined as the residual solution concentration.

The Kinleith <2kD fraction adsorption data were fitted to these modified isotherms, with C_{emin} being set at a best estimate of the residual non adsorbable concentration. Nonlinear least squares routines were used to determine the fit of the models and these are given in Appendix A2.

C_{emin} could not be measured directly, and was therefore estimated as being 595 µg/L, a concentration just below the minimum C_e level recorded in the adsorption

experiments for this sample.

The modified Langmuir isotherm fitted the data well, returning an R^2 value of 96% on the C_e vs MLSS data, with the following parameter values

a = 520
b = 0.013

The modified Freundlich isotherm did not fit the data, with the nonlinear regression not converging at any pairing of positive K_f and 1/n values.

The modified Langmuir isotherm was therefore considered as most suitably describing the Kinleith <2 kD fraction adsorption, and was used to describe the adsorptive behaviour of the AOX in this fraction. The plot of this modelled adsorption isotherm is given in Figure 34.

4.5.6. Summary of the Adsorption Isotherms

Table XV gives a summary of the adsorption isotherms that were considered most appropriate for each fraction, and for the unfractionated samples, of the two mills' wastewaters.

Table XV: Adsorption Isotherm model for bleach plant AOX

Sample Fraction Molecular Weight	Tasman	Kinleith
<2 kD	Freundlich	Modified Langmuir
2-30 kD	Freundlich	Irreversible
30-100 kD	Irreversible	Irreversible
>100 kD	Freundlich	Irreversible
Unfractionated Sample	Irreversible	Freundlich

From Table XV it is clear that no one isotherm was capable of accurately predicting the adsorption of the AOX in the different samples onto biological solids, either between the different molecular weight fractions from the same mill's wastewater, or for the same molecular weight fractions between the two mills. This indicates that

significant differences occurred between the adsorption processes of the fractions.

Comparison of the adsorption characteristics between and within mill samples is given in the following sections:

4.6. COMPARISON OF ADSORPTION CHARACTERISTICS BETWEEN MILLS

4.6.1. Introduction

In order to enable a comparison of the adsorption occurring for each molecular weight fraction of the different mills, the results obtained were plotted on three types of axes:

1) C_e vs MLSS;
2) Relative Adsorption vs MLSS;
3) Adsorption isotherm axes.

These are shown in Figures 39-53. The abbreviations T and K in the legends refer to the Tasman and Kinleith samples repectively.

4.6.2. <2kD Fractions

The plots comparing the adsorption of the two <2kD fractions are given in Figures 39-41.

Although the <2kD fractions appear to follow a similar adsorption pattern (Figure 39), Figure 41 shows the difference in adsorption isotherms between the two. The Freundlich isotherm is able to be fitted to the Tasman data but not to the Kinleith data (Table XIV and Figure 24), as the latter fraction reaches an effluent AOX concentration C_{emin} below which no further adsorption takes place. That is, a non adsorbable fraction appears to exist. The modified Langmuir adsorption isotherm, discussed in Section 4.5.5, adequately fits the Kinleith fraction's data.

This non adsorbable fraction could be defined in terms of the Freundlich equation, with the constant 1/n taking on a value that approaches infinity. The constant n can be used as an indicator of the intensity of the adsorption, and a large 1/n value signifies that the intensity of adsorption is therefore approaching zero, resulting in minimal adsorption taking place.

There are very few data from the literature with which to compare the adsorption isotherms obtained for any of the AOX samples analysed. Amy *et al.*, (1988) carried out isotherm studies using AOX with molecular weight less than 1000 Daltons, using only three data points, and did not specify the value of the Freundlich constants. No indication of the pulp bleaching conditions, from which the effluents used in the experiments were derived from, was given by the authors. Tentative analysis of the data from the graphs given in Amy *et al.*, (1988) revealed that 1/n was approximately 9 for adsorption onto biomass cells from a bench scale bioreactor with a 1 day mean cell residence time (MCRT), and 17 for the experiment using biomass with a 10 day MCRT. These values are much higher than the 1/n values found for the Tasman <2kD fraction in the present work, but they do support the observation that 1/n is significantly greater than unity for low molecular weight AOX adsorption onto biomass, and the large values of 1/n give some credence to the result found for the Kinleith effluent.

Figure 39: Adsorption of <2kD Fractions

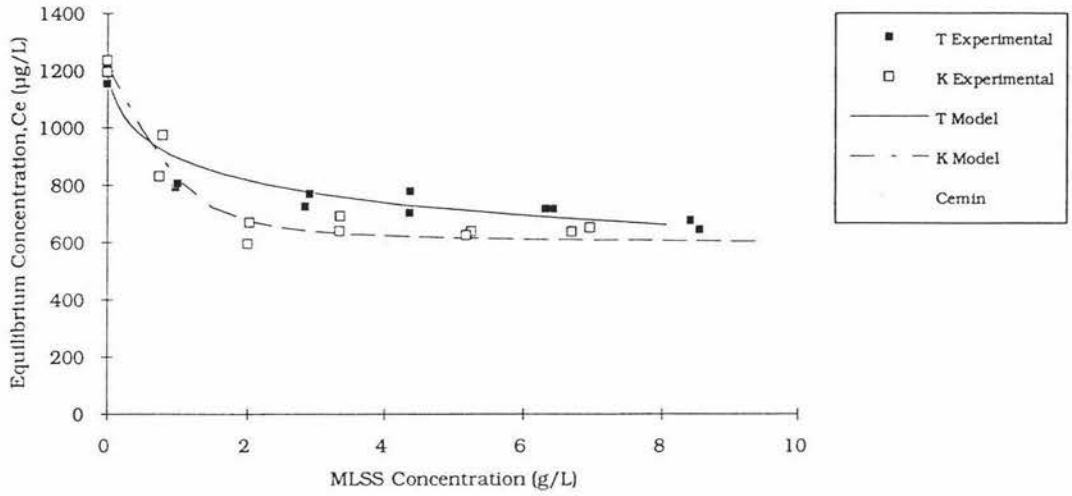


Figure 40: Relative Adsorption of <2kD Fractions.

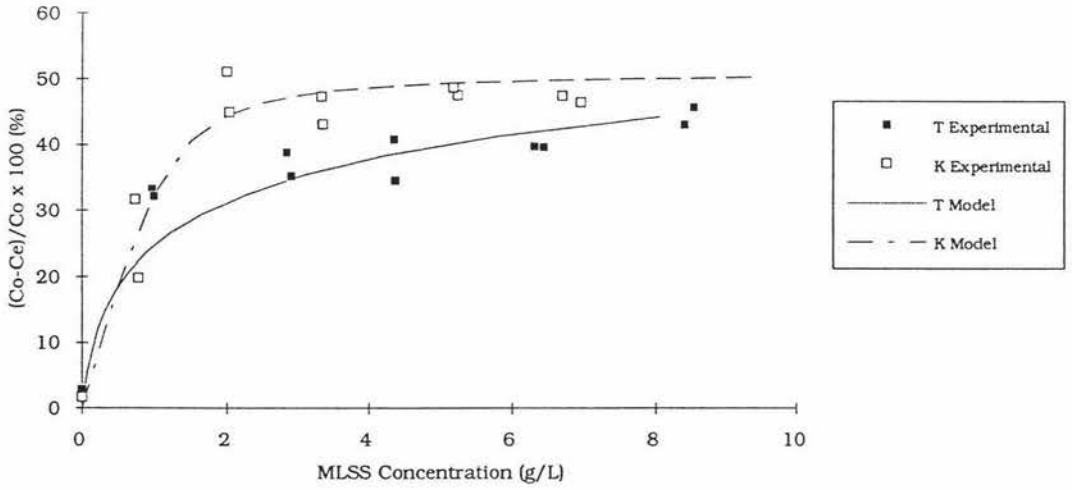


Figure 41: Adsorption Isotherm, <2kD Fractions

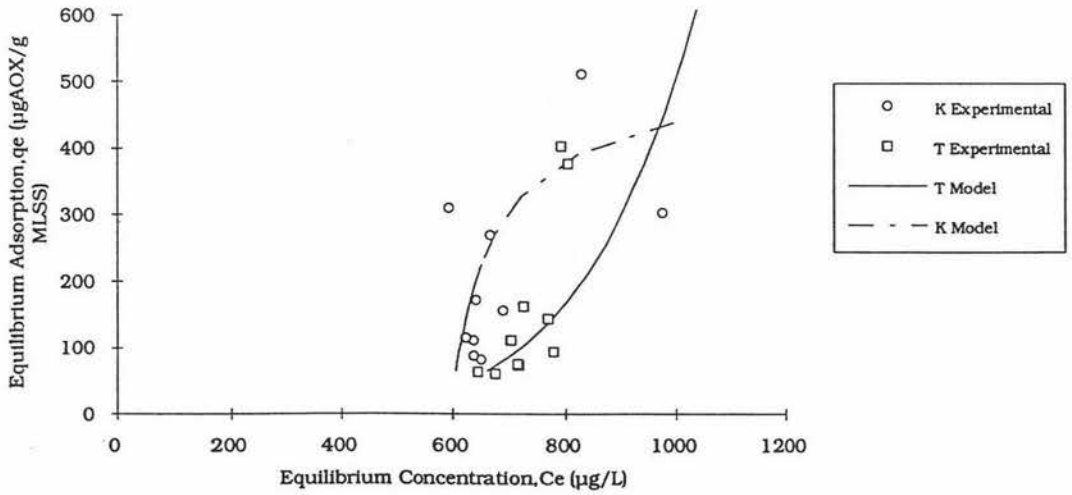


Figure 40 shows the relative adsorption of the <2kD fractions at the various MLSS levels used in the experiments. The relative adsorption is defined for a particular sample as being the reduction in liquid phase AOX due to the adsorption process, expressed as a percentage fraction of the initial AOX present prior to addition of the biomass. Over the MLSS ranges analysed the Kinleith sample showed a slightly higher overall relative adsorption, but this was observed to have reached a maximum value at 2g/L MLSS of approximately 50%, beyond which increases in MLSS had no impact on removal of AOX. This indicates that over half of the total AOX in this molecular weight range was not adsorbable under the experimental conditions.

The Tasman <2kD fraction also showed an initial sharp increase in relative adsorption at the low biomass levels with the uptake rate decreasing after 1g/L MLSS, but still showing removal of AOX at higher biomass levels. This effect is characteristic of a sample portraying typical Freundlich type isotherm behaviour.

Amy *et al.*, (1988) hypothesised that molecules of small enough molecular size could theoretically be transported into the biological cell material, rather than merely adsorbing on the surface. Wang *et al.*, (1993) also proposed that the mechanism of sorption on wastewater solids is a combination of adsorption to the surface of the solid and subsequent partitioning into the cell interior. Tsezos and Bell (1989) found that sorption of pesticides onto activated sludge and a fungal microorganism involved not only adsorption onto cell wall material, but also uptake by other cellular components of the microorganisms, indicating some movement of the molecules through the cell wall into the intracellular material. Therefore it would appear to be reasonable that a portion of AOX in the <2kD fractions of the wastewaters studied would have the capability of being absorbed into the cell material.

The <2kD fraction can therefore be considered as consisting of two portions; the first of molecular size such that the molecules in the portion could be transported into the cell interior, and the second portion with molecular size too large to be capable of intracellular transport. This can be postulated as accounting for the difference in the adsorptive uptakes of these two samples. Yin *et al.*, (1990) showed that the average molecular weight of chlorolignins from a modern OD/CED bleach plant is lower than those from a conventional CEDED sequence. If this trend were observed within the <2kD fraction, that is, if this modern bleach sequence's fraction had an average molecular weight that was lower than that of the conventional sequence, then the proportion of material of such a size that it could pass into the cell material should be greater for the modern sequence. The Kinleith fraction (modern bleach sequence)

should therefore exhibit greater removal of AOX at the lower biomass levels, as more material in this mill's fraction is capable of transport into the cell interior. Figures 39 and 40 shows that this is the case for MLSS concentrations below 2g/L.

At higher MLSS concentrations, the only additional removal of AOX to that observed at lower biomass levels would be that carried out by adsorption of the portion unable to pass into the cell material. The adsorption observed at MLSS concentrations above 2g/L (Figure 39) indicates that the Tasman fraction displays greater adsorption affinity than the Kinleith fraction AOX.

It is recommended that further work be carried out to determine the validity of the hypothesis that the AOX in the <2kD fraction undergoes both adsorption onto the surface of the biological cell, and, if the molecule is of small enough size, absorption into the interior of the cell. Analysis of the <2kD fractions of wastewaters from the two types of bleach sequence should also be carried out to verify whether a modern bleach sequence yields a greater proportion of AOX capable of being absorbed into the cell interior.

4.6.3. 2-30kD Fractions

The plots comparing the adsorption of the two 2-30kD fractions are given in Figures 42-44.

The AOX fraction adsorption behaviour of the Tasman mill fraction followed a Freundlich isotherm with parameters similar to the <2kD fraction, as can be seen from Table XIV. The Kinleith mill fraction was less amenable to fitting to a standard isotherm. The best fit for this fraction was an irreversible isotherm. This implies that, unlike the Tasman fraction, the initial AOX and biomass concentrations of the biological treatment systems are not significant in affecting the equilibrium AOX loading of the Kinleith 2-30kD fraction.

Figure 42 indicates that, overall, the samples from both mills displayed very similar equilibrium concentrations of AOX at the various biomass levels, suggesting little difference in adsorptive behaviour between the two, despite the different isotherm forms fitted to the experimental data.

Figure 42: Adsorption of 2-30kD Fractions.

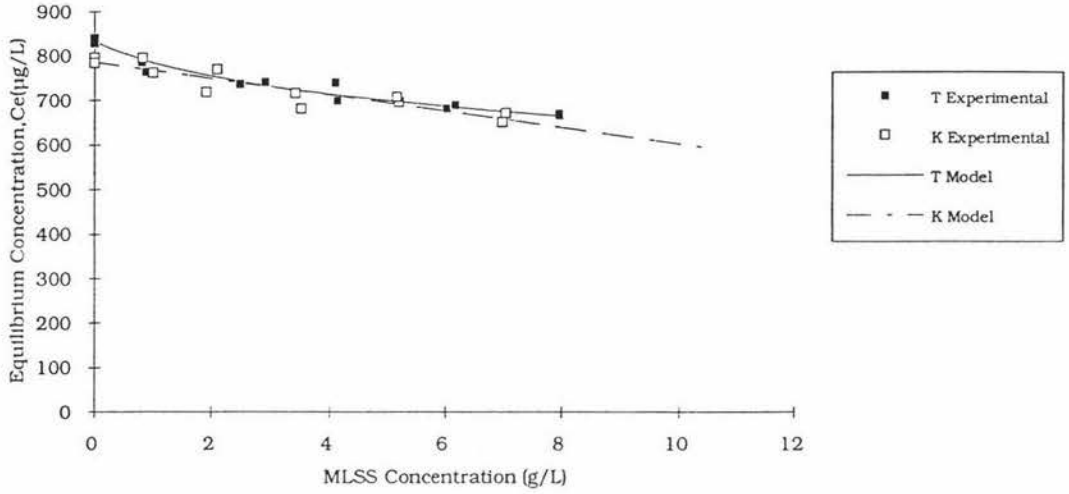


Figure 43: Relative Adsorption of 2-30kD Fractions.

