ADSORPTION-DESORPTION CHARACTERISTICS OF PHENOXYACETIC ACIDS AND CHLOROPHENOLS IN A VOLCANIC SOIL

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requirements for the degree of *Doctor of Philosophy*
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To my Late Father

ABSTRACT

A study on the adsorption and desorption behaviour of 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP) and *para*-chloro-*ortho*-cresol (PCOC), found in high concentrations in a New Zealand landfill. Volcanic soil with an organic matter content of 8.7% was used as adsorbent.

Results of studies to determine the equilibrium sorption behaviour for each chemical showed the adsorption data for both phenoxyacetic acids and chlorophenols could be described by a Freundlich-type isotherm equation, the adsorption capacity followed the order: 2,4,5-T > MCPA > 2,4-D > 2,4,5-TCP > PCOC > 2,4-DCP at all pH and temperature values. Sorption capacity decreased with increasing pH and temperature; the heat of adsorption values indicating chemicals were adsorbed either by physical or hydrogen bonding to the soil surface. Results show only 2-4% of the total surface was occupied indicating chemical adsorption to specific sites present in the soil organic matter. The desorption results indicate isotherm parameters were dependent on the amount of each chemical adsorbed onto the soil. A linear relationship was developed to obtain the desorption parameters from the adsorption isotherm parameters. Desorption experimental results reveal that all the solutes adsorbed could not be desorbed, indicating a fraction of the chemical was resistant to desorption.

A modified Freundlich-type equation described the competitive equilibrium adsorption and desorption of 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC mixtures. The model incorporated competition coefficients and was found to fit measured data, satisfactorily. The competition coefficients were linearly related to the initial concentration of the solutes in case of adsorption, and on the amount of chemical adsorbed for desorption. The results showed that the adsorption capacity of each solute decreased by about 8-12% in presence of the other competing solutes. However, in case of MCPA, the capacity decreased by 31% in the presence of 2,4-D. The desorption results reveal that 2,4-D and MCPA desorbed to a lesser extent in the bicomponent system compared to the corresponding single solute system. Similarly, the desorption of

PCOC was less in the presence of 2,4-D than of MCPA compared to single solute system.

A spinning basket reactor determined the kinetics of sorption for phenoxyacetic acids and chlorophenols. The film-mass transfer coefficients determined from the initial uptake rate data for the first 45 seconds, while the surface diffusion coefficients were obtained by fitting the experimental results with a homogeneous surface diffusion model solution. The desorption diffusion coefficients were found to be of the same order of magnitude as those of adsorption diffusion coefficients. The bicomponent surface diffusion coefficients were found to be slightly smaller (less than 10%) than single solute surface diffusion coefficients and this was due to competition between the solutes.

A surface diffusion model based on equilibrium sorption, film-mass transfer and surface diffusion coefficient along with dispersion was used to predict the soil column data. All the parameters in the model were determined from independent experiments or calculated from literature correlations. The results from the column studies indicate that an increase in the concentration and flow rate resulted in the solutes moving faster in the column. A significant tailing of the chemical was observed at low concentrations for all the solutes. The results indicate that sorption played a dominant role in the transport of chemicals in columns. The breakthrough and elution for phenoxyacetic acids was in the order: 2,4-D > MCPA > 2,4,5-T. For chlorophenols the order was: 2,4-DCP > PCOC > 2,4,5-TCP. The HSDM also used to predict the adsorption and desorption of bicomponent mixtures and the results indicated that the breakthrough and elution occurred earlier than in single solute systems. The order of breakthrough and elution was PCOC > 2,4-D > MCPA.

To conclude, this thesis presents a detailed investigation of the adsorption and desorption characteristics of phenoxyacetic acids and chlorophenols for single and dual component systems in a volcanic soil. This study has identified the mechanisms and processes responsible for the leaching of the chemicals and can be used in remediation of a contaminated soil.

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CHAPTER 1
INTRODUCTION

1.1 Introduction

The disposal of solid wastes containing toxic chemicals into landfills is commonly practised by many chemical and other industries. However, these discarded chemicals, over a period, trickle through the soil and sometimes reach the groundwater. The behaviour and fate of these chemicals are strongly affected by the sorption characteristics of the soil. Therefore, sorption phenomena constitutes the first step in understanding the fate of these chemicals.

Data on organic chemicals in surface waters and groundwaters in New Zealand are sparse. In recent years major soil and surface water contamination, was caused by DowElanco Ltd. (New Zealand), manufactures of phenoxy herbicides for weed control, disposed of wastes containing phenoxy herbicides and sludges in a landfill, constructed on an elevated coastal site. In 1982, odours from these chemicals were reported at the adjacent foreshore; subsequent investigations revealed herbicide chemicals seeping from the base of the cliff top. DowElanco immediately shifted the contaminated soil and chemicals into a secure landfill and is currently investigating various options for decontamination. An analysis of the contaminated soil revealed a large number of chemicals were present in the landfill, of which three phenoxyacetic acids namely, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2-methyl-4-chlorophenoxyacetic acid (MCPA) and three chlorophenols, 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP) and *para*-chloro-*ortho*-cresol (PCOC) are in high concentrations.

The migration of organic chemicals is affected by a number of processes taking place in the soil profile. For example, the sorption processes can prevent the chemicals from moving with water. Soil microbial populations can degrade the chemicals, the degradation products sometimes posing additional pollution problems in the environment. Organic chemicals can also be transported to the atmosphere by volatilization or into the surface water by run off from soil, or be removed from the soil by plant uptake. The transport of organic chemicals to groundwater will further depend upon a combination of factors including the nature of the chemical, the properties of the soil, climatic and environmental factors. The potential for organic chemicals to reach groundwater include evaluation of all the processes and factors having an impact on the transport through the soil. The present study investigates the adsorption/desorption characteristics and leaching of these chemicals using volcanic soil which is taken from the landfill site.

Sorption and transport of organic chemicals in soils has been studied extensively (Bailey and White, 1970; Van Genuchten *et al.*, 1977; Rao and Davidson, 1980; Khondaker *et al.*, 1990; Weber *et al.*, 1991), although it is not yet fully understood. While the equilibrium, kinetics and transport of different pesticides are well documented in literature, in most studies only single component systems are considered. In the majority of the single solute transport models, the parameters were determined from curve fitting techniques, which is the major limitation in these studies.

The objectives of this research are:

- to examine the equilibrium adsorption and desorption of phenoxyacetic acids and chlorophenols;
- to investigate the kinetics of sorption processes; and
- to predict transport through laboratory soil columns. Wherever possible, independently determined model parameters will be used to predict the transport of solutes in soil columns.

Three phenoxyacetic acids and three chlorophenols, as mentioned earlier, were chosen to examine the sorption behaviour in a single component system, and three bicomponent mixtures, namely 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC were chosen to determine the fate of these chemicals in soil.

1.2 Thesis arrangement

After a brief explanation of the pollution problem due to discarded agricultural chemicals (Chapter 1), the thesis proceeds to give a general review of the literature of organic chemical-soil interactions, kinetics and solute transport (Chapter 2). Soil characteristics and chemicals used in this study are provided in Chapter 3 together with details of the experimental and analytical methods.

Chapter 4 describes the results of equilibrium adsorption-desorption in single and bicomponent systems. The effect of various environmental factors, such as pH and temperature is given. A brief discussion on the mechanisms of adsorption of phenoxyacetic acids and chlorophenols is presented. The results of bicomponent sorption, for a range of initial concentrations, are also presented and a model, available in the literature, is modified to predict the adsorption and desorption processes.

The discussion on sorption kinetics is presented in Chapter 5 for single and bi-component systems. A basket-type batch adsorber is used to obtain the kinetic data. A widely used homogeneous surface diffusion model (HSDM) is applied to predict the single solute mass transfer and surface diffusion coefficients. The single component model equations were extended to bicomponent systems to evaluate the bicomponent surface diffusion coefficients.

The transport of phenoxyacetic acids and chlorophenols in laboratory soil columns is given in Chapter 6. A number of experiments were carried out to examine the movement of single and bisolutes in fixed bed columns. The effects of initial concentration and flow rate on the breakthrough and elution of solutes were studied for single component systems. The equilibrium and kinetic parameters developed in Chapters 4 and 5 were used to predicted the transport in single and bicomponent systems. The results of transport of solutes in bicomponent mixtures are also presented. Finally, in Chapter 7, conclusions from this study are presented.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Environmental pollution from agricultural chemicals is of growing concern today due to the excessive use of pesticide chemicals. Once the chemical reaches the soil environment, it is subjected to various physico-chemical interactions of which adsorption-desorption characteristics are the most important (Weber *et al.,* 1991). This chapter gives a review of various factors that influence the adsorption-desorption in soil.

2.2 Soil constituents

A typical soil environment contains solid, liquid and gaseous phases (Hamaker and Thompson, 1972). For the adsorption and desorption of organic chemicals the characteristics of the solid phase are the most important. The major adsorbing surfaces in soil are clays, organic matter (OM) and amorphous minerals (Wu *et al.*, 1975; Morrill *et al.*, 1982). As clays and OM in soils do not exist as separate entities, it is often not possible to know which soil component is involved in the sorption process (Kliger and Yaron, 1975).