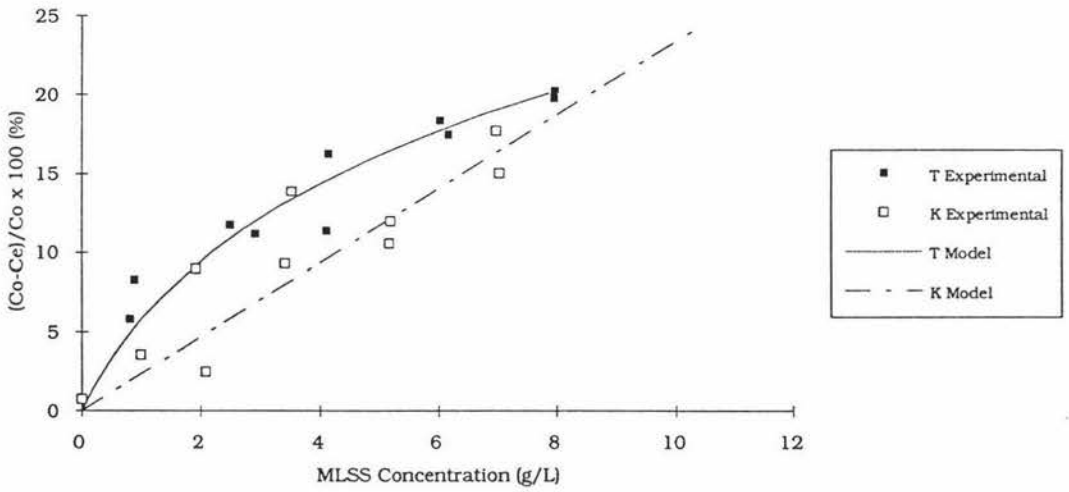
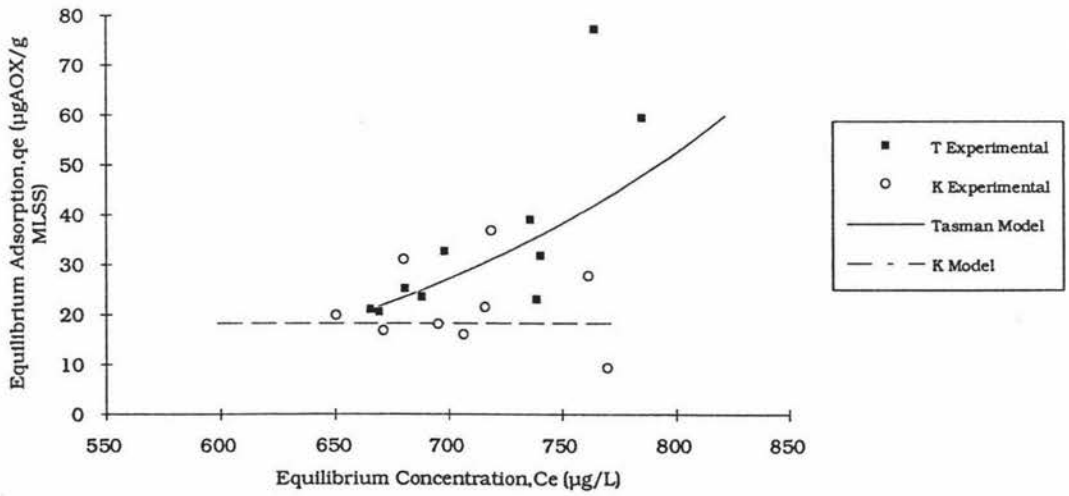


Figure 44: Adsorption Isotherm, 2-30kD Fractions.



The relative adsorptions of the two samples, shown in Figure 43, reveal that the 2-30kD fraction was very poorly adsorbed onto biomass, with less than 25% being removed at the highest recorded biomass levels. The Tasman sample displayed a slightly higher uptake over the entire solids concentration range, suggesting that this sample had a greater adsorption affinity. This is more clearly seen in Figure 44, with the adsorption isotherm of the Tasman sample indicating a higher biomass loading of AOX, q_e, than the Kinleith sample.

4.6.4. 30-100kD Fractions

The plots comparing the adsorption of the two 30-100kD fractions are given in Figures 45-47.

Figures 45 and 47 reveal that both 30-100kD fractions fit irreversible type adsorption patterns. The values obtained for Ki, 27.8 and 8.95 for the Tasman and Kinleith fractions respectively, reveal that the Tasman permeate underwent greater adsorption per unit of biomass weight than the fraction from the Kinleith mill. This can also be determined from the relative adsorption of the two samples, shown in Figure 46, revealing that the uptake for the Tasman sample was greater than for the Kinleith mill. This suggests that the Tasman 30-100kD fraction had a higher affinity for the biomass than the same fraction from the Kinleith mill.

4.6.5. >100kD Fractions

The plots comparing the adsorption of the two >100kD fractions are given in Figures 48-50.

The C_e vs MLSS and relative adsorption plots for the >100kD fractions are shown in Figures 48 and 49 respectively. The trend for these graphs is similar to those found for the 30-100kD fractions. That is, the Tasman sample showed significantly higher uptake than the sample fractionated from the Kinleith bleach effluent.

Figure 50 shows the fit of the adsorption isotherms assigned to the >100kD fraction samples. The Tasman data fitted a typical Freundlich isotherm form while the Kinleith data were consistent with an irreversible isotherm. At all MLSS concentrations, the AOX loading of the Kinleith sample onto the biomass of 19µg/g, as determined by the constant K_i, was lower than the loadings of the Tasman sample. This indicates lower adsorption affinity of the Kinleith AOX sample onto the biomass.

Figure 45: Adsorption of 30-100kD Fractions.

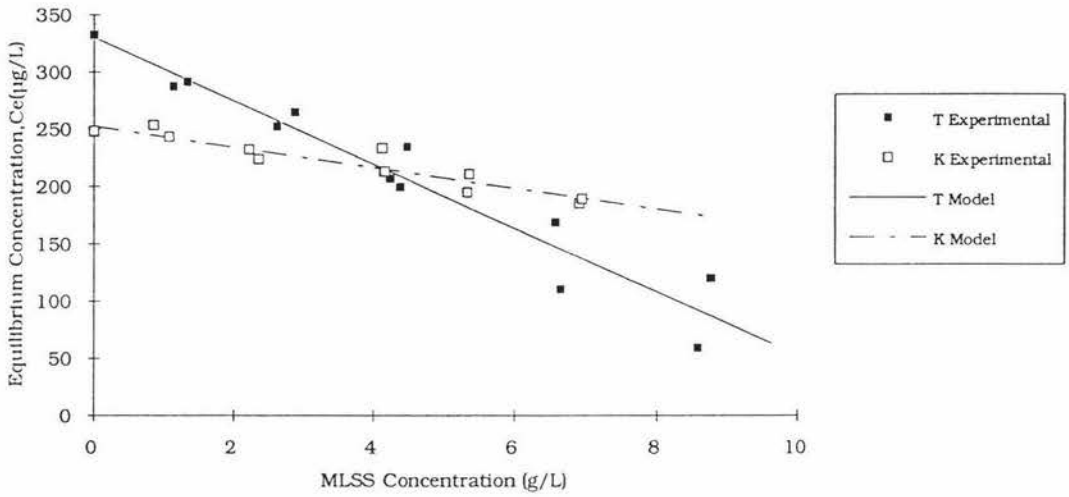


Figure 46: Relative Adsorption of 30-100kD Fractions.

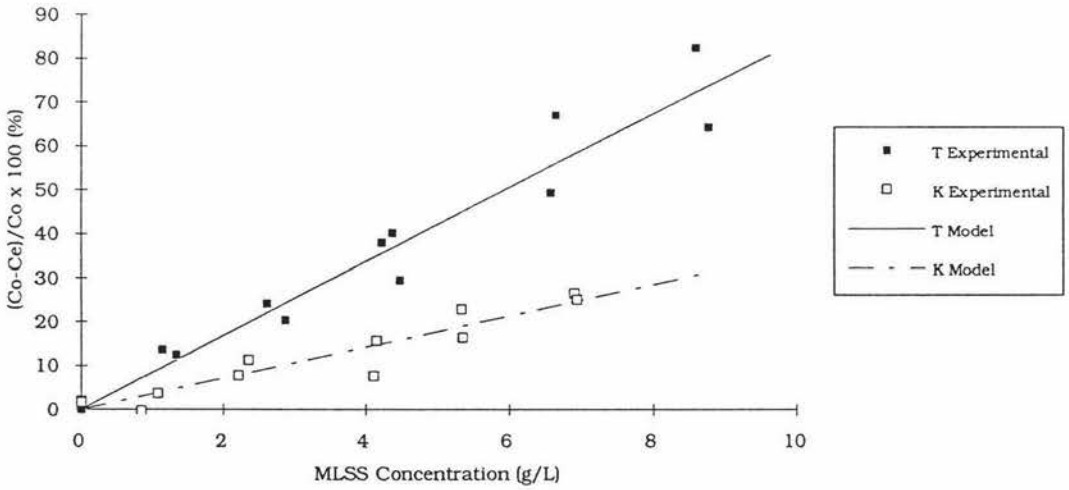


Figure 47: Adsorption Isotherm, 30-100kD Fractions

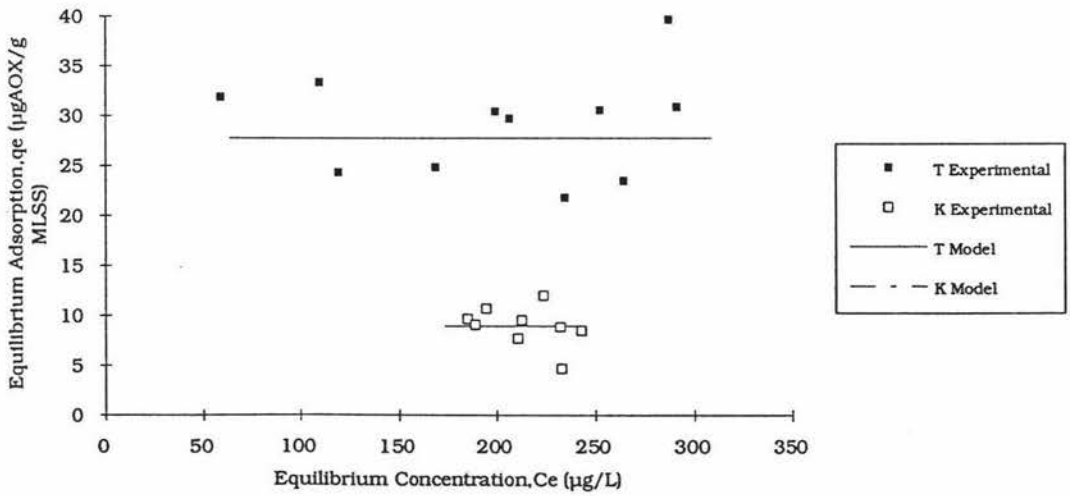


Figure 48: Adsorption of >100kD Fractions.

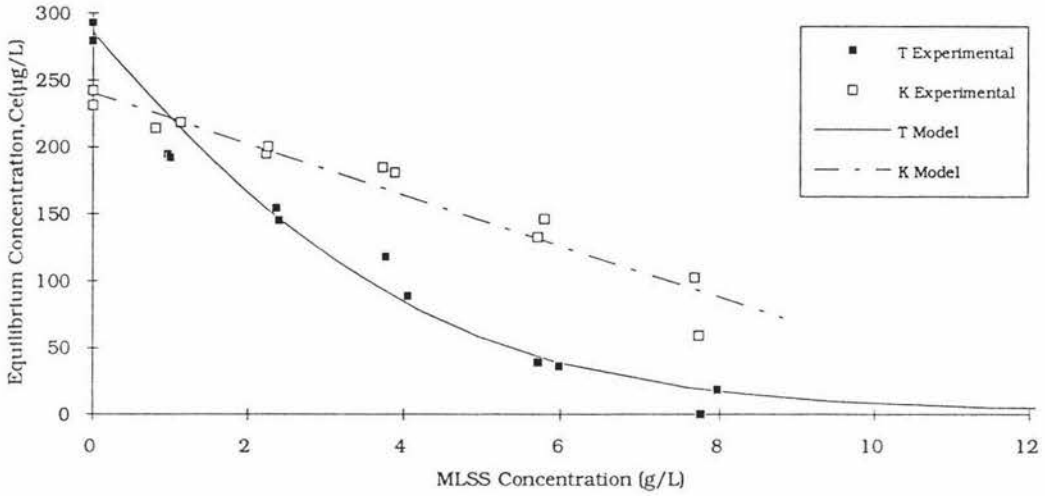


Figure 49: Relative Adsorption of >100kD Fractions.

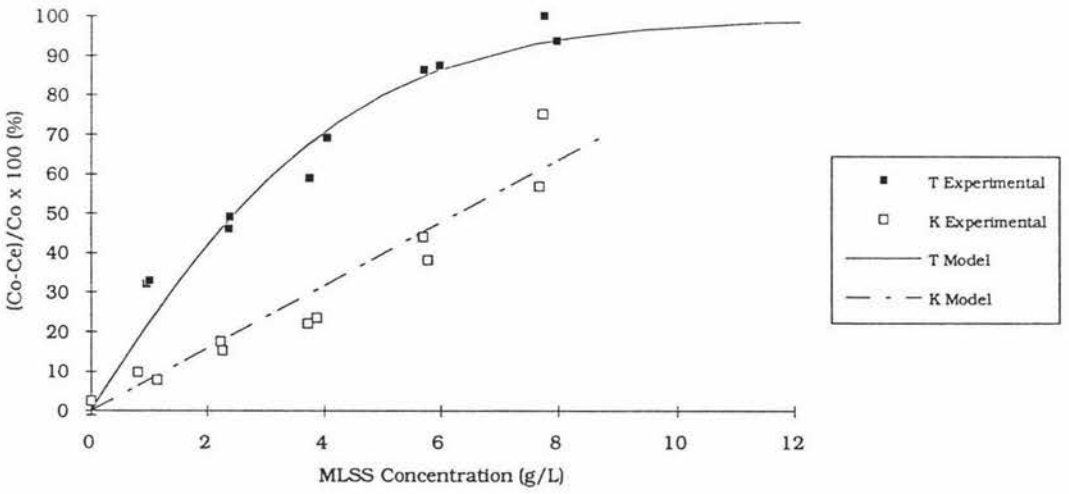
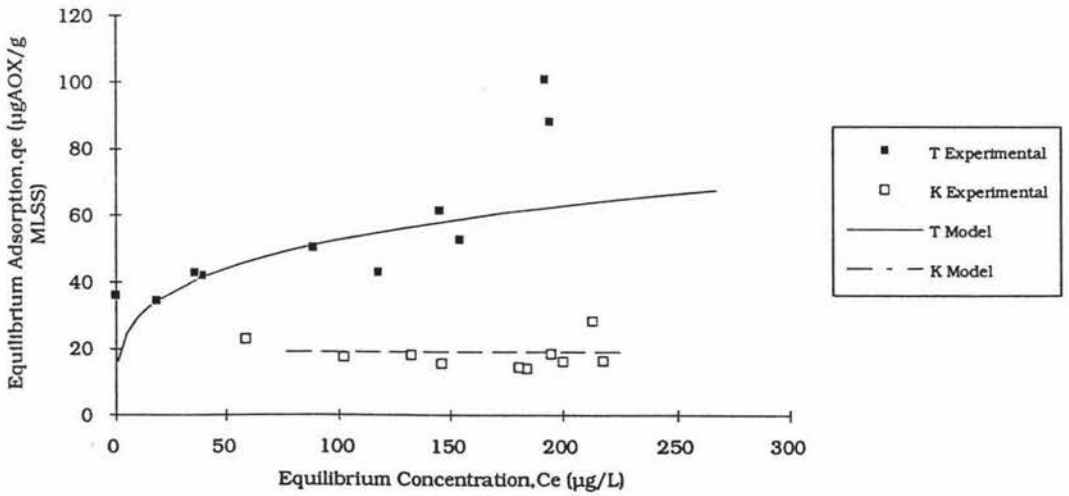


Figure 50: Adsorption Isotherm, >100kD Fractions



4.6.6. Unfractionated Samples

In comparing the adsorption of the unfractionated wastewaters, Figures 51-53 indicate the behaviour of the two mill samples.

The adsorption of the Kinleith sample follows a Freundlich isotherm, with parameters summarised in Table XIV. The difference between the isotherm for this sample and for the Tasman unfractionated wastewater, which follows irreversible type adsorption behaviour, may be attributed to differences in the proportions of the molecular weight fractions, as shown in Figure 15, and also the chlorination levels of the organics.

The adsorption isotherm of the Tasman sample would be significantly affected by the high molecular weight fraction material, with 23% of the total AOX being greater than 30kD. Bryant *et al.*, (1987) analysed the ratios of organic halide (measured as TOX) to organic carbon (measured as TOC) in a pulp and paper wastewater. Their results are shown in Table XVI.

Table XVI: Average Ratios of TOX/TOC of Kraft Mill Wastewater (Bryant *et al.*, 1987)

Sample Fraction	TOX/TOC Ratio
>0.5kD	0.073
0.5-1kD	0.590
1-5kD	0.387
5-10kD	0.280
10-30kD	0.383
>30kD	0.197
Unfractionated	0.191

Apart from the smallest molecular weight fraction, whose TOX/TOC ratio suggests the presence of significant amounts of non-chlorinated compounds such as methanol, the TOX/TOC ratios indicate that the organic molecules are chlorinated to a lesser extent as the molecular weight increases. McFarlane *et al.*, (1991) suggested that higher molecular weight molecules would have a greater affinity for adsorption onto biomass than those of lower molecular weight, due to their greater hydrophobicity and lipophilicity. From the work on the rates of adsorption (Section 4.4) the high molecular weight material was found to adsorb at a faster rate than the low molecular weight fraction, also indicating the former's higher affinity for adsorption.

Figure 51: Adsorption of Unfractionated Samples.

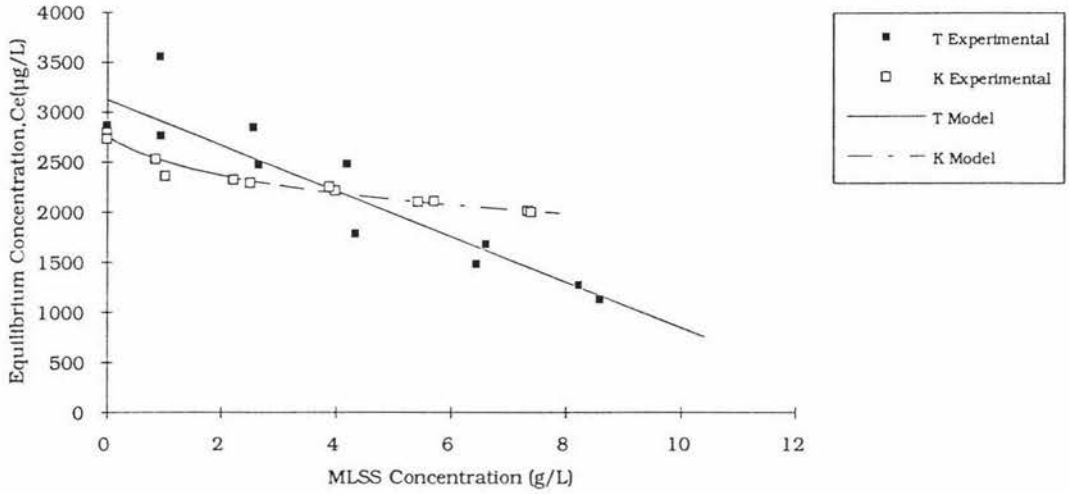


Figure 52: Relative Adsorption of Unfractionated Samples.

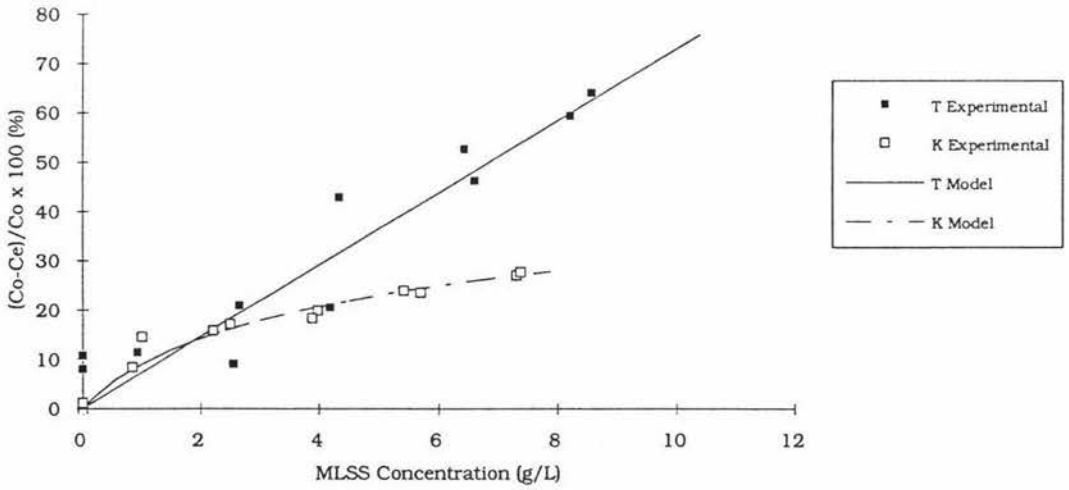
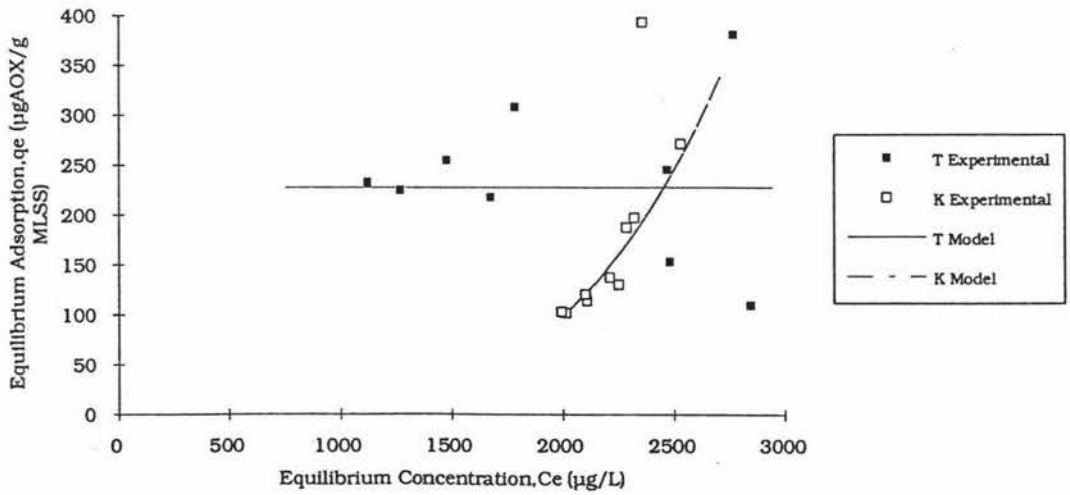


Figure 53: Adsorption Isotherm, Unfractionated Samples



These guidelines suggest that high molecular weight material should be preferentially adsorbed onto the biomass. Figure 53 implies that at high C_e (low biomass) levels, the adsorption of the Kinleith wastewater higher than Tasman's. This lower uptake of the Tasman sample at the low biomass levels may be attributed to the effect of preferential adsorption of high molecular weight material. At low biomass levels the competition for adsorption sites is most intense, and preferential adsorption of high molecular weight molecules is expected reduce the adsorption of AOX, due to the lower chlorination levels of high molecular weight material. This effect should be greater for the Tasman wastewater, as it has significantly higher proportions of high molecular weight material in the unfractionated sample, thus reducing the adsorption of Tasman's unfractionated sample relative to Kinleith's.

At higher biomass concentrations, less competition for adsorption sites should occur and the effect of preferential adsorption reduced. Under such conditions, in comparing the adsorption of AOX from two samples, that with higher average molecular weight should show greater adsorption. This behaviour can be observed in the comparison of the unfractionated wastewaters, with the Tasman sample AOX being adsorbed to a greater extent than the Kinleith AOX, as the biomass concentration increased (Figures 52, 53).

4.6.7. Overall Comparison of Adsorptive Behaviour Between the Two Mill's Effluents

The comparison of the ultrafiltered fractions reveals that, for all but the <2kD fraction, the Tasman samples show higher affinity for the biomass than the Kinleith samples. This result is most significant for the fractions greater than 30kD. This is most clearly seen from the plots of the relative adsorptions, Figures 40, 43, 46, 49, and 52. Valtilla (1991), showed that increasing the chlorine dioxide substitution in a bleaching sequence results in a decrease in the average AOX/TOC ratio in the different molecular weight fractions of bleaching wastewaters. From this it is reasonable to assume that the Tasman bleach plant wastewaters contain molecules that are chlorinated to a greater extent than those from the Kinleith mill. McFarlane *et al.*, (1991), in reviewing literature on the adsorption of chlorinated organic material, found that increasing the extent of chlorine substitution in a molecule increases its lipophilicity, and hence should increase its affinity for adsorption onto biological solids. Under the assumption that the organic fractions from the Kinleith mill would be chlorinated to a lesser extent than those from the Tasman mill, due to

the use of chlorine dioxide in the former's bleaching sequence (Valtilla, 1991), the Kinleith wastewater fractions are therefore predicted to adsorb to a lesser extent than the same molecular weight fractions from the conventional Tasman bleach plant wastewaters. The results of these adsorption experiments therefore reinforce the prediction that the higher the chlorination level of a molecule, the more effectively it is removed by adsorption onto biomass.

The <2kD sample fractions displayed different behaviour, with the Kinleith sample exhibiting higher relative adsorption than the Tasman sample, over the range of biomass concentrations used in the experiment. The Kinleith sample also revealed behaviour indicative of a non adsorbable fraction within the sample AOX. Because of the differences in behaviour of this fraction, the possibility exists of an AOX removal mechanism for the low molecular weight fraction that is different to that of the other samples, as discussed in Section 4.6.2.

4.7. COMPARISON OF ADSORPTION CHARACTERISTICS: WITHIN MILL SAMPLES

4.7.1. Tasman

Figures 54 to 56 allow comparison of the adsorptive characteristics of the Tasman wastewater samples.

The adsorption isotherms of all Tasman fractions are given in Figure 54. The two lowest molecular weight fractions from this mill behave in a similar manner, as the calculated values of K_f and 1/n Freundlich constants reveal (Table XIV). The <2kD and 2-30 kD fractions' adsorption isotherms suggest that the interactions of the molecules with the biomass are similar for both fractions. This reinforces the speculation made in the rejection coefficient analysis, Section 4.2.3, that a large proportion of the 2-30kD fraction has a molecular weight close to the 2,000 MWCO of the UM2 ultrafiltration membrane.

The >100kD fraction also exhibited Freundlich isotherm behaviour, with a calculated 1/n, shown in Table XIV, that was significantly smaller than for the lower molecular weight fractions. The trend in 1/n values from smallest to largest molecular weight fractions indicates increasing intensity of adsorption with increasing molecular weight.

Figure 54: Adsorption Isotherm, Tasman Samples

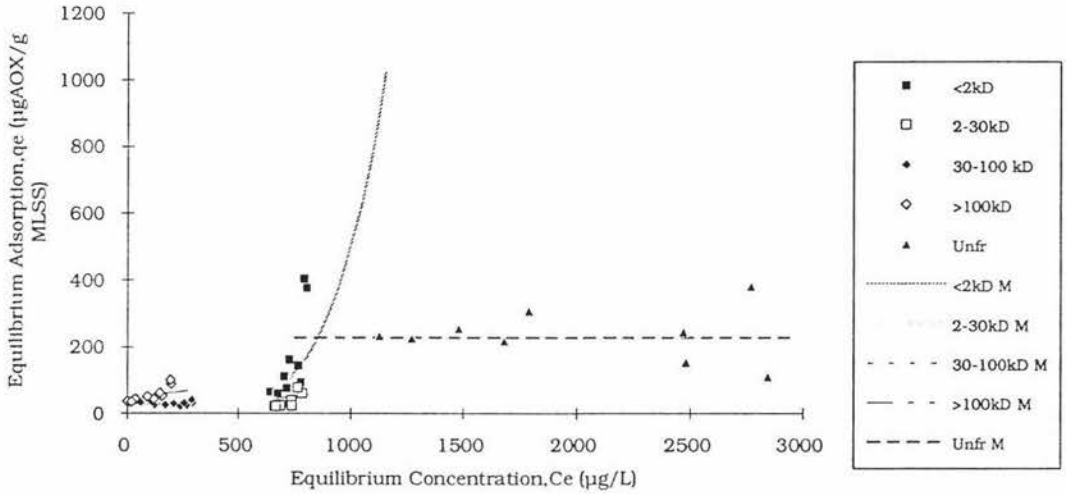


Figure 55: Relative Adsorption of Tasman Samples.