Clays represent layers of silica and aluminium sheets, each silica sheet consists of a silicon atom surrounded by four oxygen atoms in a tetrahedral symmetry. On the other hand, the alumina sheet has aluminium atoms coordinated by six oxygen or hydroxyl groups in an octahedral fashion. Isomorphic substitution of Al^{3+} or Fe^{3+} for Si^{4+} in the tetrahedral layer, and Mg^{2+} for Al^{3+} in the octahedral layer, produce a change in the net charge on the surface, the generated negative charge being responsible for organic chemical adsorption. Clays are characterized by properties such as lattice expansion, cation exchange capacity (CEC) and surface area. The typical surface area of clays is between 600 and 800 m^2/g. Adsorption of organic chemicals by clays differs from other soil components because of CEC, strength of the negative charge, specificity of adsorption sites and the nature of the cation on the exchange complex (Calvet, 1980).

Soil organic matter is formed by the degradation of plant and animal tissues. The major constituents of OM are polymeric organic acids, which are mainly humic acid, fulvic acid and humin. OM is characterized by its solubility in an alkali or in an acid. The acid component of OM is commonly known as fulvic acid, whereas the alkali component is humic acid. Humin is the insoluble component. Soil OM also possesses a large surface area (500-800 m^2/g) and its cation exchange capacity is in the range of 200-400 meq/100 g. The large surface area and the presence of various functional groups are responsible for high adsorption capacity (Haque, 1974). The adsorption of organic chemicals onto OM varies from soil to soil because of differences in composition, presence of various functional groups and the degree of cation saturation (Morrill *et al.*, 1982).

Amorphous mineral colloids are oxides of aluminium, silicon and iron. These are formed by the weathering of soil minerals often serving as cementing agents (Wada and Harward, 1974). Amorphous materials are amphoteric in nature and their reactivity is strongly influenced by pH (Morrill *et al.*, 1982). Presence of Al and Fe in amorphous minerals can influence organic chemical behaviour by acting as exchangeable ions on the exchange complex (Adams, 1972). The CEC of amorphous minerals varies from 5 to 30 meq/100 g and is responsible for most of the anion adsorption in soils. The surface area of amorphous minerals is in the range of 100-800 m^2/g (Morrill *et al.,* 1982).

2.3 Adsorption-desorption characteristics

The literature on sorption of organic chemicals in soil and on soil components is voluminous. Literature citations in this review are limited to studies that appear to be significant in natural soil systems, recognizing the complexity of soil-solute interactions.

2.3.1 Adsorption

Adsorption may be defined as the spontaneous deposition of a solute onto a solid surface resulting from the interaction between the fields of force of the adsorbent and the molecules or ions of the adsorbate (Rao, 1990). It is either positive (favourable) or negative (unfavourable) depending whether the adsorbate is attracted or repelled by the adsorbent. Positive adsorption from a solution occurs when there is an attraction between the adsorbate and the adsorbent resulting in higher concentration of adsorbate at the liquid-solid interface than in bulk solution. Negative adsorption occurs when there is a higher adsorbate concentration in the bulk solution than at the liquid-solid interface (Hamaker and Thompson, 1972).

The adsorption process of organic chemicals including phenoxyacetic acids and chlorophenols onto soils and sediments, has been critically evaluated and summarized in several review articles (Hamaker and Thompson, 1972; Calvet, 1980; Karickhoff, 1981, 1984; Morrill *et al.*, 1982; Rao *et al.*, 1982; Chiou, 1989; Weber *et al.*, 1991). The major factors influencing adsorption are:

- physical and chemical characteristics of the soil constituents - pH, % organic carbon (OC), clay fraction, surface area, and surface charge;
- nature of the organic chemical - ionization constant (pK_a), solubility, charge on the molecule, molecular size, and polarity; and
- pH and temperature of the system.

The prevailing hypothesis is that, for sorption of nonionic organic chemicals, organic matter is the dominant sorbent. Sorption is envisioned as a partitioning process, in which the sorbate permeates into the organic matter. The majority of the reported studies (Karickhoff, 1981; Chiou, 1989; Che *et al.,* 1992; Haderlein and Schwarzenbach, 1993; Dell *et al.,* 1994; and Kan *et al.,* 1994) on organic chemical sorption onto soils were done at low concentrations. The important conclusions from these investigations are:

- linear sorption isotherms over a considerable concentration range;
- existence of an inverse, linear relationship between solute aqueous solubility and adsorption capacity;
- low heats of adsorption (4-7 kcal/mole); and
- absence of competitive sorption when solutes are present as mixtures.

The adsorption of phenoxyacetic acids, 2,4-D, 2,4,5-T and MCPA, on clay materials was investigated by Frissel (1961), Weber *et al.* (1965), Bailey *et al.* (1968) and others. Bailey *et al.* (1968) found no significant adsorption of phenoxyacetic acids by montmorillonite clay at high pH values. The authors also report that positive adsorption of these acids occurs when the pH is below the dissociation constant (pK_a) of the acids, i.e., when compounds are in molecular form.

Harris and Warren (1964) examined the adsorption of 2,4-D and other herbicides in relation to pH, temperature, and the nature of the adsorbent. All herbicides investigated by them showed increased adsorption at low pH values. Also, an organic soil was found to adsorb more in comparison to a clay soil. The adsorptive behaviour of 2,4-D onto various synthetically prepared organo-clay complexes, which are similar to naturally occurring organo-complexes of soil, was investigated by Miller and Faust (1972) and Khan (1974). Khan (1974) reports that the adsorption of 2,4-D onto these complexes is higher than onto clays. Similar results are reported in Miller and Faust (1972). The adsorption of 2,4,5-T onto four different soils was examined by O'Connor and Anderson (1974). The results of their study indicate that when 2,4,5-T is adsorbed to the organic matter in the soil, adsorption capacity increased with increasing organic matter content.

The adsorption of 2,4-D and some other selected herbicide chemicals, at high concentration were investigated by Rao and Davidson (1979) on three different soils. They conclude that Freundlich-type isotherms describe pesticide adsorption over the concentration range, and the adsorption isotherms are favourable and nonlinear. The uptake of 2,4-D onto Ohakea silt loam is described by a Freundlich isotherm (Bhamidimarri and Petrie, 1992). Mallawatantri and Mulla (1992) report similar results for 2,4-D adsorption onto Naff silt loam.

The sorption studies of chlorophenols onto soils are limited. Boyd (1982) investigated the adsorption of chlorophenols including 2,4-DCP and 2,4,5-TCP, the results indicating that the adsorption capacity increased as the number of chlorine atoms increased on the molecule. Schellenberg *et al.* (1984) found that the sorption of chlorophenols by sediments and aquifer materials is due to solute partitioning. The resulting isotherms are linear over a wide range of solute concentrations and dependent on the soil organic matter. The adsorption of PCOC onto Ohakea silt loam is described by a nonlinear Freundlich type isotherm (Bhamidimarri and Petrie, 1992). Bellin *et al.* (1990) reports that the adsorption of pentachlorophenol (PCP) onto soil is described as a Freundlich isotherm.

While studies on the competitive sorption of organic chemicals onto soils has been investigated by several researchers, their results have generally shown no competition for nonionic solutes (Karickhoff *et al.*, 1979; Chiou *et al.*, 1983). However, some researchers report relatively small decreases in sorption resulting from competition (McGinley *et al.*, 1993). The sorption of trichloroethene (TCE) and p-xylene from single and bicomponent solutions by two aquifer materials was examined by Lee *et al.* (1988). They observed no difference in sorption between the single and binary systems. The sorption of trichloroethylene by a sandy aquifer material in single and ternary-solute systems is the same (Brusseau and Rao, 1991).

2.3.2 Desorption

The reversibility of the sorption process plays a significant role in determining the behaviour and fate of an organic chemical in the soil, that is, whether the chemical is adsorbed permanently onto the solid phase or released back into solution in reaction to a decrease in solution concentration.

Studies of solute desorption from soils are scarce and inconclusive (Voice and Weber, 1983). Desorption experiments are usually performed in conjunction with adsorption studies to determine the reversibility of freshly adsorbed compounds onto soil matrix. However, in many instances the time frame and conditions usually encountered in the field are difficult to simulate in the laboratory.

In modelling solute transport, the adsorption/desorption process is often simplified by assuming ideal conditions of instantaneous equilibrium, isotherm linearity and desorption reversibility (Brusseau and Rao, 1989). However, considerable field and laboratory data deviate from that predicted by this simple model approach. As a result, the assumption of ideal behaviour has been challenged by many researchers (Ball and Roberts, 1991; Pavlostathis and Jaglal, 1991).