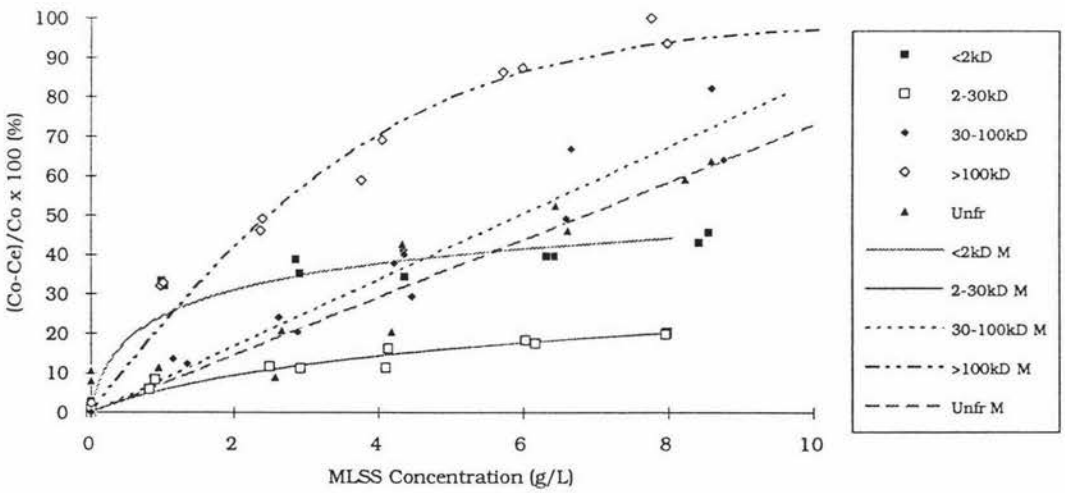


Figure 56: Adsorption of Tasman Samples.

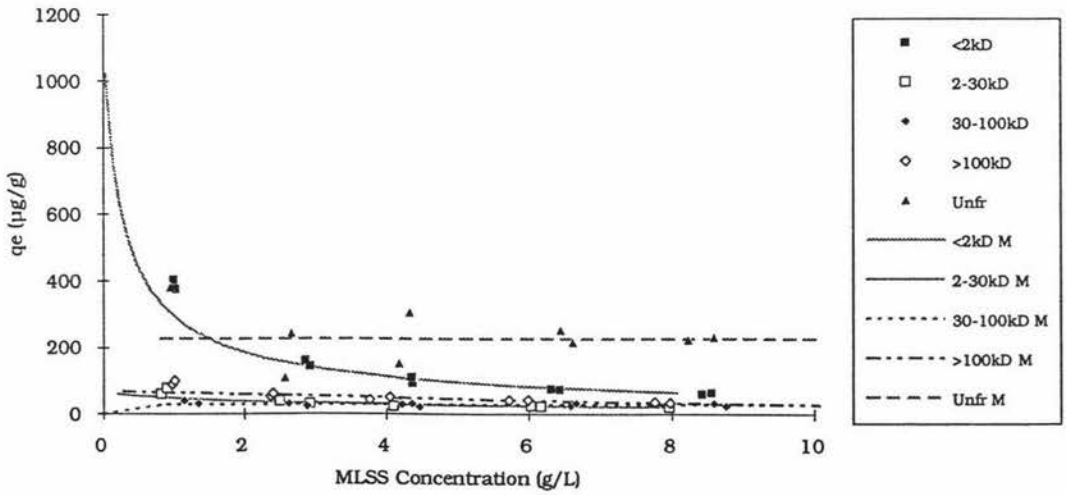


Table XIV reveals that the trend in K_f values for the three samples displaying typical Freundlich type behaviour is for K_f to decrease with increasing molecular weight fraction. K_f can be used to compare the relative adsorption capacity of different systems but comparison of the derived values without regard to the units of the constants under comparison is misleading. Bowman (1982) points out that too often the units of K_f are not taken into account, which can result in the mistaken belief that it is a unitless constant. He also showed that the usefulness of K_f in comparing the adsorption of different systems is limited as it only defines the adsorption capacity of samples at one equilibrium concentration, that where the log of C_e equals zero. Thus, a comparison of K_f values alone disregards the effect that the exponent 1/n has in the Freundlich equation, which may cause significant differences in the relative adsorption of the systems under comparison, depending on the value of C_e at which the comparison is made. In discussing the application of a physical meaning to the Freundlich constants, Bailey and White (1970) point out that the Freundlich isotherm is derived on the assumption that the decrease in heat of adsorption with increasing surface coverage is due to surface heterogeneity. This heterogeneity of the adsorbent remains an unknown factor in adsorption from solutions, making all efforts to treat the Freundlich constants as anything more than empirical descriptions very speculative. Therefore, from the above arguments, it is difficult to relate the observed trends in K_f to specific characteristics of the fractions studied and no attempt has been made in this work to do so.

Figure 55 allows comparison of the relative adsorption of each of the Tasman fractions, with the curves shown being derived from the modelled equations for the adsorption isotherms. Using relative adsorption as a measure involves comparison of values normalised for the effect of the original concentration. As a result, comparison between samples of widely different initial concentrations is somewhat tenuous. Despite this limitation, information can be obtained from comparison of relative adsorptions, as it gives an indication of the proportional adsorption of each fraction at AOX levels similar to those that they would be found in an unfractionated bleach plant effluent. Although competitive effects would be significant in an unfractionated effluent, the relative adsorptions can give an indication of the expected behaviour of the different fractions in the unfractionated wastewater.

For the sample fractions with molecular weights greater than 2kD, Figure 55 indicates that as the molecular weight increases, the proportion of the total AOX that is adsorbed also increases. The 2-30kD fraction showed the lowest relative removal,

with less than 25% being removed at the highest recorded MLSS concentration of 8 g/L.

At MLSS concentrations greater than 4g/L, the fractions with molecular weights greater than 30kD were removed to a greater extent than the molecules in the <2kD and 2-30kD fractions. Almost total removal of the >100kD fraction was observed at high solids concentrations. These findings indicate that the high molecular weight material has a greater affinity for adsorption onto biomass than the lower molecular weight material, as suggested in Section 4.6.6. Assuming minimal competitive effects at MLSS concentrations greater than 4g/L, the high molecular weight AOX component of an unfractionated effluent from the Tasman bleach plant could be expected to adsorb to a greater extent than the lower molecular weight components at these biomass loadings, thus reducing the proportion of high weight AOX in the adsorbed sample. At lower biomass loadings, the situation becomes more confused, with a large proportion of the molecules found in both the <2kD fraction and in the >100kD fractions being expected to adsorb. Competitive effects would be expected to be much more significant at low MLSS, as discussed in Section 4.6.6.

At all MLSS concentrations, the relative adsorption of the 2-30kD fraction was the lowest of all the molecular weight fractions. From this, it could be expected that the proportion of the AOX in this fraction relative to the total AOX of the sample would increase on exposure of an unfractionated bleach plant sample to biomass for adsorption.

It must be noted that the above suggestions are only speculative, and it is recommended that work be carried out to quantify any effects that adsorption of unfractionated effluent has on the overall molecular weight distribution.

Figure 56 shows the plot of biomass loading as a function of MLSS level for the Tasman effluent fractions. The biomass loadings for the 2-30kD, 30-100kD and >100kD fractions show adsorption of AOX of a similar magnitude. The <2kD fraction had significantly higher biomass loading at low biomass concentrations, decreasing at high MLSS concentrations to a level slightly higher than that of the other fractions.

The effect of the high molecular weight fractions on the adsorption of the AOX in the unfractionated wastewater is demonstrated in Figure 56, with the loading at low biomass levels being very much lower than that of the <2kD fraction, indicating significant competitive effects. The very low magnitude of AOX removal at these low

MLSS values, when compared with the <2kD fraction loading, possibly indicates the impact of an effect other than purely competition between molecules of different sizes for the limited adsorption sites. This effect at low MLSS may be caused by reduction in the ability of the low molecular weight molecules to be transported through the cell walls, due to the interference of the high molecular weight material in the unfractionated Tasman sample.

4.7.2. Kinleith Samples

Figures 57 to 59 allow comparison of the adsorptive characteristics of the Kinleith wastewater samples.

Figure 57 shows the adsorption isotherms of the Kinleith samples. The 2-30kD fraction, 30-100kD fraction and >100kD fraction have very similar adsorption loadings, as can also be observed from Table XIII and Figure 59. These three fractions follow an irreversible type of adsorption isotherm, which indicates that the loading of AOX onto the biomass has reached a saturation level at all levels of biomass used in this study. The loading onto the adsorbent remains constant and removal of adsorbate is directly proportional to the amount of adsorbent present in the system.

The <2kD fraction acts in a distinctly different manner to the other three fractions. The presence of the non adsorbable fraction, as discussed in Section 4.6.2, greatly affects the behaviour of the overall isotherm for this sample. The difference is also expected to be due to the mechanisms of removal. It has been suggested (Section 4.6.2) that the smaller molecules in the <2kD fraction may diffuse into the cell material of the biomass, and this process would affect the shape and extent of the uptake curves. The higher molecular weight fractions, because of the size of their molecules, are not expected to display this type of removal mechanism, and hence the uptake behaviour could be expected to be different.

The initial concentrations of the Kinleith effluent were chosen to match those of the Tasman fractions, not as a representation of their concentrations in the 2D:1E unfractionated mixture. Nevertheless, comparison of the relative adsorptions between the fractions of this sample was carried out as for the Tasman samples. Figure 58 shows that the relative adsorption of the <2kD fraction was greater than for all other fractions, apart from at high MLSS concentrations (greater than 6g/L), where the >100kD fraction showed a greater uptake. In contrast, the Tasman high molecular weight fractions (30-100 and >100kD) showed relative adsorption that was much

Figure 57: Adsorption Isotherm, Kinleith Samples

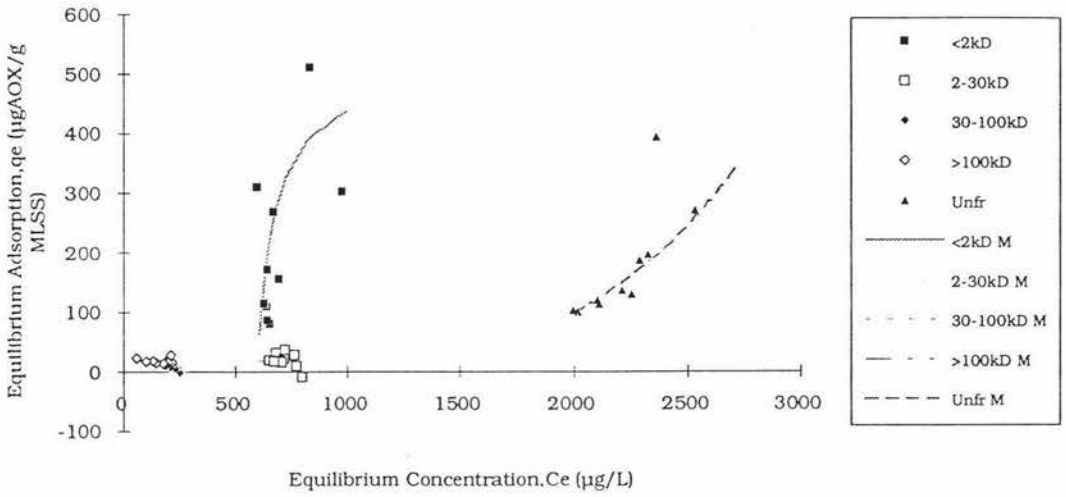


Figure 58: Relative Adsorption of Kinleith Samples.

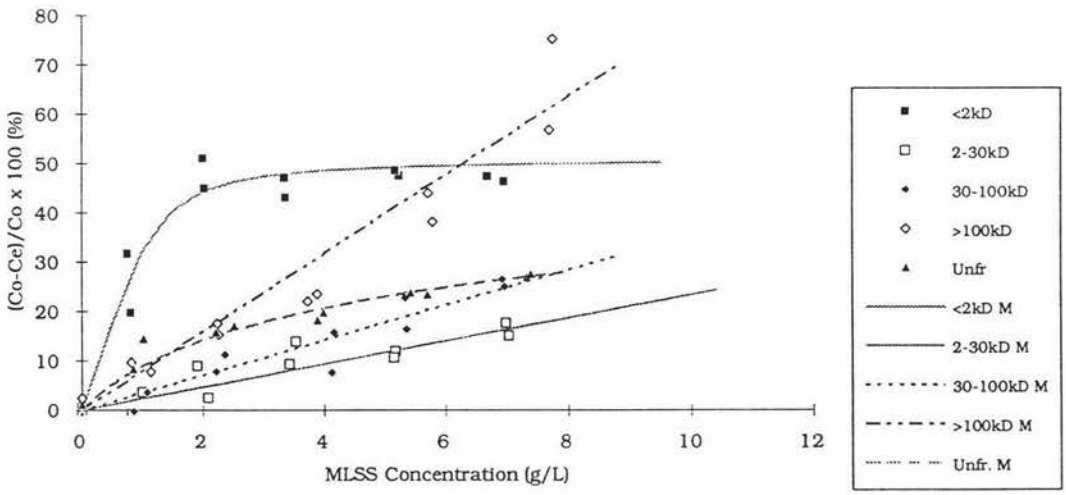
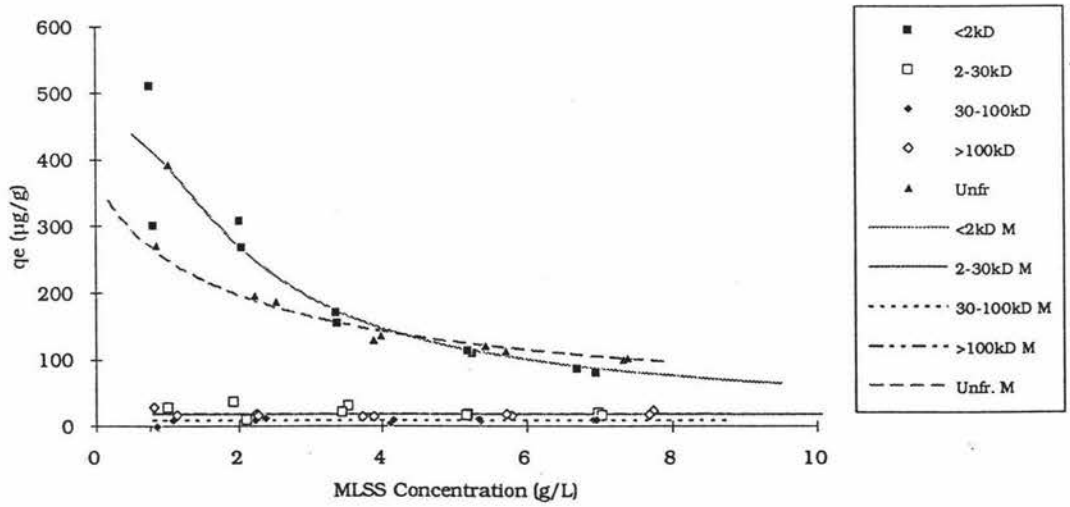


Figure 59: Adsorption of Kinleith Samples.



more significant when compared with that of their respective low molecular weight fractions. This lower relative affinity of the Kinleith samples may be due to the lower chlorination levels of the AOX in this wastewater.

As for the Tasman samples, the 2-30kD fraction showed the lowest relative adsorption (Figure 58), with the relative adsorptions for the fractions greater than 2kD increasing with increasing molecular weight.

Figure 59 shows that the AOX loadings of the Kinleith fractions greater than 2000 Daltons were all of similar magnitude and much lower than the <2kD fraction.