Adsorption/desorption behaviour of a solute which does not conform to the ideal conditions has been attributed to several different factors, including the following:

- varying adsorption energies, leading to isotherm nonlinearity, i.e., a Freundlich type isotherm (Brusseau and Rao, 1989);
- failure to attain equilibrium in either the adsorption or the desorption directions due to slow kinetics in either step (Wu and Gschwend, 1986);
- chemisorption of the solutes to various components of the soil matrix, leading to irreversible adsorption (Brusseau and Rao, 1989);
- either biotic or abiotic degradation of the solute being studied, causing an apparent irreversible adsorption (Miller and Pedit, 1992);
- adsorption/desorption hysteresis (Brusseau and Rao, 1989); and
- experimental procedures, such as centrifugation *versus* dilution (Bowman and Sans, 1985).

Harris and Warren (1964) studied the desorption of 2,4-D from muck soil and report that successive extractions with distilled water desorbed only half of the initially adsorbed 2,4-D; the concentrations of the herbicide in the final extracts are extremely low. Van Genuchten *et al.* (1974) and O'Connor *et al.* (1980) investigated the adsorption and desorption characteristics of 2,4,5-T on Glendale clay loam and observed that the adsorption and desorption isotherms are different, desorption depending strongly on the amount adsorbed onto the soil at equilibrium. Karickhoff and Morris (1985) studied the long-term desorption of organic contaminants, reporting that the final portion of the sorbed material (10% of the initial sorbed mass) tended to desorb very slowly.

Che *et al.* (1992) examined the desorption of the herbicides, imazaquin and imazethapyr, from clays and found that most of the desorption occurred in the first cycle with 100% of the adsorbed herbicide desorbed after five desorption cycles. Bhamidimarri and Petrie (1992) report that the desorption of 2,4-D and PCOC from Ohakea silt loam is 82 and 84%, respectively, the desorption rate of these compounds was found to be a function of the amount of solute adsorbed onto the soil. Chen and Maier (1992) observed that only 15% of phenanthrene is desorbed after first re-equilibration; after 7 days, 55% of the total adsorbed could be desorbed.

Grathwohl and Reinhard (1993) examined the desorption behaviour of TCE onto aquifer materials for different time scales. When the equilibration time is short (23 min) 96% of the adsorbed solute was removed from the soil. However, when the equilibration time is longer than 5 days, only 73% of the TCE was desorbed. When desorption of naphthalene from a contaminated soil was examined, Connaughton *et al.* (1993) report that 70-80% of the sorbed naphthalene could be easily desorbed, the remainder showing increased resistance to desorption.

2.3.3 Hysteresis

Hysteresis is observed when, for a given equilibrium concentration solution, more chemical is retained on the soil during the desorption phase than the adsorption phase. The concept and existence of *true* hysteresis in adsorption and desorption is well documented (Brusseau and Rao, 1989; Adamson, 1990). Adamson (1990) suggests that there are three major types of hysteresis loop shapes: two types of closed-loop hysteresis where the desorption is 100% complete, and one type where a fraction of the solute is irreversibly bound to the adsorbent (even at zero solution-phase concentration). While most of these observations are based upon the adsorption of gases onto various solids, the same arguments are extended to the adsorption of organic solutes from aqueous solution onto porous adsorbents (Kan *et al.*, 1994).

Kan *et al.* (1994) suggests that the open-loop type of hysteresis, observed in soil-solute systems, is probably due to a mechanical or structural rearrangement of the adsorbent, i.e., the solid from which desorption takes place is different from that during adsorption. This type of hysteresis is simply termed as irreversible adsorption. Based on experimental results, Kan *et al.* (1994) suggests three types of anomalous adsorption/desorption behaviour: apparent hysteresis, which is the result of some experimental artifact; true hysteresis, which is time invariant and repeatable; and irreversible adsorption, which is generally associated with some rather permanent change in the adsorbent/adsorbate system.

Swanson and Dutt (1973) and Hornsby and Davidson (1973) were the first to report hysteresis in soil systems. Hysteresis in sorption isotherms of hexachlorobiphenyl on sediments is observed by Horzempa and Di Toro (1983). A number of studies show - that a fraction of the sorbed solute at the end of adsorption cycle is difficult to remove after several desorption steps, attributing this to hysteresis in adsorption-desorption (Swanson and Dutt, 1973; Rao and Davidson, 1980). Pavlostathis and Jaglal (1991) also observed hysteresis in the adsorption and desorption of TCE from silty clay. Recently, Kan *et al.* (1994) reports hysteresis in adsorption and desorption behaviour of naphthalene, phenanthrene and p-dichlorobenzene from soils and sediments.

2.3.4 Effect of pH

The acidity of an adsorbent system is usually measured by the pH of the solution in contact with the solid phase. Calvet (1980) found the pH of the solution has a marked effect on adsorption of organic chemicals onto soil, reporting three variations of adsorption: adsorption of weak bases on negatively charged adsorbents - clays, humic acids; adsorption of weak acids on positively charged adsorbents - oxides and hydroxides; and adsorption of neutral molecules on clays and soils.

The important feature of weak acids and weak bases is that they exist as ions or neutral molecules depending on solution pH. Weak acids are in molecular form at low solution pH, whereas weak bases are converted to cations at low pH (Hamaker and Thompson, 1972). The degree of association or dissociation of an organic chemical is a function of its pK_a. A compound, when present in molecular form or in ionic form, affects the extent and magnitude of adsorption and the strength by which it is held, because the adsorption can be different between the associated and dissociated forms (Hermosin and Cornejo, 1993).

The influence of pH on phenoxyacetic acids adsorption onto clays was studied by several researchers (Bailey *et al.*, 1968; Hermosin and Cornejo, 1993). These authors report that the positive adsorption of phenoxyacetic acids occur when the pH of the solution is near or below the pK_a of the compound. Fontaine *et al.* (1991) observed a clear trend of increasing sorption with decreasing pH for the acid herbicide, flumetsulam. The authors attribute this to the presence of a large proportion of neutral molecules at low pH values. Also, the flumetsulam sorbs to the soil more strongly than the anionic form. The pH dependence of adsorption has been reported for other acid herbicides (Walker *et al.*, 1989; Stougaard *et al.*, 1990). Che *et al.* (1992) evaluated the effect of pH on sorption for two herbicides and observed that sorption increased as pH decreased. The amount of 2,4-D adsorbed onto clays decreased continuously when pH increased from 0.7 to 8 (Hermosin and Cornejo, 1993).

Hassett and Banwart (1989) investigated the adsorption of chlorophenols on soils and report that chlorophenols are also adsorbed below their pK_a values. For chlorophenols with low pK_a values, especially PCP, the overall uptake at normal soil pH is relatively low because a high fraction of the compound is ionized. The sorption of pentachlorophenol is shown to depend on the proportion of anion to neutral forms (Lee *et al.*, 1990). Haderlein and Schwarzenbach (1993) report that the sorption of nitrophenols onto kaolinites is strongly influenced by the solution pH with maximum sorption occurring below the pK_a value of the respective compounds.

The observed increase in adsorption capacity at low pH is explained by the effects of hydrogen ions on solute and on the adsorbent. Protons cause conformational modifications of humic substances and hydrolyse the clay lattices. Hydrolysis of clays brings Al^{+3} and Fe^{+3} ions to the surface, which are more or less covered by hydroxides. These compounds are highly adsorbent and are frequently responsible for observed increases in adsorption at low pH (Calvet, 1980). When adsorption is maximum the corresponding pH is sometimes the pK_a value. However, this is not a general rule as it is sometimes coincidental.

2.3.5 Effect of temperature

In general, adsorption processes are exothermic, while desorption processes are endothermic (Rao, 1990). This variation of temperature effects surface-solute, and water-solute interactions, the balance between the two effects resulting in adsorption increasing, decreasing or remaining unaffected (Calvet, 1980). In general, for neutral organic compounds, the isosteric heats of adsorption (ΔH), which measure the strength of sorption, are relatively low; increased sorption capacity is not associated with comparable increases in ΔH (Chiou *et al.*, 1979).

Harris and Warren (1964) studied the effect of temperature on the adsorption of 2,4-D by clays and a muck soil and found that the adsorption of 2,4-D by bentonite is greater at 0°C than at 50°C, while in muck soil (high organic matter soil) the extent of adsorption at 0°C and 50°C is similar. The authors attribute this lack of temperature dependence for muck soil to its ion-exchange mechanism. Khan (1973, 1974) also examined the adsorption of 2,4-D at two different temperatures onto organo-clay complexes and reports that the adsorption capacity decreased as the temperature was increased from 5 to 25°C. The above results indicate that the sorption capacity is generally influenced by temperature.

On the other hand, the sorption of nonpolar organics was found to be independent of temperature (Chiou *et al.*, 1979; Hassett *et al.*, 1980). While these authors have obtained identical isotherms and constants at 15, 25 and 35°C for this class of compounds, the lack of temperature dependence is attributed to similar enthalpies of the solutes in solution and in the organic phases of soil (Chiou *et al.*, 1979). Nonpolar organic solutes form weak van der Waal bonds with the solvent (water) as well as with the sorbent - hence the sorption is independent of temperature (Hassett *et al.*, 1983).

2.3.6 Adsorption mechanisms

Sorption processes are driven by a variety of forces and/or mechanisms effecting the relative bonding of the solute and sorbent *versus* the solvent and solute (Hassett and

Banwart, 1989). The mechanisms and bond energies of organic chemicals adsorption onto soils are listed in Table 2.1.

Table 2.1 Bonding mechanisms of organic chemicals in soils (Morrill *et al.*, 1982).

Mechanism	Reported Bonding Energies (kcal/mole)	Chemical Types
Hydrogen bonding	0.5-15	Carbonyls, aliphatic amines, chlorophenols.
van der Waals	1-2	Larger molecules: 2,4-D on OM, picloram, linuron.
Coordination	-	Amitrol, ureas, amino acids, alcohols.
Ion exchange	upto 50	Amines, acids and/or ionized bases, hydroxides, sulfonate and sulphite surfactants.
Chemisorption	30-190	Amines and pyridines on Mg- and Ca saturated clays.

Physical adsorption results from electrostatic interactions between atoms, ions and molecules due to the electron fluctuations producing instantaneous dipoles. The van der Waals interactions are weak and decrease rapidly with the distance between the interacting species. Examples of physical adsorption are linuron and 2,4-D on humic acids (Morrill *et al.*, 1982).

Hydrogen bonding is a partial charge transfer interaction in which the hydrogen atom serves as a bridge between two electronegative atoms, one held by covalent bond, the other by electrostatic forces (Hadzi *et al.*, 1968). The presence of oxygen-containing functional groups and amino groups on organic matter indicates that the adsorption could occur by the formation of a hydrogen bond with the organic chemicals containing similar groups (Morrill *et al.*, 1982). The energy of adsorption in hydrogen bonding varies from 0.5 to 15 kcal/mole. The adsorption of 2,4-D on clays (e.g., montmorillonite) involves hydrogen bonding of the C=O group to the hydroxyls of the clay surface (Hermosin and Cornejo, 1993).

Ion (cation/anion) exchange is a process in which one type of ion is taken from solution in exchange of another type present on soil. The columbic forces of attraction are very large (50 kcal/mole). When organic molecules become positive by protonation (amine, alcohol, carbonyl groups), ions are adsorbed on clays depending on the CEC of the clay minerals. Protonated forms of atrazine and prometryn are adsorbed on clay complexes by ion exchange mechanism (Morrill *et al.*, 1982). Anion exchange reactions are not well defined as cation exchange reactions in soils, in general, anions are adsorbed either electrostatically or with a degree of chemical bonding by soils (Hassett and Banwart, 1989).

Coordination is an important mechanism in the adsorption of nonionic polar molecules. The coordination complexes are formed by the donation of electron pairs by the ligand and the acceptance by the metal resulting in the filling or partial filling of orbitals. Khan (1974) reports that the adsorption of linuron on montmorillonite is due to coordinate bonding.

In chemisorption, electrons are redistributed in new orbitals and a permanent chemical bond is formed. Chemisorption is exothermic with an energy range of 30-190 kcal/mole (Calvet, 1980). The adsorption of nemagon on illites is due to chemisorption (Morrill *et al.,* 1982).

Hydrophobic sorption is due to partitioning of the nonpolar organic from the polar aqueous phase into hydrophobic surfaces in the soil (Hassett and Banwart, 1989). A feature of hydrophobic bonding is the weak interaction between the solute and the solvent. The primary force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the solute from solution. The adsorption of a number of nonpolar organic chemicals is due to hydrophobic sorption (Chiou *et al.*, 1979; Chiou, 1989).

The two important mechanisms by which phenoxyacetic acids and chlorophenols adsorb onto soils are hydrogen bonding and physical adsorption (Boyd *et al.*, 1989; Hermosin and Cornejo, 1993).

2.3.7 Single component isotherm models

The first and the most important characterization of soil-chemical interaction due to adsorption is in terms of equilibrium behaviour. An equilibrium isotherm is obtained by plotting the amount of chemical adsorbed per unit mass of adsorbent *versus* the solution phase concentration at constant temperature under equilibrium conditions (Weber *et al.*, 1991). Examples of different equilibrium patterns are shown in Figure 2.1. Some of the models frequently used to describe equilibrium patterns of organic chemicals in soils are described below.

2.3.7.1 Linear isotherm

Linear isotherm is frequently used to describe adsorption of chemicals onto soils at low concentrations. In this model, the amount of chemical adsorbed onto adsorbent is directly proportional to the equilibrium concentration as,

$$q = K_d C_e \tag{2.1}$$

where, K_d is the distribution coefficient indicating the retention of the chemical by the soil. The linear isotherm model was used by Rebhun *et al.* (1992) to describe the uptake of di- and tri-chlorobenzene (DCB and TCB) onto various soils. The authors explain that the linearity is due to low surface coverage of DCB and TCB. Farrell and Reinhard (1994a) also obtained linear isotherms for the adsorption of trichloroethylene and tetrachloroethene (PCE) onto Norwood soil attributing this to the organic matter partitioning of solutes.

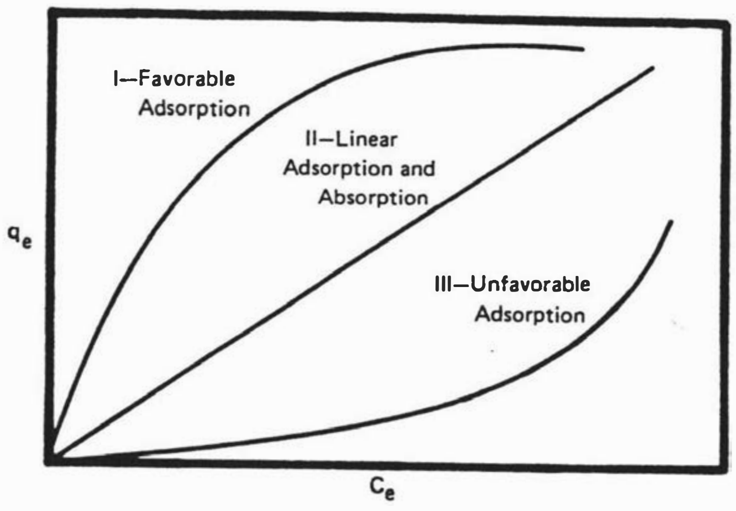


Figure 2.1: Types of equilibrium sorption separations; q_e = amount sorbed and C_e = amount in solution (Weber *et al.*, 1991).

2.3.7.2 Freundlich isotherm

The Freundlich isotherm is the oldest of the nonlinear isotherms used to describe the sorption of organic chemicals onto soils. The Freundlich isotherm is defined by the relationship,

$$q = KC_e^{\frac{1}{n}} \tag{2.2}$$

where, K indicates sorption capacity and 1/n sorption intensity. Higher values of K means the adsorption capacity for the chemical is high and low values of 1/n indicates low intensity of adsorption. O'Connor *et al.* (1980) used the Freundlich isotherm to describe the adsorption of 2,4,5-T onto Glendale clay loam. Adsorption and desorption isotherms of pentachlorophenol onto three different soils is also described by a nonlinear Freundlich isotherm (Bellin *et al.*, 1990). The sorption of substituted phenylureas from aqueous solution onto three soils followed a Freundlich type isotherm (Spurlock and Biggar, 1994).

2.3.7.3 Langmuir isotherm

The isotherm model was developed by Langmuir (1918) to describe the adsorption of gases onto solids. The model is based on the assumptions that the energy of adsorption of each molecule is the same and independent of surface coverage, sorption occurring only on localized sites, involving no interaction between the adsorbed molecules. With these assumptions, the Langmuir isotherm is expressed as,

$$q = \frac{Q^o f C_e}{1 + f C_e} \tag{2.3}$$

where, Q^o represents the adsorbed solute concentration corresponding to complete monolayer coverage; *f* is a sorption coefficient related to the enthalpy of adsorption. The adsorption of trichlorobenzene by Ann Arbor I soil is described using the Langmuir isotherm (Weber *et al.*, 1991), while Haderlein and Schwarzenbach (1993) report that the adsorption of substituted nitrobenzenes and nitrophenols onto mineral surfaces follows the Langmuir isotherm.

2.3.8 Multicomponent isotherm models

In multicomponent systems, competition between solutes for sorption sites occurs due to differences in adsorption energies. Models have been proposed based on linear, Langmuir and Freundlich isotherms to describe multicomponent sorption.

The Langmuir isotherm for competitive sorption is based on the same assumptions as those for single solutes (Jain and Snoeyink, 1973). The Langmuir model for the competitive sorption of two solutes is expressed as,

$$q_1 = \frac{Q_1^0 f_1 C_1}{1 + f_1 C_1 + f_2 C_2} \tag{2.4}$$

$$q_2 = \frac{Q_2^0 f_2 C_2}{1 + f_1 C_1 + f_2 C_2} \tag{2.5}$$

where, Q_1^0, f_1, Q_2^0 and f_2 are Langmuir constants obtained from pure component adsorption for solutes 1 and 2, respectively and C_1 and C_2 are the equilibrium concentrations of the respective solutes in the mixture. Sorption experiments with binary mixtures of nitrophenols and nitrobenzenes onto mineral surfaces is described by the competitive Langmuir isotherm (Haderlein and Schwarzenbach, 1993).