The unfractionated Kinleith sample, with only 9% of the total AOX having molecular weight greater than 30kD, showed an adsorption isotherm that revealed the effect of the large proportion of low molecular weight material in the sample, and Figure 59 shows that the adsorption followed closely that of the <2kD fraction. The much higher relative adsorption of the <2kD components at most MLSS levels, coupled with the significantly lower proportion of high molecular weight material in the Kinleith sample, indicated that the low molecular weight material was the main influence in the adsorption of the Kinleith unfractionated wastewater. This contrasted with the Tasman effluent, where the high molecular weight fraction appeared to exert a significant impact on the overall adsorption of the unfractionated wastewater.

4.8. IMPLICATIONS OF RESULTS IN BIOLOGICAL TREATMENT OF PULP AND PAPER WASTEWATERS

The discussion on the implications of the results found in this work will focus around the potential effects of adsorption of chlorinated organic molecules in three types of biological treatment systems; aerated lagoons, conventional activated sludge, and oxygen activated sludge systems. Typical characteristics of the three systems are outlined in Table XVII

Table XVII: Characteristic Parameters of Three Treatment Systems

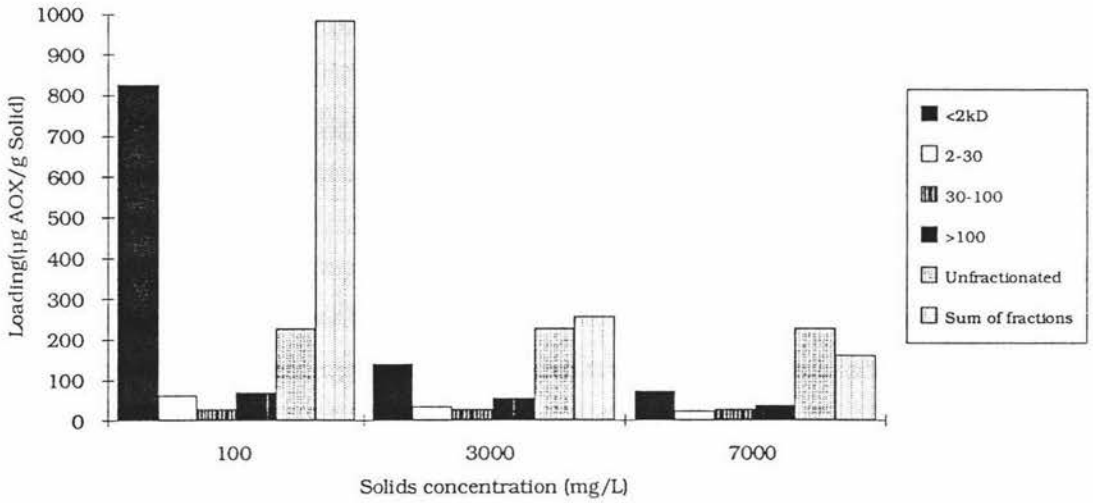
System	MLSS Concentration (mg/L)	Hydraulic Retention Time (HRT)	Solids Retention Time (SRT)	Reference
Aerated lagoon	50-200	2-20 d	long	Valtilla (1991)
Conventional Activated Sludge	2000-5000	6-24 hr	5-15 d*	Valtilla (1991) *Metcalf and Eddy (1979)
Oxygen Activated Sludge	6000-8000	1-3 hr	8-20 d	Metcalf and Eddy (1979)

With respect to attainment of adsorption equilibrium, the long SRT's and HRT's of the aerated lagoons suggest that a position could be attained that closely resembles that of a batch adsorption isotherm. The activated sludge systems are not likely to attain such an equilibrium, with the biomass obtaining lower adsorptive loadings of the AOX compounds, due to the short HRT's of these systems. However, the work carried out on the rates of adsorption, discussed in Section 4.4, suggests more than 85% of the total adsorption should have occurred after 6 hours. Similarly Stuthridge and McFarlane (1993) found that the time to equilibrium for the adsorption of AOX from a pulp and paper mill onto biological solids was 4 hours. From these considerations, it is suggested that only the oxygen activated sludge systems would suffer from adsorptive behaviour that was greatly affected by the time of contact between the adsorbate and adsorbent.

As adsorption equilibrium is not likely to occur in the activated sludge systems, any suggestions as to the likely implications of this work, carried out using batch adsorption isotherms, must be considered as speculation. It is therefore recommended that research be carried out using the appropriate treatment systems to verify any of the following implications.

Figure 60 shows the adsorptive loadings, predicted from the adsorption models, of the Tasman AOX fractions at solids concentrations indicative of each of the biological systems under discussion. Also included in Figure 60 is the sum total of each of the individual fraction's adsorptive loadings, for comparison with the unfractionated sample adsorptive loading.

Figure 60: Tasman AOX Loadings at Different Biomass Concentrations.



Because of their low MLSS concentrations, the aerated lagoons could be expected to suffer most from competitive effects amongst the differing molecular weight AOX fractions. Figure 60 reveals that, at an MLSS of 100mg/L, a representative solids concentration for aerated lagoons, the Tasman unfractionated samples had biomass loadings predicted as being 77% lower than the sum of the biomass loadings for the individual molecular weight fractions, suggesting that significant interference between AOX fractions of different molecular weights would occur in an aerated lagoon system. As discussed in Section 4.6.6, the high molecular weight fractions would be expected to preferentially adsorb onto biomass, and at the low MLSS concentrations of an aerated lagoon the low molecular weight fractions could be substantially precluded from adsorption onto the biomass.

At the high solids concentrations associated with the activated sludge systems, competitive effects should be minimised. Figure 60 supports this by showing that for the Tasman wastewater, at an MLSS concentration of 3000mg/L (conventional activated sludge systems), the unfractionated sample loading is only 11% lower than the sum of the individual AOX loadings. At an MLSS concentration of 7000mg/L (oxygen activated sludge systems), the unfractionated sample was predicted to adsorb more AOX than the sum of the individual fractions, possibly indicating a synergistic effect occurring. Because of the reduction in competition, the adsorption of the different molecular weight fractions in the activated sludge systems may be expected to resemble the adsorption of the individual fractions.

The effect of competition in the Kinleith samples cannot be determined by the same type of comparison, as the initial AOX concentrations of the fractions in the adsorption studies were chosen to match those of the Tasman fractions, and not as representative of their concentrations in the 2D:1E mixture. However, Figure 59 supports the prediction of minimal competitive effects at higher biomass concentrations, as the adsorptive loadings for the <2kD fraction follow closely that of the unfractionated wastewater. The <2kD fraction loadings would have revealed an even closer alignment with those of the unfractionated sample had its initial AOX concentration been the same as that of the <2kD AOX present in the unfractionated sample, as this latter concentration was higher and would result in higher biomass loadings for a given solids concentration.

Table XVIII gives the relative adsorptions, from the batch adsorption data, of the molecular weight fractions from both mills, at MLSS concentrations comparable with those found in the three different treatment systems.

Table XVIII: Percent of AOX in Each Fraction that Could Potentially be Adsorbed in Different Treatment Systems

Treatment System	Tasman					Kinleith				
	<2kD	2-30kD	30-100kD	>100kD	Unfractionated	<2kD	2-30kD	30-100kD	>100kD	Unfractionated
Aerated Lagoon (100mg/L)	7.0	0.73	0.84	2.3	0.73	3.8	0.23	0.36	0.79	1.3
Conventional Activated Sludge (3000mg/L)	35	12	25	58	22	47	7.0	11	24	18
Oxygen Activated Sludge (7000mg/L)	43	19	59	91	51	50	16	25	56	27

This shows the potential significance of adsorption as a removal mechanism for AOX. Aerated lagoons, with low MLSS concentrations and therefore significant competitive effects, would not be expected to show adsorption of individual fractions comparable to the percentages given in Table XVIII in the treatment of bleach plant wastewaters,

The activated sludge systems may yield similar percentage removals of the individual fractions to those given in Table XVIII and these will be discussed below.

Removals of the <2kD fraction should be fairly similar between the two types of activated sludge systems. A significant amount of the AOX in this fraction should be removed by the adsorption process, approximately one third for the Tasman wastewater and nearly half of the total for the Kinleith wastewater.

The removal of the 2-30kD fraction is the lowest of all the AOX in the wastewater samples, with neither system removing more than 20% of the available AOX in this fraction. The AOX in the Tasman fraction would be expected to be removed by adsorption to a slightly greater extent than the Kinleith fraction.

The results from Table XVIII for both the 30-100kD and >100kD fractions reveal that the oxygen activated sludge systems should remove approximately twice the amount of AOX than the conventional activated sludge systems. Comparison of the percentage removals between the mills for both activated sludge treatment systems reveals that adsorptive processes can potentially remove approximately twice the amount of AOX in these fractions from the Tasman bleach plant wastewaters than from the Kinleith wastewaters.

Comparison of the percentage removals from the unfractionated samples reveals that the aerated lagoon does not appear to have the potential to remove significant amounts of AOX by the mechanism of adsorption onto biological solids, with less than 2% being removed for either mill's wastewater sample. The overall removal from a conventional activated sludge system is predicted to be fairly similar for both the Kinleith and Tasman wastewaters. At 15-20% removal, the adsorption process can be considered a significant removal process for AOX in this treatment system. In an oxygen activated sludge system, the Tasman wastewater could be expected to be adsorbed to a much greater extent than a wastewater from the Kinleith bleaching sequence. At a predicted 51% removal, the adsorption process for Tasman AOX is potentially highly significant mechanism of removal. The adsorption of the Kinleith wastewater, at 27% removal, in the oxygen activated sludge system is predicted to be

of lower significance, but still contributing to the AOX removal process.

A number of inferences may now be drawn in assessing the potential significance of AOX removal by adsorption onto biological solids and whether changes to bleaching sequences alters the significance of this removal mechanism:

- The AOX from a conventional bleach plant effluent should be adsorbed to a greater extent than that from a modern bleaching sequence.

- Aerated lagoons are not expected to display significant removal of AOX by adsorption onto biological solids.

- Conventional activated sludge systems could be expected to remove 15-20% of AOX by adsorption onto biological solids, a significant contribution. The removal of AOX by this process is expected to be slightly greater for conventional bleach sequence wastewaters.

- Oxygen activated sludge systems could be expected to remove up to 50% of AOX from wastewaters of a conventional bleach sequence by way of adsorption onto biological solids, making this a highly significant removal mechanism in this type of treatment system. The potential for adsorptive removals from a modern bleach plant wastewater is predicted to be only half that of a conventional bleach plant wastewater, indicating that the adsorptive characteristics of the AOX has changed significantly on alteration of the type of bleaching process used.

- A significant decrease in the proportion of AOX with molecular weights greater than 30kD should be noticed in the effluent from the activated sludge treatment of conventional bleach wastewater, with a corresponding increase in the proportions of the fractions in the 2-30 kD molecular weight range. This can be postulated by comparing the relative adsorptions of the individual fractions with that of the unfractionated sample, for the Tasman samples (Figure 55). A fraction with a higher relative adsorption than the unfractionated sample at a given solids concentration would be expected to undergo a reduction in its proportion of the total AOX upon adsorption of the unfractionated sample. Conversely, a fraction with a lower relative adsorption should be present in higher proportions in the liquid effluent from the treatment system than in its influent.

- Figure 58 indicates that all three biological treatment systems of a modern bleach

sequence wastewater should result in the relative proportions of the AOX in the <2kD fraction to be significantly lower in the effluent than in the influent. At the higher biomass loadings associated with the activated sludge systems, the >100kD AOX fraction, as well as the <2kD fraction should undergo a reduction in their proportion of the total AOX due to adsorption of the unfractionated wastewater onto the solids in the system. In all treatment systems, the 2-30kD fraction should be observed to increase in its proportion of the total, as it is adsorbed to a low extent at all biomass levels.

- It is suggested that the modern bleaching sequence wastewater adsorption will be dominated by the uptake of the <2kD fraction, as the biomass loadings for this fraction in the Kinleith samples are very similar to the loadings of the unfractionated sample (Figure 59). As discussed above, the similarity between the two would have been even more marked in the experimental work completed if the initial AOX concentration of the <2kD fraction of the adsorption flasks had been the same as the concentration of <2kD AOX in the Kinleith unfractionated sample adsorption flasks. The suggested AOX fraction loadings from the modern bleaching sequence wastewaters contrasts with the predicted loadings of the AOX from a conventional bleaching sequence, where the higher molecular weight material must make a much greater contribution to the overall uptake, as evidenced by the Tasman sample loadings shown in Figure 56. This Figure shows that the <2kD fraction, although exhibiting the greatest loadings of any of the fractions, has loadings significantly lower than the unfractionated wastewater sample at most MLSS concentrations.

It is important to note that the above implications for adsorption of AOX onto biomass in biological treatment systems do not take into consideration the effect of biodegradation of the compounds in the systems. This is known to be an important phenomenon and the interaction of adsorption with biodegradation will significantly affect the fate of chlorinated organic molecules entering the treatment systems.

Also of importance is the fact that the work was carried out using biomass collected from a domestic activated sludge plant. The adsorptive behaviour observed is a function of the adsorbent characteristics, and so the specific characteristics of the biomass used in this work must be acknowledged as affecting the results obtained and conclusions drawn. The results may therefore not be applicable to situations where the biomass characteristics differ greatly from those used in this work.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

1. Considerable differences existed between the concentration and molecular weight distribution of AOX from the mixed C and E wastewater of a conventional CEH (Tasman) bleaching sequence, and that from the mixed D_1 and E_1 wastewater of a modern $OODE_OD$ (Kinleith) bleach sequence. The AOX concentration was significantly lower in the wastewaters from the $OODE_OD$ bleaching process. The wastewater from the conventional sequence had significantly greater proportions of high molecular weight AOX than the modern sequence wastewater. Consequently, the modern sequence wastewater's AOX had a much greater proportion of the low molecular weight material than the wastewater from the conventional plant.

2. The rate of adsorption for the Tasman 2kD fraction and >100kD fraction was found to be adequately described by the following model:

$$dq(t)/dt = m(q_e - q(t))^j$$

The high molecular weight fraction displayed a faster rate of reaction, implying a higher affinity for adsorption than the low molecular weight fraction.

3. Equilibrium adsorption onto biological solids of the different molecular weight AOX fractions contained in the above mixtures was characterised, and can be defined by the models describe in Table XIX:

Table XIX: Adsorption Isotherms for Bleach Plant AOX

Sample Fraction Molecular weight (daltons x 1000)	Tasman	Kinleith
<2	Freundlich	Modified Langmuir
2-30	Freundlich	Irreversible
30-100	Irreversible	Irreversible
>100	Freundlich	Irreversible
Unfractionated Sample	Irreversible	Freundlich

The major conclusion to be drawn from Table XIX is that no one isotherm was capable of accurately predicting the adsorption of the different samples, either

between the different molecular weight fractions from the same mill's wastewater, or for the same molecular weight fractions between the two mills. This indicates that significant differences occurred between the adsorption processes of the fractions.

4. The following conclusions were made as to the significance of adsorption of AOX onto biological solids in various treatment systems.

   • Adsorption is not expected to be a significant removal mechanism in an aerated lagoon treatment of bleach plant wastewaters, due to the low solids concentrations present in the system.

   • Conventional activated sludge treatment systems could be expected to remove 15-20% of the available AOX by adsorption, with AOX from conventional bleach plants adsorbing to a slightly greater extent than that from modern bleach plants. Adsorption could be concluded to be having a significant role in the removal of AOX in such a treatment system.

   • Oxygen activated sludge treatment systems, could be expected to remove up to 50% of the AOX from a conventional bleach plant wastewater by adsorption, making this a highly significant removal mechanism for this type of wastewater. The potential removal of AOX from modern bleach plant wastewaters is predicted to be considerably lower than that of a conventional sequence, but still contributing significantly to the removal of AOX from the wastewater.

5. It is concluded that changes to the bleaching sequence, by addition of oxygen delignification and chlorine dioxide substitution, significantly alters the adsorptive characteristics of the AOX in the wastewaters from the bleach plant. This is evidenced by the following conclusions as to the adsorption characteristics of the molecular weight fractions of the Tasman (conventional) and Kinleith (modern) bleach plant wastewaters.

   • The adsorption of the Kinleith <2kD sample showed indications of a non adsorbable fraction. The Tasman sample did not show evidence of this.

   • For the fractions with molecular weights greater than 2kD, the Tasman samples showed greater affinity for adsorption than the Kinleith samples. It is

postulated that the greater adsorption of the Tasman AOX is due to higher chlorination levels of the molecules in this wastewater.

- Similarly, for the unfractionated samples, the Tasman sample adsorption was greater than that from the Kinleith mill, except at low biomass concentrations where the effect of preferential adsorption of high molecular weight material appears to cause the AOX adsorption of the Tasman wastewater to be lower than Kinleith's. The generally greater adsorption by the Tasman sample is considered to be due to the higher chlorination levels and the greater average molecular weight of the sample.

- The unfractionated wastewater adsorption was greatly affected by the high molecular weight AOX for the Tasman sample, while for the Kinleith sample the adsorption appears to be mainly influenced by the <2kD fraction.

Overall, the AOX from conventional bleach plant wastewater shows greater affinity for adsorption than that from a modern bleach plant, indicating that modernisation of bleach sequences has reduced the significance of adsorption onto biological solids as an AOX removal mechanism.

6. Adsorption is expected to alter the molecular weight distribution of the AOX present in the wastewater passing through a biological treatment system in the following manner.

- Conventional bleach plant wastewater should reveal a decrease in the proportion of material with molecular size greater than 30,000 daltons, on passing through the system. For modern bleach plant wastewaters, this effect is only expected to occur in the fraction with molecular weight greater than 100,000 daltons.

- Modern bleach plant wastewater should reveal a significant decrease in the proportion of the <2kD fraction. This effect is not expected to be as notable for conventional bleach plant wastewaters.

- Both wastewater types should exhibit an increase in the proportion of 2-30kD AOX.

7. Further conclusions to be drawn from the work are:

   - Biological treatment systems with low biomass levels, such as aerated lagoons, are expected to exhibit adsorption that is significantly affected by competition for the limited adsorption sites on the solids' surfaces. Systems with higher biomass concentrations, such as activated sludge systems, may not be subject to such significant competition.

   - Comparison of the adsorption of the different molecular weight fractions within the mill samples revealed that, for the fractions greater than 2kD, the proportion of the total AOX in a particular fraction that was adsorbed onto biomass increased with increasing molecular weight. This implies that increasing molecular weight results in greater adsorption affinity.

   - The total adsorption loading onto the biomass is expected to be dominated by the <2kD molecular weight fraction, for both conventional and modern bleach plant wastewater.

5.2. RECOMMENDATIONS FOR FURTHER WORK

1. Further work should be carried out to assess the rates of adsorption of AOX onto biological solids, both to evaluate the suitability of the proposed model and to determine the adsorption rates of the molecular weight fractions not studied in this work. It would be of interest to compare the rates of adsorption of the fractions from a conventional bleach plant wastewater with those from a modern sequence.

2. The sorption of AOX in the <2kD fraction appears to consist of two mechanisms:

   - adsorption onto the cell walls
   - absorption of those compounds small enough to pass through the cell wall into the cell interior.

   The Kinleith sample displayed sorption characteristics that indicated that it contained a greater proportion of material capable of being absorbed into the cell than the Tasman sample. It is recommended that further work be carried out to determine the validity of this hypothesis on the mechanism of sorption, and to verify that a modern bleaching sequence yields a wastewater with a greater

proportion of absorbable AOX in the <2kD fraction than does a conventional bleach sequence.

It is recommended that attempts be made to verify the presence of a non adsorbable fraction in the Kinleith bleach mill effluent, as this may have consequences as to the treatability of this fraction in biological systems system.

3. It is recommended that work be carried out to determine the effect that adsorption in an unfractionated mixture has on the individual fractions' adsorption. A procedure of adsorption and then fractionation of the liquid at equilibrium should clarify these effects.

   Determination of the significance of the process of adsorption and the study of the adsorptive behaviour of the chlorinated organic compounds in actual biological treatment systems is the main aim of this area of research. Attempts should be made to evaluate the implications suggested within this work, obtained from batch adsorption studies, in order to determine their relevance and applicability to full scale treatment systems.

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APPENDIX

APPENDIX A1

EXAMPLE OF CONDUCTIVITY ADJUSTMENT

K(sample) = 2.0

K(0.2g/L NaCl solution) = 3.2

Equivalence of Phosphate buffer to NaCl solution: 0.2g/L NaCl equivalent to $2.66*10^{-3}$M PO_4 solution.

65 mL stock solution A and 41.5 mL stock solution B diluted to 2 L with water gives an ESCC of 0.2 g/L.

$$\text{ESCC} = \frac{2}{3.2} \times 2 = 0.125 \text{ g NaCl equivalent/L}$$

Therefore require ionic strength equivalent to 0.2-0.125 = 0.075 g/L NaCl to obtain an ESCC of 0.2 g/L.

Require addition of

$$\frac{0.075}{0.2} \times 2.66\times10^{-3} = 9.975 \times 10^{-4} \text{ Mol/L } PO_4$$

$$\text{volume Stock A to be added} = \frac{9.975 \times 10^{-4} \times 65 \times 1000}{.05 \times 106.5} = 12.2 \text{ mL/L}$$

$$\text{volume Stock B to be added} = \frac{9.975 \times 10^{-4} \times 41.5 \times 1000}{.05 \times 106.5} = 7.8 \text{ mL/L}$$

APPENDIX A2

SAS PROGRAMS USED FOR NON LINEAR ANALYSIS OF ADSORPTION ISOTHERMS

The following programs were used in the nonlinear analysis of the data to determine the form of the adsorption isotherms.

A spreadsheet named Freundli.XLS was used for the data.
Nomenclature used was the same as that defined in Section 3, unless otherwise stated.

M = MLSS concentration
mgCe = Ce expressed as mg/L
mgCo = Co expressed as mg/L
Cr = C_{min}
k = K_f (Freundlich parameter)
n = 1/n (Freundlich parameter)

FREUNDLICH ISOTHERM SAS PROGRAM

```
filename dat dde 'Excel|p:\thesis\xlisothe\Freundli.XLS!R100C2:R111C3';

data dat;
  infile dat;
  input M Ce;
  mgCe=.001*Ce;
  Co=1215.2;
  mgCo=.001*Co;
  Cr=590;
  mgCr=.001*Cr;
proc nlin;
  parameters k=.3 n=3;
  model M=(mgCo-mgCe)/(k*(mgCe-mgCr)**n);
run;
```

Note that the Freundlich isotherm procedures used values for Ce and Co in mg/L. The resultant values for K_f and 1/n relate to q_e expressed in mg/g. To alter the parameters to allow calculation of q_e in µg/g, the following transformation to K_f must be made

$$K_f = K_{f\ model} \times 1000^{(1 - 1/n)}$$

LANGMUIR ISOTHERM SAS PROGRAM

```
filename dat dde 'Excel|p:\thesis\xlisothe\freundli.XLS!R13C2:R22C3';

data dat;
  infile dat;
  input M Ce;
  mgCe=.001*Ce;
  Co=1188;
proc nlin;
  parameters a=4 b=3;
  model Ce=(-1*(Co*b-1-M*a*b)-((Co*b-1-M*a*b)**2-(4*(-1*b)*Co))**.5)/(2*(-1*b));
run;
```

MODIFIED LANGMUIR ISOTHERM SAS PROGRAM.

```
filename dat dde 'Excel|p:\thesis\xlisothe\Freundli.XLS!R100C2:R111C3';

data dat;
  infile dat;
  input M Ce;
  mgCe=.001*Ce;
  Co=1215.2;
  Cr=590;
proc nlin;
  parameters a=2 b=4;
  model Ce=(-1*(Cr*b+Co*b-1-M*a*b)-((Cr*b+Co*b-1-M*a*b)**2-(4*(-
1*b)*(M*a*b*Cr+Co-Co*b*Cr)))**.5)/(2*(-1*b));
run;
```

MODIFIED FREUNDLICH ISOTHERM SAS PROGRAM.

```
filename dat dde 'Excel|p:\thesis\xlisothe\Freundli.XLS!R100C2:R111C3';

data dat;
  infile dat;
  input M Ce;
  mgCe=.001*Ce;
  Co=1215.2;
  mgCo=.001*Co;
  Cr=590;
  mgCr=.001*Cr;
proc nlin;
  parameters k=.3 n=3;
  model M=(mgCo-mgCe)/(k*(mgCe-mgCr)**n);
run;
```

APPENDIX A3. ERROR ANALYSIS OF SAMPLE AOX.

Error Analysis of Tasman Sample AOX Determination

Measured AOX (µg/	Std error (s.e)	s.e squared	Measured AOX (µg/	Std error (s.e)	s.e squared	Measured AOX (µg/	Std error (s.e)	s.e squared
74.11	1.21	1.475	70.1	2.079	4.323	18.9	2.102	4.42
72.39			73.04			21.88		
67.68	2.32	5.371	75.06	0.811	0.658	6.676	0.072	0.005
70.95			76.21			6.778		
63.44	0.25	0.063	70.56	0.089	0.008	63.2	1.722	2.965
63.8			70.68			65.63		
47.1	1.92	3.7	70.33	1.544	2.384	45.55	0.807	0.651
49.82			72.51			46.69		
57.17	2.15	4.601	70.86	1.358	1.844	35.72	1.881	3.537
60.2			68.94			33.06		
63.68	2.23	4.977	72.12	2.607	6.799	14.13	0.17	0.029
60.52			68.43			14.37		
58.58	0.02	5E-04	56.75	0.583	0.34	57.26	0.25	0.062
58.55			55.92			57.61		
62.79	0.32	0.1	58.96	0.476	0.227	104.5	3.348	11.21
63.23			59.64			109.2		
58.69	2.22	4.91	61.88	1.96	3.841	88.27	3.713	13.78
55.55			59.1			83.02		
59.47	1.5	2.249	40.84	1.309	1.715	104.2	5.748	33.03
57.35			38.99			96.04		
33.06	0.24	0.056	65.02	0.395	0.156	40.41	1.421	2.019
33.4			65.58			38.4		
55.04	0.83	0.687	60.45	1.147	1.316	56.06	0.354	0.125
56.22			58.83			55.56		
58.74	0.01	2E-04	51.18	1.71	2.925	84.02	1.261	1.59
58.76			53.6			82.23		
83.47	0.98	0.952	17.24	0.81	0.657	73.36	1.595	2.542
82.09			18.39			75.62		
83.49	0.63	0.395	37.66	2.046	4.187	54.35	0.226	0.051
84.38			40.55			54.04		
78.67	0.29	0.082	39.89	0.198	0.039	51.68	0.55	0.302
79.07			39.61			50.91		
77.26	0.58	0.334	39.69	1.823	3.324	48.77	3.148	9.911
76.44			42.27			44.32		
76.24	1.32	1.754	40.13	0.573	0.328			
74.37			40.94					
73.83	1.19	1.41						
75.51								

Statistical analysis of errors

Pooled std dev	1.691071
t statistic for n=2, 90% C.I.	6.314
Average measured AOX (µg/L)	58.79139
% Coefficient of Variation (for 60µg/L sample.)	2.818451
90% Confidence Interval on Average expressed as a Percentage.	12.58346
90% CI expressed as a Percentage. 50µg sample	15.10015
90% CI expressed as a Percentage. 90µg sample	8.388973

Error Analysis of Kinleith Sample AOX Determination

Measured AOX (µg/l	Std error (s.e)	s.e squared	Measured AOX (µg/l	Std error (s.e)	s.e squared	Measured AOX (µg/l	Std error (s.e)	s.e squared
71.32	0.53	0.277	57.26	0.069	0.005	52.49	0.049	0.002
72.06			57.16			52.56		
76.43	3.26	10.6	72.95	0.47	0.221	54.38	0.174	0.03
71.83			72.29			54.62		
49.28	1	1.006	68.77	1.536	2.359	52.21	2.21	4.884
50.7			66.6			55.34		
58.15	0.74	0.549	70.79	1.375	1.89	43.09	0.722	0.521
59.2			68.85			44.11		
48.97	1.1	1.215	77.44	3.121	9.744	43.53	2.502	6.262
47.41			73.03			47.07		
53.63	0.71	0.506	66.95	1.154	1.332	34.12	1.637	2.678
54.64			65.31			31.81		
52.45	0.16	0.027	71.42	2.628	6.908	36.14	0.181	0.033
52.22			75.14			36.4		
57.3	1.37	1.879	70.53	1	1.001	83.1	0.904	0.817
55.36			69.11			84.38		
51.93	0.94	0.883	65.51	2.751	7.568	81.08	1.171	1.371
53.26			69.4			82.73		
52.04	0.74	0.55	71.91	1.055	1.114	77.42	2.03	4.12
50.99			73.4			74.55		
55.26	1.45	2.109	71.94	0.039	0.001	71	0.119	0.014
53.21			71.89			70.83		
52	1.55	2.405	73.21	3.123	9.752	93.68	0.693	0.481
54.19			68.8			92.7		
64.74	1.54	2.385	62.93	5.41	29.26	91.56	0.353	0.125
62.55			70.58			92.06		
78.73	0.46	0.21	63.68	3.215	10.34	91.02	2.957	8.746
78.08			59.13			86.84		
63.78	0.3	0.093	62.85	1.906	3.634	90.76	0.294	0.087
64.21			65.54			90.35		
60.49	1.09	1.179	64.35	0.685	0.47	85.67	0.949	0.901
62.03			65.32			84.33		
73.68	1.49	2.223	66.81	0.812	0.659	84.19	0.718	0.516
71.57			67.96			85.21		
77.14	0.97	0.95	60.26	0.433	0.188	79.95	2.02	4.081
78.52			59.64			82.81		
69.53	0.22	0.047	58	0.761	0.579	81.68	1.491	2.222
69.22			56.92			79.57		
60.11	2.47	6.117	56.94	1.147	1.315			
56.61			55.31					

Statistical analysis of errors

Pooled std dev	1.654159
t statistic for n=2, 90% C.I.	6.314
Average measured AOX (µg/L)	65.81377
% Coefficient of Variation (for 65µg/L sample.)	2.544859
90% Confidence Interval on average AO expressed as a Percentage.	11.36196
90% Confidence Interval expressed as a Percentage. 50µg sample	13.63435
90% Confidence Interval expressed as a Percentage. 90µg sample	7.574642

APPENDIX A4

DETERMINATION OF ADSORPTION RATE

The routine for determining the parameters m and j for each sample is given below.