Sheindorf *et al.* (1981) developed a Freundlich-type multicomponent isotherm model assuming that each component, individually, follows a Freundlich-type isotherm in a pure component system, and that for each component in a multicomponent adsorption an exponential distribution of energy exists. For a bicomponent system, the sorption of each component is expressed as,

$$q_1 = K_1 C_1 (C_1 + a_{12} C_2)^{\frac{1}{n_1} - 1} \qquad (2.6)$$

$$q_2 = K_2 C_2 (C_2 + a_{21} C_1)^{\frac{1}{n_2} - 1} \qquad (2.7)$$

Sheindorf *et al.* (1981, 1982) successfully applied this model to the competitive equilibrium adsorption of *p*-nitrophenol and benzenesulphonate onto activated carbon.

Randtke and Prausnitz (1972) developed a multicomponent isotherm based on ideal adsorption solution theory (IAST) to predict the competitive adsorption. The IAST model incorporating Freundlich isotherms is expressed as,

$$C_1 = \frac{q_1}{q_1 + q_2} \left(\frac{q_1 + q_2 \frac{n_1}{n_2}}{K_1} \right)^{1/n_1} \qquad (2.8)$$

$$C_2 = \frac{q_2}{q_1 + q_2} \left(\frac{q_2 + q_1 \frac{n_2}{n_1}}{K_2} \right)^{1/n_2} \qquad (2.9)$$

An example of the application of the IAST model to equilibrium data for competitive adsorption of lindane and *p*-dichlorobenzene on humic acid is reported by Weber *et al.* (1991). McGinley *et al.* (1993) also describes the competitive adsorption of tetrachloroethylene (TTCE) and dichlorobenezene adsorption onto soils by IAST model.

Yonge and Keinath (1986) modified IAST model to account for non-ideal competition for adsorption sites by adding a competition factor. The equation is expressed as:

$$q_i = K^{(n'-1)/n'} \left[\frac{K_i}{\eta_i} C_i^{n_i} \right]^{1/n'} \left[\sum \left(\frac{K_i/\eta_i}{K'} C_i^{n_i} \right)^{1/n'} \right]^{n'-1}$$

where

Yonge, D.R. and Keinath, T.M., 1986. The effects of non-ideal competition on multi-component adsorption equilibria, *Journal WPCF*, 58, 77-81.

$$K' = \frac{\sum (K_i/\eta_i)}{N}$$

where, n' = average value of n_i, K' = average value of K_i and η = competition coefficient. Nonlinear statistical analysis is required to determine the values of η_i which provide the lowest residual sum of squares of the competitive data. The authors have found that inclusion of a competition factor did not significantly improve the model predictions when compared to IAST model.

The comparisons of bicomponent isotherms can be based on theoretical derivations, on convenience of application and on successful prediction. The Langmuir and IAST isotherms contain no interaction parameter, but the multicomponent Sheindorf' model and the modified ISAT model contain one parameter each. The Langmuir and IAST isotherms are derived from basic principles but are limited to low concentrations. Multicomponent Freundlich isotherm is derived with the same assumptions employed in the derivation of the single-solute isotherm, namely exponential distribution of energies, the interaction parameter can be determined from the experimental data. On the other hand, the interaction parameter in modified IAST must be estimated from the observed data. The decision whether to determine experimentally or to estimate the competition coefficient depends on the adsorption properties of the two solutes. Estimation in general limits the predictive power as in the case of modified IAST model. Therefore, the multicomponent Freundlich isotherm presented by Sheindorf *et al.* (1981) represents a good compromise of convenience and accuracy. Its derivation enables to extend to many soluble systems while the experimental information required to determine the competition coefficient is minimal.

2.4 Sorption kinetics

Sorption kinetics are important because of the major role that sorption plays in the fate of organic compounds. In addition, the kinetic studies lead to a better understanding of sorption mechanisms and improve the ability to predict the contaminant fate and transport in soils (Brusseau and Rao, 1990).

A two-phase pattern of adsorption/desorption of organic chemicals from soils has been observed by kinetic studies (Pavlostathis and Jaglal, 1991). An initial fast stage (in hours) and a subsequent longer, slow phase (days) has been reported. The second stage is attributed to the slow solute diffusion into/from internal sorption sites (Wu and Gschwend, 1986). The biphasic desorption pattern is more pronounced in soils contaminated for longer periods (Brusseau and Rao, 1990). The kinetics of desorption of a sorbed compound appears to be related to its residence time in the soil (Farrell and Reinhard, 1994b). Ideal conditions for linear isotherms and complete reversibility are usually assumed in theoretical adsorption/desorption models and are dubious in cases of long-term contamination with organic chemicals (Voice and Weber, 1983).

Karickhoff (1980) and Karickhoff and Morris (1985) studied the sorption of pyrene, phenanthrene and naphthalene to aquifer materials. They report that roughly half of the final equilibrium sorption is achieved in a short time (minutes), while the remainder required periods of up to weeks. These observations proposed a two-site model in which sorbed chemical is fractioned into fast and slow uptake. McCall and Agin (1985) show that picloram desorption from soil is biphasic, with the slow fraction giving a decreased rate with increasing time. A similar two-site sorption model is used to describe the kinetics.

Rijnaarts *et al.* (1990), Overcash *et al.* (1991), Brusseau *et al.* (1991), and Pavlostathis and Mathavan (1992) report the use of an intraparticle diffusion model to describe the adsorption and desorption kinetics for several organic chemicals from soils and aquifer materials. The main conclusions from these studies are: adsorption and desorption diffusion rates are different; mechanism of diffusion is through intraorganic matter; and resistance to desorption with increase in residence time.

Ball and Roberts (1991) examined the sorption kinetics for PCE and 1,2,4,5-tetracholorobenzne (TeCB) on sandy aquifer material, the rates interpreted using an intraparticle diffusion model. The authors report that intraorganic matter diffusion is the main mechanism of sorption. Grathwohl and Reinhard (1993) used an intraparticle diffusion model to describe the adsorption and desorption kinetics of trichloroethylene from aquifer material. The authors assumed the adsorbent particles as homogeneous spheres and the intraparticle diffusion is described by a constant diffusion coefficient. Some of the models frequently used to describe the sorption kinetics are discussed below.

2.4.1 Models

The sorption of organic chemicals from solution by porous adsorbents (e.g. activated carbon, soil) is assumed to occur in three consecutive mass transport steps (Weber *et al.*, 1991), are illustrated schematically in Figure 2.2. The first step, bulk transport of a chemical in the solution phase, is usually rapid because of mixing. The second step, film-mass transport, involves diffusion of the solute through a hypothetical film surrounding the particle. The third step, diffusion of a chemical from the exterior surface to an active adsorption site (intraparticle transport) within the particle by surface or pore diffusion. The actual adsorption of a chemical on adsorption sites is assumed to be rapid, and is described by an equilibrium adsorption isotherm (Crittenden *et al.*, 1986). Of the three steps, film-mass transfer and intraparticle transport are the major factors controlling the adsorption of chemicals onto porous adsorbents.

Single-resistance models based on film-mass transfer are able to describe the kinetics for a short period, usually the first few minutes (Peel and Benedek, 1981). Other single resistance models adopt internal mass transfer only, i.e., surface or pore diffusion mechanisms (Overcash *et al.*, 1991).

Surface diffusion model pictures the adsorption process as occurring at the outer surface of the adsorbent, followed by the diffusion of the chemical in the adsorbed state. Although the adsorbent particle is assumed to be homogeneous, this does not preclude the use of this model for porous particles. However, in this model no attempt is made to relate the transport processes to the structure in terms of properties such as surface area and pore size distribution; even though the adsorbent may be porous, there are no sinks for the adsorbate since it diffuses into them in the adsorbed state. The entire process might be pictured as an adsorption at the outer surface of the particle followed by a sponge-like absorption of the chemical into the pores (Brusseau and Rao, 1989).