The adsorption rate equation used was:

$$\frac{-dq(t)}{dt} = m(q_e - q(t))^j$$

An estimate of j was made.

Using this estimate, values of m were calculated for each time recorded from the solution of the above differential equation:

$$\frac{1}{(qe - q(t))^{(j-1)}} - \frac{1}{qe^{(j-1)}} = (j-1)mt$$

$$\frac{((qe - q(t))^{(1-j)} - qe^{(1-j)}}{(j-1)t} = m$$

The average of these m values was taken and used to calculate q(t) at each time, from the following rearrangements:

$$\frac{1}{(qe - q(t))^{(j-1)}} - \frac{1}{qe^{(j-1)}} = (j-1)mt$$

$$\frac{1}{(qe - q(t))^{(j-1)}} = (j-1)mt + \frac{1}{qe^{(j-1)}}$$

$$(1-j)\ln(qe - q(t)) = \ln((j-1)mt + qe^{(1-j)})$$

$$qe - q(t) = \exp(\ln((j-1)mt + qe^{(1-j)})/(1-j))$$

$$q(t) = qe - \exp(\ln((j-1)mt + qe^{(1-j)})/(1-j))$$

These modelled q(t) values were compared with those obtained from the experimental work, and using a least squares routine, the values of the parameters m and j were determined that resulted in the closest fit of the model to the data.

The spreadsheet set up for the modelling of the rate parameters is given in the following pages.

Note that in the modelling equations used, qe was defined as Q

ADSORPTION RATE CALCULATIONS FOR TASMAN <2kD FRACTION

Sample	Time (minutes)	Time (hours)	MLSS(g/L)	Eff. AOX (ug/L)	Adsorbed AOX (ug/g) q(t)	Percent of Total Adsorbed
Blk2			6.770667	0		
Control	0	0	0	1234.479	0	0
1	15	0.25	7.58	1128.034	14.04281	19.23673
2	45	0.75	7.499333	1032.006	26.99883	36.98469
3	82	1.366667	7.417333	968.0878	35.91465	49.19815
4	144	2.4	7.504667	895.0059	45.2349	61.96562
5	214	3.566667	7.566	846.1276	51.32847	70.31297
6	277	4.616667	7.343333	737.346	67.69852	92.7377
7	394	6.566667	7.230667	762.4219	65.28539	89.43204
8	848	14.13333	7.200667	749.0905	67.4088	92.34082
9	1359	22.65	6.971333	730.197	72.33649	99.09108

j	1.39
qe	73

Time (hr)	q(t)	Q-qe	m	qmod	(q-qmod)^2	(qmod-qemean)^2
0	0	73	#DIV/0!	1.42E-14	2.02E-28	
0.25	14.04281	58.95719	0.167217	10.07095	15.77571	1561.218
0.75	26.99883	46.00117	0.126586	25.12275	3.519651	598.3138
1.366667	35.91465	37.08535	0.106414	37.58046	2.7749	144.066
2.4	45.2349	27.7651	0.091793	50.12023	23.8664	0.288389
3.566667	51.32847	21.67153	0.08172	57.93225	43.60987	69.70645
4.616667	67.69852	5.301478	0.185585	62.11706	31.15276	157.0974
6.566667	65.28539	7.714612	0.102746	66.48205	1.432005	285.571
14.13333	67.4088	5.591202	0.058678	71.33602	15.42307	473.1848
22.65	72.33649	0.663508	0.111605	72.3746	0.001452	519.4475
Means	49.58321		0.114705			

Sum of residuals of B Residual ss	resid2
137.5558	137.5558

Regression ss	Total ss	R squared
3808.894	3946.45	0.965144

<2kD Fraction
Model of adsorption rate

m=	0.114705	
j=	1.39	Modelled q(t)
Q=	73	

Time (hrs)	q(t)	% Adsorbed	Rate
0	1.42E-14	1.95E-14	44.62726
0.2	8.218597	11.25835	37.80049
0.4	15.20543	20.82936	32.25554
0.6	21.18733	29.02374	27.71069
0.8	26.34218	36.08517	23.95446
1	30.8109	42.20671	20.82619
1.2	34.70623	47.54277	18.20244
1.4	38.11908	52.21792	15.98743
1.6	41.12341	56.33344	14.10611
1.8	43.77979	59.97232	12.49917
2	46.1382	63.20301	11.11935
2.2	48.24012	66.08236	9.928686
2.4	50.12023	68.65784	8.896503
2.6	51.80762	70.96934	7.997816
2.8	53.32688	73.05052	7.212159
3	54.69888	74.92998	6.522668
3.2	55.94142	76.63208	5.915371
3.4	57.06973	78.17771	5.378628
3.6	58.09692	79.58483	4.902696
3.8	59.03431	80.86892	4.479381
4	59.89172	82.04345	4.101758
4.2	60.67767	83.1201	3.763955
4.4	61.39962	84.10907	3.46097
4.6	62.06409	85.01931	3.188523
4.8	62.67682	85.85866	2.942945
5	63.24285	86.63404	2.721074
5.2	63.76665	87.35157	2.520177
5.4	64.25216	88.01666	2.337887
5.6	64.7029	88.63412	2.172144
5.8	65.122	89.20822	2.021154
6	65.51224	89.7428	1.883347
6.2	65.87613	90.24127	1.757344
6.4	66.21589	90.7067	1.641938
6.6	66.53354	91.14183	1.53606
6.8	66.83088	91.54916	1.43877
7	67.10956	91.93091	1.349232
7.2	72	98.63014	0.114705
8.2	72	98.63014	0.114705
9.2	72	98.63014	0.114705
10.2	72	98.63014	0.114705
11.2	72	98.63014	0.114705
12.2	72	98.63014	0.114705
13.2	72	98.63014	0.114705
14.2	72	98.63014	0.114705
15.2	72	98.63014	0.114705
16.2	72	98.63014	0.114705
17.2	72	98.63014	0.114705
18.2	72	98.63014	0.114705
19.2	72	98.63014	0.114705
20.2	72	98.63014	0.114705
21.2	72	98.63014	0.114705
22.2	72	98.63014	0.114705
23.2	72	98.63014	0.114705
24.2	72	98.63014	0.114705
25.2	72	98.63014	0.114705
26.2	72	98.63014	0.114705

ADSORPTION RATE CALCULATIONS FOR TASMAN >100kD FRACTION

Sample	Time (hours)	MLSS(g/L) (g/L)	AOX (ug/L) (ug/L)	Adsorbed AOX (ug/g) q(t)	Percent of Total Adsorbed
1	0.283	8.242	133.5085	14.9571	15.74432
2	0.85	8.339333	104.2547	38.16873	40.17761
3	1.73	8.335333	87.26516	51.77544	54.50047
4	2.37	8.134	90.79015	50.1679	52.80831
5	3.72	8.202	69.61284	66.9651	70.48958
6	5.53	8.252	54.48246	78.78295	82.92943
7	6.82	8.169333	65.69802	70.4276	74.13432
8	15.43	7.944	40.28559	93.75161	98.6859
9	22.72	7.917333	40.35512	94.00882	98.95666
BLK1		7.584667	-3.77743		
BLK2		7.728	3.848818		
CONTROL		0	152		

j	1.395
Q=	95

Time (hr)	q(t)	Q-qe	m	qmod	(q(t)-qmod)	(qmod-qemean)^2
0	0	95	#DIV/0!	0	0	
0.283	14.9571	80.0429	0.103653	12.59747	5.567859	2451.658
0.85	38.16873	56.83127	0.110913	31.65472	42.43235	927.6273
1.73	51.77544	43.22456	0.088365	50.83865	0.877579	127.0815
2.37	50.1679	44.8321	0.061047	60.0324	97.30852	4.323455
3.72	66.9651	28.0349	0.069766	72.28572	28.30905	103.5109
5.53	78.78295	16.21705	0.076547	80.98319	4.841057	356.1335
6.82	70.4276	24.5724	0.043372	84.56741	199.9342	504.2591
15.43	93.75161	1.248394	0.123152	92.41393	1.78938	918.2254
22.72	94.00882	0.991176	0.093377	93.8097	0.03965	1004.763
mean	62.1117		0.085577			

Sum of residuals of B Residual ss
381.0996

Regression ss	Total ss	R squared
6397.583	6778.683	0.94378

>100 kD Fraction
Model of adsorption rate

m=	0.085577
j=	1.395
Q=	95

Time (hrs)	q(t)	% Adsorbed	Rate
0	0	0	49.12263
0.2	9.15724	9.6392	42.64556
0.4	17.1285	18.03	37.22462
0.6	24.10387	25.3725	32.65695
0.8	30.23753	31.82898	28.78414
1	35.65548	37.53208	25.48139
1.2	40.46143	42.59098	22.64951
1.4	44.74134	47.09615	20.20907
1.6	48.56686	51.12301	18.09599
1.8	51.99807	54.73481	16.25821
2	55.08565	57.98489	14.65319
2.2	57.87252	60.91844	13.24593
2.4	60.39526	63.57396	12.00746
2.6	62.68515	65.98436	10.91373
2.8	64.76905	68.17795	9.944602
3	66.67016	70.17912	9.083176
3.2	68.40855	72.009	8.315194
3.4	70.00166	73.68596	7.628573
3.6	71.46471	75.22601	7.013033
3.8	72.81102	76.64318	6.459794
4	74.05228	77.94977	5.961328
4.2	75.19877	79.1566	5.511156
4.4	76.25959	80.27325	5.103688
4.6	77.24277	81.30818	4.734081
4.8	78.15546	82.26891	4.398126
5	79.00402	83.16212	4.092158
5.2	79.79411	83.9938	3.812973
5.4	80.5308	84.76927	3.557764
5.6	81.21865	85.49331	3.324063
5.8	81.86172	86.17023	3.1097
6	82.46369	86.80388	2.912756
6.2	83.02787	87.39776	2.731533
6.4	83.55725	87.955	2.564526
6.6	84.05454	88.47846	2.410398
6.8	84.52219	88.97072	2.267957
7	84.96243	89.43413	2.136138
7.2	85.37729	89.87083	2.01399
8.2	87.1302	91.716	1.521342
9.2	88.46779	93.12399	1.173183
10.2	89.50835	94.21931	0.920965
11.2	90.33146	95.08574	0.734286
12.2	90.99215	95.78121	0.593498
13.2	91.52935	96.34669	0.485546
14.2	91.97119	96.81178	0.401543
15.2	92.33834	97.19825	0.335309
16.2	92.64626	97.52238	0.282463
17.2	92.90666	97.79649	0.239843
18.2	93.12857	98.03008	0.205134
19.2	93.31899	98.23052	0.176615
20.2	93.48343	98.40361	0.152989
21.2	93.62627	98.55397	0.133269
22.2	93.75102	98.68528	0.116695
23.2	93.86051	98.80054	0.102676
24.2	93.95706	98.90217	0.090746
25.2	94.04257	98.99218	0.080538
26.2	94.11861	99.07223	0.071757

APPENDIX A5

ANALYSIS OF ADSORPTION ISOTHERMS FOR ALL COLLECTED DATA

TASMAN DATA

SAMPLE	Solids Conc (MLS	Effl. Conc (Ce)	qe	Experimental (Co-Ce)/Co*100	
	g/L	µg/L	µg/g		Average Ce
	T<2kD	T<2kD	T<2kD	T<2kD	µg/L
U3	0	1221		-2.77778	1188
U4	0	1155		2.777778	
U5	0.982667	792.9476	402.0208	33.25357	
U6	1.015333	805.8794	376.3499	32.16504	
U7	2.860667	727.0252	161.1424	38.80259	
U8	2.919333	769.9026	143.2167	35.19338	
U9	6.426	718.5786	73.05033	39.51359	
U10	4.376667	778.8588	93.48237	34.43949	
U11	4.36	704.8937	110.8042	40.66552	
U12	6.314667	716.8111	74.61817	39.66236	
U13	8.548667	646.1452	63.38472	45.61068	
U14	8.415333	677.4236	60.67215	42.97781	

					Average Ce
	T2-30kD	T2-30kD	T2-30kD	T2-30kD	µg/L
P3	0	827.8425		0.692244	833.6131
P4	0	839.3837		-0.69224	
P5	0.813333	785.2775	59.42897	5.798321	
P6	0.892	764.7383	77.21389	8.262201	
P7	2.921333	740.6543	31.82069	11.15132	
p8	2.496667	736.0977	39.05824	11.69792	
P9	4.141333	698.1873	32.70101	16.24564	
P10	4.106	738.9599	23.05241	11.35457	
P11	6.03	680.6365	25.36926	18.35104	
P12	6.17	688.0646	23.58971	17.45996	
P13	7.976	665.2422	21.10969	20.19773	
P14	7.965333	669.0172	20.66404	19.74488	

					Average Ce	
	T30-100kD	T30-100kD	T30-100kD	T30-100kD	µg/L	Ki=
Control	0	332.601		0	332.601	
X3A	1.335333	291.38	30.86948	12.39354		
X4A	2.882	264.8738	23.50007	20.3629		
X5A	4.471333	234.9268	21.84452	29.36676		
X6A	6.588667	168.8374	24.85535	49.23726		
X7A	8.759333	119.4789	24.33086	64.07741		
X3B	1.134667	287.5658	39.69024	13.54031		
X4B	2.623333	252.4261	30.56222	24.10543		
X5B	4.367333	199.4749	30.48225	40.02578		
X5C	4.226667	206.7758	29.76936	37.83066		
X6B	6.662667	110.3206	33.36207	66.83094		
X7B	8.586667	59.12126	31.84935	82.22457		

SAMPLE	Solids Conc (M) g/L T>100kD	Effl. Conc (Ce) µg/L T>100kD	qe µg/g T>100kD	Experimental (Co-Ce)/Co*100 T>100kD	Average Ce
2A	0	279.3053		2.359524	µg/L
2B	0	292.8043		-2.35952	286.0548
3A	0.964	194.2228	88.25984	32.10294	
4A	2.373333	154.0943	52.75743	46.1312	
5A	3.754667	117.4669	43.10325	58.93552	
6A	5.724	38.87586	42.00374	86.40965	
7A	7.764	0	35.9744	100	
3B	0.999333	191.9641	100.9075	32.89254	
4B	2.401333	145.2131	61.46219	49.23591	
5B	4.054	88.46279	50.40492	69.07488	
6B	5.988	35.81804	42.91688	87.47861	
7B	7.976667	18.35247	34.40684	93.58428	

				qe using model Co (3123.9) µg/g		Experimen (Co-Ce)/Co
	Tunfr	Tunfr	Tunfr	Tunfr		Tunfr
T2A	0	2871.858			Average Ce	8.068176
T2B	0	2790.638			µg/L	10.66815
T3A	0.922667	3556.747	-742.292	-469.126	2831.248	-13.856
T4A	2.570667	2841.74	11.7161	109.7614		9.032298
T5A	4.188667	2481.439	93.2084	153.3807		20.56598
T6A	6.446667	1480.149	215.8804	254.9768		52.61854
T7A	8.225333	1271.637	194.5479	225.19		59.29328
T3B	0.937333	2766.509	25.74156	381.2845		11.44053
T4B	2.661333	2470.94	120.127	245.3508		20.90208
T5B	4.336	1786.725	231.5297	308.3891		42.80467
T6B	6.615333	1679.626	167.9449	218.3221		46.23303
T7B	8.579333	1124.41	194.2141	233.0589		64.0062

KINLEITH DATA

SAMPLE	Solids Conc (M) g/L K<2kD	Effl. Conc (Ce) µg/L K<2kD	qe µg/g K<2kD	Experimental (Co-Ce)/Co*100 K<2kd	Average Ce µg/L
U3	0	1194.874		1.672525	1215.199
U4	0	1235.523		-1.67253	
U5	0.753333	830.3951	510.8013	31.6659	
U6	0.796667	975.0779	301.407	19.75981	
U7	2.006	595.0832	309.1304	51.02997	
U8	2.035333	669.2618	268.2298	44.92573	
U9	3.344667	642.0014	171.3765	47.16902	
U10	3.360667	691.8694	155.7219	43.06533	
U11	5.252	638.3298	109.838	47.47116	
U12	5.186667	625.1058	113.7711	48.55938	
U13	6.95	652.6458	80.94288	46.29308	
U14	6.688	639.3764	86.09784	47.38503	

	K2-30kD	K2-30kD	K2-30kD	K2-30kD	Average Ce µg/L
P3	0	795.5763		-0.73197	789.7953
P4	0	784.0142		0.731971	
P5	0.825333	796.8294	-8.52279	-0.89063	
P6	1.004667	761.8926	27.77308	3.532902	
P7	1.919333	718.935	36.91918	8.971973	
p8	2.095333	770.3268	9.291323	2.464996	
P9	3.524667	680.3175	31.06044	13.86153	
P10	3.425333	716.4906	21.40074	9.281477	
P11	5.19	695.3609	18.19544	11.95681	
P12	5.169333	706.476	16.118	10.54948	
P13	6.985333	650.217	19.98161	17.67271	
P14	7.038	671.3818	16.82488	14.99294	

	K30-100kD	K30-100kD	K30-100kD	qe using Co=252.3 µg/g K30-100kD	Average Ce µg/L	Experimen (Co-Ce)/Co K30-100kD
X3	0	247.4815	#VALUE!		247.8599	1.909843
X4	0	248.2384	#VALUE!			1.609847
X5	0.851333	253.1141	-6.17175	-0.9563		-0.32268
X6	1.074667	243.1663	4.367512	8.499109		3.620178
X7	2.362	223.899	10.14435	12.02415		11.25685
X8	2.222667	232.6427	6.846386	8.844027		7.79125
X9	4.116667	233.1235	3.57969	4.658255		7.600667
X10	4.154	212.7499	8.452108	9.520979		15.67584
X11	5.361333	210.972	6.880362	7.708531		16.3805
X12	5.342	194.9813	9.898658	10.72982		22.71848
X13	6.917333	185.4005	9.029402	9.671281		26.51584
X14	6.953333	189.2025	8.435864	9.074419		25.0089

SAMPLE	Solids Conc (M)	Effl. Conc (Ce)	qe	Experimental (Co-Ce)/Co*100	
	g/L	µg/L	µg/g		Average Ce
	K>100kD	K>100kD	K>100kD	K>100kD	µg/L
3	0	241.9145		-2.3575	236.3427
4	0	230.7709		2.357501	
5	1.132	217.8797	16.31007	7.811962	
6	0.808	213.5	28.27065	9.66507	
7	2.235333	194.8548	18.56007	17.55415	
8	2.259333	200.1868	16.00291	15.29808	
9	3.721333	184.2342	14.00265	22.04787	
10	3.881333	180.7027	14.33529	23.5421	
11	5.793333	146.0371	15.58785	38.2096	
12	5.716	132.4113	18.18254	43.97487	
13	7.743333	58.62688	22.95082	75.19412	
14	7.688667	102.1773	17.44976	56.7673	

					Average Ce
	Kunfr	Kunfr	Kunfr	Kunfr	µg/L
T3	0	2791.434		-1.10869	2760.825
T4	0	2730.217		1.108688	
T5	0.847333	2530.706	271.5809	8.335171	
T6	1.015333	2361.221	393.5696	14.47409	
T7	2.216667	2323.98	197.073	15.82299	
T8	2.514	2288.853	187.7375	17.09533	
T9	3.983333	2212.937	137.5453	19.84511	
T10	3.885333	2253.884	130.4756	18.36194	
T11	5.707333	2110.299	113.9808	23.56275	
T12	5.430667	2103.589	121.0232	23.8058	
T13	7.330667	2015.667	101.6495	26.99042	
T14	7.392667	1996.561	103.3815	27.68248	

Modelled Ce vs M results for Tas <2kD

Calculated Freundlich constants

Kf=	6.18E-13	1/n=	4.97	
M	Ce	(Co-Ce)/Co*100		qe(model)
g/L	µg/L			µg/g
0	1188	0		
0.034339	1153	2.946128		1019.249
0.080049	1118	5.892256		874.4686
0.140636	1083	8.838384		746.6067
0.220772	1048	11.78451		634.1384
0.326716	1013	14.73064		535.6331
0.466925	978	17.67677		449.7515
0.652912	943	20.6229		375.2421
0.900498	908	23.56902		310.939
1.231633	873	26.51515		255.758
1.677092	838	29.46128		208.6946
2.280531	803	32.40741		168.8203
3.104671	768	35.35354		135.28
4.240882	733	38.29966		107.289
5.824332	698	41.24579		84.12981
8.058396	663	44.19192		65.14944

Modelled Ce vs M results for Tas 2-30kD

Calculated Freundlich constants

Kf=	2.56E-13	4.93	
M	**Ce**	**(Co-Ce)/Co*100**	**qe(model)**
g/L	µg/L		µg/g
0	833.6131	0	
0.200277	821.6131	1.439517	59.917
0.430688	809.6131	2.879033	55.72476
0.695387	797.6131	4.31855	51.76973
0.999131	785.6131	5.758067	48.04176
1.347376	773.6131	7.197584	44.53099
1.746393	761.6131	8.6371	41.22784
2.203394	749.6131	10.07662	38.12301
2.726692	737.6131	11.51613	35.20749
3.325888	725.6131	12.95565	32.47253
4.01208	713.6131	14.39517	29.90967
4.798134	701.6131	15.83468	27.5107
5.698983	689.6131	17.2742	25.26766
6.732004	677.6131	18.71372	23.17289
7.917454	665.6131	20.15323	21.21894

Modelled Ce vs M results for Tas 30-100kD

Calculated Irreversible constants

Ki =	27.8	Co(Model)=	330.4	
M	**Ce**	**(Co-Ce)/Co*100**		**qe(model)**
g/L	µg/L			µg/g
0	330.4	0		#DIV/0!
0.8	308.16	6.731235		27.8
1.6	285.92	13.46247		27.8
2.4	263.68	20.1937		27.8
3.2	241.44	26.92494		27.8
4	219.2	33.65617		27.8
4.8	196.96	40.38741		27.8
5.6	174.72	47.11864		27.8
6.4	152.48	53.84988		27.8
7.2	130.24	60.58111		27.8
8	108	67.31235		27.8
8.8	85.76	74.04358		27.8
9.6	63.52	80.77482		27.8

Modelled Ce vs M results for Tas >100kD

Calculated Freundlich constants

Kf= 16.3 1/n= 0.255

M	**Ce**	**(Co-Ce)/Co*100**	**qe(model)**
g/L	µg/L		µg/g
0	286.0548	0	
0.280403	267.0548	6.642084	67.75958
0.571461	248.0548	13.28417	66.49626
0.874788	229.0548	19.92625	65.15866
1.192425	210.0548	26.56834	63.73565
1.527006	191.0548	33.21042	62.21325
1.882011	172.0548	39.85251	60.57349
2.262185	153.0548	46.49459	58.79272
2.674231	134.0548	53.13667	56.83876
3.12808	115.0548	59.77876	54.66613
3.639348	96.05479	66.42084	52.20715
4.234721	77.05479	73.06293	49.3539
4.965563	58.05479	79.70501	45.91624
5.951582	39.05479	86.34709	41.50157
7.59676	20.05479	92.98918	35.01493
8.336163	15	94.75625	32.51553
9.414726	10	96.50417	29.3216
11.43842	5	98.25208	24.57112
17.48802	1	99.65042	16.3

Modelled Ce vs M results for Tas Unfractionated sampl

Calculated Irreversible constants

Ki= 227.9 Co(Model)= 3123.9

M	**Ce**	**(Co-Ce)/Co*100**	**qe(model)**
g/L	µg/L		µg/g
0	3123.9	0	
0.8	2941.58	5.836294	227.9
1.6	2759.26	11.67259	227.9
2.4	2576.94	17.50888	227.9
3.2	2394.62	23.34518	227.9
4	2212.3	29.18147	227.9
4.8	2029.98	35.01777	227.9
5.6	1847.66	40.85406	227.9
6.4	1665.34	46.69036	227.9
7.2	1483.02	52.52665	227.9
8	1300.7	58.36294	227.9
8.8	1118.38	64.19924	227.9
9.6	936.06	70.03553	227.9
10.4	753.74	75.87183	227.9

Modelled Ce vs M results for Kin<2kD

Calculated Modified Langmuir constants

a= 519.9 b= 0.0133

Co 1215.2
Cr 595
a= 519.9
b= 0.0133

Langmuir model

M	A	B	C	Ce µg/L	:o-Ce)/Co*100	qe(model) µg//g	Cemin µg/L
0	-0.0133	23.07566	-8401.29	1215.2	-1.9E-14		595
0.5	-0.0133	19.61833	-6344.17	996.2716	18.01584	437.8569	595
1	-0.0133	16.16099	-4287.06	823.8642	32.20341	391.3358	595
1.5	-0.0133	12.70366	-2229.94	723.3834	40.47207	327.8778	595
2	-0.0133	9.24632	-172.828	675.989	44.3722	269.6055	595
2.5	-0.0133	5.788985	1884.286	652.4171	46.31196	225.1132	595
3	-0.0133	2.33165	3941.401	639.0447	47.41238	192.0518	595
3.5	-0.0133	-1.12569	5998.515	630.5904	48.1081	167.0313	595
4	-0.0133	-4.58302	8055.629	624.808	48.58393	147.598	595
4.5	-0.0133	-8.04035	10112.74	620.6195	48.92861	132.129	595
5	-0.0133	-11.4977	12169.86	617.4521	49.18926	119.5496	595
5.5	-0.0133	-14.955	14226.97	614.9757	49.39305	109.1317	595
6	-0.0133	-18.4124	16284.09	612.988	49.55662	100.3687	595
6.5	-0.0133	-21.8697	18341.2	611.358	49.69075	92.89877	595
7	-0.0133	-25.327	20398.32	609.9975	49.80271	86.4575	595
7.5	-0.0133	-28.7844	22455.43	608.8451	49.89754	80.84731	595
8	-0.0133	-32.2417	24512.54	607.8566	49.97888	75.91792	595
8.5	-0.0133	-35.699	26569.66	606.9995	50.04942	71.553	595
9	-0.0133	-39.1564	28626.77	606.2492	50.11116	67.6612	595
9.5	-0.0133	-42.6137	30683.89	605.587	50.16566	64.16979	595

Modelled Ce vs M results for Kin 2-30 kD

Calculated Irreversible constants

Ki= 18.4 Co(Model)= 786.1

M g/L	**Ce** µg/L	**(Co-Ce)/Co*100**	**qe(model)** µg/g
0	786.1	0	
0.8	771.38	1.872535	18.4
1.6	756.66	3.745071	18.4
2.4	741.94	5.617606	18.4
3.2	727.22	7.490141	18.4
4	712.5	9.362677	18.4
4.8	697.78	11.23521	18.4
5.6	683.06	13.10775	18.4
6.4	668.34	14.98028	18.4
7.2	653.62	16.85282	18.4
8	638.9	18.72535	18.4
8.8	624.18	20.59789	18.4
9.6	609.46	22.47042	18.4
10.4	594.74	24.34296	18.4

Modelled Ce vs M results for Kin 30-100 kD

Calculated Irreversible constants

Ki= 8.96 Co(Model)= 252.3

M g/L	**Ce** µg/L	**(Co-Ce)/Co*100**	**qe(model)** µg/g
0	252.3	0	
0.8	245.132	2.841062	8.96
1.6	237.964	5.682124	8.96
2.4	230.796	8.523187	8.96
3.2	223.628	11.36425	8.96
4	216.46	14.20531	8.96
4.8	209.292	17.04637	8.96
5.6	202.124	19.88744	8.96
6.4	194.956	22.7285	8.96
7.2	187.788	25.56956	8.96
8	180.62	28.41062	8.96
8.8	173.452	31.25168	8.96

Modelled Ce vs M results for Kin >100 kD

Calculated Irreversible constants

Ki= 19.1 Co(Model)= 240.4

M	**Ce**	**(Co-Ce)/Co*100**	**qe(model)**
g/L	µg/L		µg/g
0	240.4	0	
0.8	225.12	6.356073	19.1
1.6	209.84	12.71215	19.1
2.4	194.56	19.06822	19.1
3.2	179.28	25.42429	19.1
4	164	31.78037	19.1
4.8	148.72	38.13644	19.1
5.6	133.44	44.49251	19.1
6.4	118.16	50.84859	19.1
7.2	102.88	57.20466	19.1
8	87.6	63.56073	19.1
8.8	72.32	69.91681	19.1

Modelled Ce vs M results for Kin unfractionated

Calculated Freundlich constants

Kf= 4.25E-12 1/n= 4.05

M	**Ce**	**(Co-Ce)/Co*100**	**qe(model)**
g/L	µg/L		µg/g
0	2760.825	0	
0.162615	2705.825	1.992158	338.2229
0.353435	2650.825	3.984316	311.2308
0.577137	2595.825	5.976473	285.8938
0.839239	2540.825	7.968631	262.1422
1.146272	2485.825	9.960789	239.9081
1.50599	2430.825	11.95295	219.1249
1.927627	2375.825	13.9451	199.7275
2.422209	2320.825	15.93726	181.6523
3.002957	2265.825	17.92942	164.8375
3.68577	2210.825	19.92158	149.2226
4.489845	2155.825	21.91374	134.7485
5.438456	2100.825	23.90589	121.358
6.559932	2045.825	25.89805	108.995
7.888917	1990.825	27.89021	97.60529