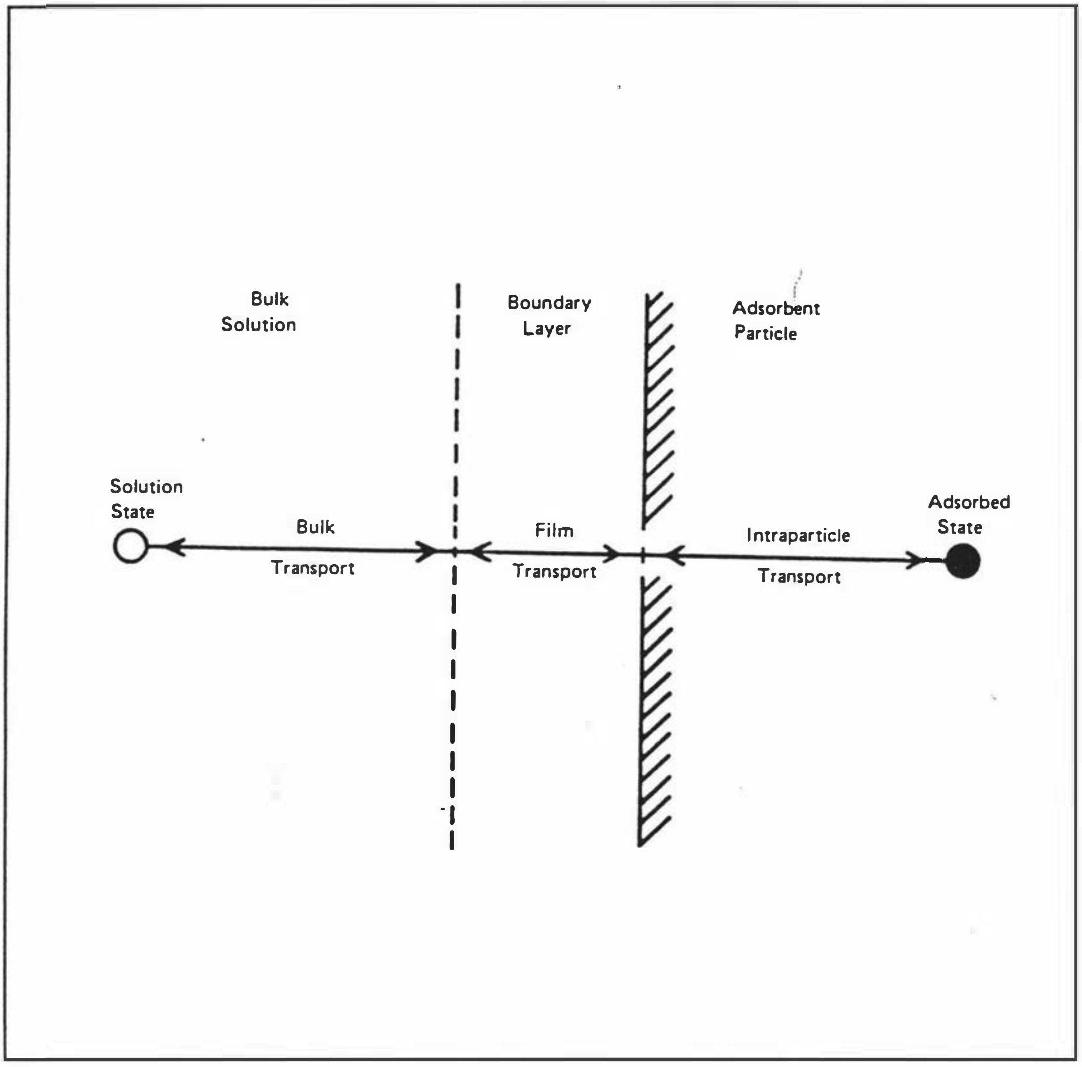


Figure 2.2: Mass transport steps in adsorption by porous adsorbent (Weber *et al.*, 1991).

The pore diffusion model pictures the adsorbent particles as consisting of a solid phase interspersed with very small pores. Most researchers have assumed that the adsorbate diffuses into the pores in the fluid phase, but, with the addition of an extra term, surface diffusion in the adsorbed state is also accounted for.

The serious limitation of the pore diffusion model is the assumption that the distribution of pores can be characterized by a representative, average diffusion coefficient. However, this assumption breaks down as pore diameters approach molecular dimensions. Assuming homogeneity among the pores can be a oversimplification for porous adsorbents (Farrell and Reinhard, 1994b). However, Wu and Gschwend (1986) found that the pore diffusion model is adequate to describe both adsorption and desorption kinetics for several nonpolar organic solutes on soils and sediments. A comparison of various model and their limitations are given in Table 2.2.

Table 2.2 Comparison of sorption kinetic models

Model (Reference)	Fitting parameter	Model limitations
One-site model (Coates and Elzermann, 1986)	k_d	Cannot describe biphasic adsorption/desorption kinetic data
Two-site model (Coates and Elzermann, 1986)	k_d, K	Cannot describe the slow reversible, nonequilibrium desorption for residual sorbed compounds (Karickhoff, 1980)
Pore diffusion (Wu and Gschwend, 1986)	D_p	Cannot describe instantaneous uptake without additional correction factor (Miller and Pedit, 1992)
Surface diffusion (Miller and Pedit, 1992)	D_s	Model calibrated with sorption data, predicted more desorption data than occurred in the desorption experiments (Miller and Pedit, 1992)

Several researchers have found that for liquid systems, a surface diffusion mechanism gives a more rational description of the intraparticle transport in comparison to a pore diffusion mechanism (Crittenden, 1976; Neretnieks, 1976; Brusseau and Rao, 1989; Weber *et al.,* 1991). However, the appropriate model for sorption to soils has not been resolved (Miller and Pedit, 1992).

2.5 Solute transport

The movement of organic chemicals in a soil profile is important from the point of view of potential contamination of surface and groundwaters. Water moving through a soil profile can carry organic chemicals in solution. However, the amount of chemical reaching the groundwaters is governed by the retention and release by soil particles in contact with the solution. A number of review articles have appeared on the transport of organic chemicals in saturated and unsaturated flow systems (Brusseau and Rao, 1989, 1990; Khondaker *et al.,* 1990; Beck *et al.,* 1993). The factors responsible for organic chemical transport in soils are:

- the diffusion coefficient of the chemical;
- the sorption of the chemical by the chemically active sites on the soil particles;
- the velocity of the soil water in the inter-particle voids; and
- hydrodynamic dispersion (Beck *et al.,* 1993).

The processes of adsorption and mass transfer have been evaluated in Chapters 4 and 5. Hydrodynamic dispersion occurs when solution flows through a soil volume. On the microscopic scale, the solution does not move at the same rate throughout the soil volume. Boast (1973) and Nassar and Horton (1992) given three reasons for why this irregular flow causes hydrodynamic dispersion: within a given pore, the flow rate of the solution is slower near the walls of the pore than in the middle; flow is faster in larger pores than in smaller pores; and the solution does not flow simply in the direction of the soil volume as soil solution flows in some pores at an angle to the mean direction of soil solution flow. Excellent reviews on dispersion are available (Bear, 1980; Hillel, 1982).

A variety of solute transport models incorporating the above factors were proposed to predict the movement of organic chemicals in soils. A brief discussion on the frequently used transport models is given in the following section.

2.5.1 Models

In describing the adsorption-desorption processes, transport models usually assume either an equilibrium or kinetic (nonequilibrium) relationship. Models that assume an equilibrium between solute and sorbent require an estimation of fewer parameters and are less complex (Harmon *et al.*, 1989). While the equilibrium models are simple to use, there is an ample evidence that nonequilibrium conditions can exist during solute transport. In recent years, criteria for the use of different transport models have been described by a number of researchers (Valocchi, 1985; Brusseau and Rao, 1989; Bahr, 1990).

The convective-dispersive transport equation incorporating sorption mechanisms is the foundation upon which numerous mathematical models of solute transport in porous media have been based. The models based on a convection-dispersion equation are grouped into the following categories:

- equilibrium models;
- two-region models;
- two-site models;
- dispersed flow, film transfer, pore and surface diffusion model, (DFPSDM); and
- homogeneous surface diffusion model (HSDM).

2.5.1.1 Equilibrium models

The basic assumption of equilibrium models is that at any given depth z and time t the chemical in the liquid phase is in equilibrium with that sorbed onto the soil and there is a uniform concentration of chemical in the liquid phase. For a linear isotherm (Equation 2.1) the convective-dispersion equation is expressed as,

$$(1 + \frac{\rho_b K}{\theta}) \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \qquad (2.10)$$

where, $(1+\rho_b K/\theta)$ is referred to as the *retardation factor* (R_f) (Davidson and Chang, 1972; Brusseau and Rao, 1989). For the Freundlich isotherm (Equation 2.2) the retardation factor is concentration dependent and is expressed as,

$$R_f = 1 + \frac{\rho_b n K C^{(\frac{1}{n} - 1)}}{\theta} \qquad (2.11)$$

For linear sorption isotherms, Equation 2.11 is solved with various initial and boundary conditions (Van Genuchten and Alves, 1982; Weber and Miller, 1988). For Freundlich nonlinear adsorption, Van Genuchten *et al.* (1974), Jennigs *et al.* (1982) and Parker and Valocchi (1986) combined Equations 2.10 and 2.11 and developed numerical solutions to predict the organic chemical transport in soil columns. The numerical approach allowed greater flexibility than the analytical solutions.

Most equilibrium models (Lindstrom *et al.*, 1967; Davidson *et al.*, 1968; Parker and Valocchi, 1986 and others) have used the same Freundlich isotherm parameters for adsorption and desorption to describe the transport in soil columns. The results of Davidson *et al.* (1973) show that the shape of the concentration distribution in soil is significantly altered due to hysteresis in adsorption and desorption processes. They calculated the distribution curves for pesticides showing hysteresis in adsorption and desorption and found that the curves are asymmetrical when hysteresis is taken into account, compared with no hysteresis. Gaber *et al.* (1992) used an equilibrium model to predict the transport of picloram in a silt loam clay at different velocities. While the experimental results suggest that the model predicted the breakthrough curves adequately, it overestimated the elution time at faster velocities. The authors conclude that nonequilibrium models made a better prediction of the transport of picloram in soil columns.

Bahr (1990) and Valocchi (1985, 1989) describe the criteria for using equilibrium models for solute transport, determining that the applicability of models depends on the interaction of transport parameters such as velocity, dispersion coefficient, sorption rate, isotherm parameters and boundary conditions.

2.5.1.2 Two-region models

The convective-dispersive solute transport implies that soil and water participate freely in convective transport of solutes and that all adsorption sites are equally accessible for the solute if the adsorption reaction takes place. However, in many instances, deviations are observed with the predicted curves and often the chemical appears earlier than predicted. Some experimental conditions were found to be responsible for the early or delayed appearance of the chemical, e.g., nonlinear conditions, movement through aggregated or undisturbed cores (Van Genuchten and Wierenga, 1977; Brusseau and Rao, 1989).

To explain the observed asymmetry in breakthrough curves, the concept of solute transfer between mobile and immobile soil-water phases is proposed (Coats and Smith, 1964; Van Genuchten and Wierenga, 1976). The governing model equations are given by Coats and Smith (1964). The model assumes that the liquid phase in the soil is divided into *mobile* (macroporosity) and *immobile* (microporosity) regions. The transport of chemical in the mobile region is assumed to take place through convection-dispersion, whereas the transport in the immobile region is taken as diffusion controlled. The rate of diffusion depends on the concentration gradients between the two regions. Chemical sorption in both regions is considered to be instantaneous.

Gamerdinger *et al.* (1990, 1991) demonstrates the use of a two-region model to describe the transport of atrazine in silty loam soil at two different concentrations and velocities. An accurate prediction of the experimental data is obtained when predicting the low concentration data from the parameters estimated from the high-concentration data.

2.5.1.3 Two-site models

Instead of assuming mobile and immobile regions, Selim *et al.* (1976) and Cameron and Klute (1977) suggested a two-site model, the basic concept of which is that soil consists of different adsorptive surfaces (organic matter, clays, aluminium and other oxides) and the chemical adsorbs onto these surfaces at different rates. This model assumes the presence of two types of sites for sorption: the adsorption on type-1 is assumed to be instantaneous; the adsorption on type-2 is described by a first-order reversible kinetic reaction. At equilibrium, adsorption on both types of is related by a linear isotherm (Equation 2.1).

Cameron and Klute (1977) applied this model, in combination with a linear isotherm, for the movement of atrazine in soil columns. Neither the first-order kinetic model nor the linear isotherm model alone could predict the observed data. However, on combining the first-order and linear models, excellent agreement was observed with the experimental data. This model is also used by Gamerdinger *et al.* (1994) to describe the transport of benzene, toluene and xylene in laboratory soil columns under saturated conditions. Hatfield and Stauffer (1993) proposed a combination of two-region and two-site model, while Hatfield *et al.* (1993) used this model to predict the transport of organic chemicals in soils.

2.5.1.4 Dispersed flow, film transfer, pore and surface diffusion model (DFPSDM)

Crittenden *et al.* (1986) described a dispersed flow, film-mass transfer, pore and surface diffusion model to predict the movement of organic chemicals through a column of saturated soil. The model comprises the following mechanisms:

- axial dispersion;
- film-mass transfer resistance;

- pore and surface diffusion as intraparticle mass transport mechanisms; and
- equilibrium adsorption of solute between soil surface and the intraaggregate liquid.

Crittenden *et al.* (1986) presented mass-balance equations for the column and the adsorbent particle. The column mass-balance equation accounts for accumulation in the mobile phase, axial dispersion, convective flow and transport of solute from liquid phase by the film-mass transfer coefficient. The solid phase mass-balance accounts for pore and surface diffusion and accumulation in the intra-stationary phase. The solute in the intra-stationary phase fluid is assumed to be in equilibrium with that adsorbed onto the surface, and is related by an equilibrium isotherm.

Based on these mechanisms, equilibrium and nonequilibrium soil column models are presented for different initial and boundary conditions (Crittenden *et al.*, 1986). Hutzler *et al.* (1986) presented the predicted and measured breakthrough curves for trichloroethene, bromoform, and chloride ion in saturated soil columns using DFPSDM.

2.5.1.5 Homogeneous surface diffusion model (HSDM)

The HSDM is proposed by Hand *et al.* (1984) to describe the fate of a solute in a fixed bed adsorber. The model assumptions are the same as those for DFPSDM, except that the surface diffusion was assumed as the rate controlling the transport mechanism. The model has been verified by a number of workers to describe the transport of organic solutes in activated carbon systems (Hand *et al.*, 1984; Fettig and Sontheimer, 1987 a, b and c; Kenneth *et al.*, 1992). The advantages of this model are that all the model parameters can be obtained from independent experiments.

2.5.2 Major limitations of the models

Verification of the transport models is usually based upon the agreement between experimentally measured and calculated curves, and is valid only when all model parameters are measured and/or estimated independent of the data being simulated. However, due to lack of experimental techniques for independent measurement of parameters in each model, these are often estimated by curve-fitting the model to the measured data (Van Genuchten *et al.*, 1977; Rao *et al.*, 1979; Lee *et al.*, 1991). Using these techniques, more than one conceptual model describes the experimental data, which is one of the weaknesses of this approach (Rao *et al.*, 1979; Davidson *et al.*, 1980). Another limitation is the possibility that both physical and chemical processes contribute simultaneously to the observed asymmetry in calculated curves when model verification is attempted using breakthrough curve (BTC) data for adsorbed solutes (Rao *et al.*, 1979). Therefore, curve-fitting techniques, although useful in parameter estimation, fail to insure process identification.

Models based on two-region and two-site concepts have provided mathematically identical solutions (Nkedi-Kizza *et al.*, 1984), and hence the distinction between physical and chemical processes of sorption reaction is difficult. This can be illustrated by comparing the transport studies by Van Genuchten and Cleary (1979) for 2,4,5-T with Rao *et al.* (1979) for 2,4-D. The former study uses a physical non-equilibrium concept (two-region), while the chemical non-equilibrium (two-site) model was used by Rao *et al.* (1979). In both studies, the kinetic parameters are the same. However, two different kinetic processes are concluded, because the parameters are obtained by curve fitting to breakthrough curves. The models, considering diffusion into aggregates with well-defined geometry (spherical, Rao *et al.*, 1980; and non-spherical, Van Genuchten, 1985), also suffer from the same limitations. Independent evidence of the nature of the time dependent process is thus necessary for a proper development of transport models. In the models proposed by Hand *et al.* (1984) and Crittenden *et al.* (1986) all the model parameters can be determined, independently, from experiments or from correlations.

In addition to the above limitations, most available models are developed using laboratory conditions and fail to predict the fate and movements of contaminants in the field.

2.6 Conclusions

General conclusions from this review are:

- environmental conditions, i.e., pH, temperature and concentrations can play a major role in sorption processes;
- desorption of organic chemicals found to be slow and a fraction of the chemical is difficult to desorb, this phenomena often attributed to the hysteresis of adsorption and desorption processes; however, the desorption processes are not well understood;
- kinetics of sorption plays a dominant role in the transport of chemicals in soil, most previous modelling attempts have adopted either a surface diffusion or a pore diffusion mechanism;
- virtually all of the models in literature used curve-fitting techniques to predict the transport of solutes in laboratory and field situations; and
- very few studies reported on competitive sorption of chemicals in soil, however no attempts were made to model the observed behaviour.

CHAPTER 3
MATERIALS AND METHODS

This chapter describes the soil characteristics and properties of the chemicals used in the study, together with experimental methods and analytical techniques.

3.1 Soil characteristics

Volcanic soil was collected from the DowElanco landfill site located in New Plymouth, New Zealand, in April, 1989, from the top 15 cm, air-dried and sieved through a 850 μm screen to remove stones and plant materials. The average particle size of the soil was determined using a stack of British Standard sieves and the mass of soil retained on each screen was weighed. From a plot of $1/d_p$ *versus* cumulative mass fraction an average particle diameter of 359 μm was determined.

Rogers *et al.* (1980) and Koskinen and Chang (1982) have observed the degradation of organic chemicals during adsorption-desorption equilibration. By using the standard method of calculating adsorption-desorption without accounting for degradation losses results in an overestimation of the amount of solute adsorbed in soil. Errors resulting from the degradation losses were eliminated by steam sterilizing the soil in an autoclave at 120°C for 30 minutes.

Skipper and Westermann (1973) examined the effects of autoclaving on soil properties, their results indicating that, as a result of steam sterilizing only the pH decreases slightly due to release of organic acids, other characteristics remaining the same. The authors conclude that steam sterilization of soil is an appropriate option compared to gamma radiation, sodium azide or propylene oxide treatments.

Preliminary experiments indicated that the volcanic soil was contaminated with different organic chemicals, although no attempt was made to determine the compounds present. To avoid the possibility of leaching these chemicals during experiments, the soil was washed in a 30 cm long column with distilled water. At regular intervals the effluent from the column was collected and absorbance was measured at 280 nm. Washing was continued till the adsorbed chemicals were flushed from the soil, i.e., till zero absorbance was reached. By washing the soil with water, it was possible that the soluble organic matter present could be dissolved in the flushing solution. However, it was assumed that the loss of soluble organic matter was insignificant to cause any error in the sorption investigations. After washing, the soil was dried in an oven at 55°C for 24 h, and then steam sterilized at 120°C for 30 min, stored at 20°C and used for all experimental studies.

The soil pH was measured by mixing 10 g of soil with 25 ml distilled water. The mixture was stirred vigorously using a high speed stirrer for 10 min and allowed to stand overnight. The pH of the suspension was measured using a glass electrode. The experiments were repeated and the error between replicates was found to be less than 0.1 pH units.

The soil organic carbon was determined by a colorimetric method (Blackmore *et al*., 1987). A gram of finely ground air-dried soil was mixed with known amounts of sucrose and 12 ml of concentrated H_2SO_4 (98%) in 10 volumetric (0.2 L) flasks. After the mixtures were allowed to stand for 10 min with occasional swirling, 6 ml of 3M chromium trioxide solution was added and the mixtures were shaken thoroughly till no particles were left on the sides of the flask. Distilled water was added to make up to the 0.2 L and the mixtures left to stand overnight at 20°C. From each flask, a 10-15 ml aliquot was centrifuged at 2000 rpm for 15 min. The absorbence of each sample was measured at 600 nm using an UV spectrophotometer. A standard curve was prepared from the absorbence readings and concentrations in the samples. The percentage of organic carbon was calculated using the procedure given by Blackmore *et al.* (1987). The characteristics of the volcanic soil are given in Table 3.1.

Due to unforeseen problems, the soil collected in 1989 was exhausted. A new batch of soil was collected from the same site in November 1992. The soil was sieved and washed as described earlier and used only for column experiments. The properties of this soil are also given in Table 3.1.

Table 3.1 Soil characteristics

Property	1989	1992[b]
Mechanical analysis[a]:		
% sand (2-.02 mm)	56	
% silt (.02-.002 mm)	26	
% clay (<.002 mm)	18	
Dry bulk density, g/cc	0.82	
Total porosity %	64.5	
Macroporosity %	4.60	
Size analysis[a] %		
<0.076 mm	67	
<0.422 mm	92	
<2 mm	100	
pH	5.8 ± 0.1	5.8 ± 0.1
Cation exchange, meq/100	31.2 ± 2.8	18.0 ± 2.2
Organic matter	8.7 ± 0.8	7.6 ± 0.5
BET surface area, m^2/g	49.72[c]	
BET surface area, m^2/g (between 40 and 3000 pore diameter)	30.32	
Average particle size, µm	359 ± 25	300 ± 33
Particle density, g/cc	2.6	

[a] New Zealand Soil Bureau (1983).
[b] Soil Science Department, Massey University (1992).
[c] Detailed analysis shown in Appendix 1

As shown in Table 3.1, the soil characteristics are different for the two batches. For example, the organic matter was found to be 8.7 and 7.6%, respectively, from the same location at different times. It is reported in literature (Hamaker and Thompson, 1972; Rao, 1990) that the sorption characteristics remain relatively constant for soils having organic matter greater than 5%. Hence, the small change observed in OM may not have any significant effect on the sorption capacity. On the other hand, Bailey and White (1970), Morrill *et al.* (1982), Schellenberg *et al.* (1984), Westall *et al.* (1985), Hance (1988) report that the cation exchange capacity is mainly responsible for the sorption of basic organic compounds and has little or no effect on neutral and acidic compound sorption onto soil. There are no reported studies available on the effect of particle size on sorption; however, in general, decreasing the particle size increases the surface area and, as a result, more chemical could adsorb onto the soil (Brusseau and Rao, 1990).

3.2 Chemicals

Phenoxyacetic acids and chlorophenols used for this study were supplied by DowElanco, (New Zealand) in crystalline form, having > 99% purity. Stock solutions were prepared by dissolving the compounds in 0.1N KOH solution. Subsequent concentrations were made by diluting with distilled water. The properties of the compounds are listed in Table 3.2, where the analytical wavelengths reported were measured in an UV spectrophotometer when the absorbance was maximum by scanning.

Table 3.2 Properties of phenoxyacetic acids and chlorophenols

Compound	Molecular weight	pKa	Solubility[a] (mg/l)	Analytical wavelength (nm)	Area/ molecule(A_m)
2,4-D	221	2.73	725	283	56.1
2,4,5-T	255	2.88	238	289	60.5
MCPA	200	3.05	1174	280	56.4
2,4-DCP	163	7.85[b]	4600	285.2	48.2
2,4,5-TCP	197	6.00[b]	1190	291	49.6
PCOC	143	5.76	8000	281	48.5

a. Handbook of chemistry and physics, 54th ed. (1978-79).
b. Murin and Snoeyink (1979).

3.3 Experimental procedures

Equilibrium, kinetics and fixed-bed experiments were carried out for three phenoxyacetic acids and three chlorophenols as individual solutes, and for three bicomponent mixtures, namely, 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC.

3.3.1 Preliminary experiments

Preliminary experiments were carried out to find the change in pH during the course of the experiment. A known concentration of solution at pH 2 was contacted with 5 grams of soil and continuously shaken. At regular intervals the pH of the supernatant was measured. After 12 h, the pH of the supernatant was found to be 2.01 indicating the change in pH, during the course of the experiment, was not significant. To determine the time required to attain equilibrium, 5 grams of soil were contacted with 100 ml solution of known concentration. At frequent time intervals (30 min), flasks were taken out and analyzed for solute concentration. After four hours, the relative concentration change was not significant and the experiment was terminated. The equilibrium time for bicomponent mixtures was also determined by the same procedure.

3.3.2 Equilibrium

Equilibrium experiments were carried out in a thermostated incubator (Environ Shaker, Model No. 3597-1234) having a temperature control of ± 0.1°C. Initially, the effect of pH on the equilibrium adsorption was examined, using a 100 ml solution of known concentration of each chemical, adjusted to an initial pH between 2 to 7.5, and contacted with 5 grams of soil in conical flasks. The flasks were continually shaken till equilibrium was attained when the concentration of the chemical in supernatant was measured. The effect of pH on the adsorption was examined for three different initial concentrations.

Equilibrium adsorption-desorption experiments were conducted in shake flasks at 20°C. The equilibrium adsorption isotherm for each chemical was determined by contacting a 100 ml solution of known concentration (0-400 mg/l) with known amounts of soil (1-10 g) within the temperature range of 10-30°C. The flasks were shaken. After equilibrium 5 ml of supernatant was removed and analyzed for chemical concentration. The difference between the initial and final concentration in the supernatant was taken to be the result of adsorption. Experiments were duplicated for all the compounds.

Equilibrium desorption isotherms were obtained by using selected soil-solute mixtures from the adsorption studies. After adsorption equilibrium was attained, 20 ml of supernatant was removed from the mixture and replaced with an equal volume of distilled water adjusted to pH 2. The samples were shaken until equilibrium was reached, when the concentration of the supernatant was analyzed and the amount desorbed determined. This represented one desorption equilibrium point. The procedure was repeated to obtain a desorption isotherm. Desorption isotherms were obtained starting with three different equilibrium adsorption points.

Bicomponent solution mixtures were prepared in the desired concentration range (50-400 mg/l) and adjusted to pH 2. The sorption experimental procedure for bicomponent mixtures was the same as that of single component studies.

3.3.3 Batch kinetics

The kinetic runs for adsorption for each chemical were carried out in a baffled basket-type reactor in which the soil was held in wire baskets and rotated through the liquid phase. For each experiment, the reactor was filled with 1 L of solution of a known concentration (100 mg/l) at pH 2. A basket impeller was used to stir the liquid phase at 250 rpm. The concentration of the liquid phase was measured at 5-10 s intervals for the first minute to determine the film-mass transfer coefficient. After that, measurements were taken at increasing time intervals (5 min) until equilibrium was reached (30 min), however, experiments were continued up to four hours. To minimize errors, all samples were returned to the reactor after measurement.

Desorption kinetic experiments were carried out with the same soil-chemical mixture used for the adsorption kinetic study. After adsorption equilibrium was established, 0.2 L of solution was taken out and replaced with an equal volume of distilled water at pH 2. The initial concentration of the solution was determined and used as the initial concentration for desorption studies. The basket impeller was then lowered into the solution and rotated. Measurements were taken at regular intervals (5 min) to analyze for solute concentration. The experiment was terminated when desorption equilibrium was reached.

Bicomponent batch kinetic adsorption-desorption experiments were carried out using the above procedure for an initial concentration of 100 mg/l of each component and an initial solution pH 2.

3.3.4 Column studies

Fixed bed adsorption-desorption experiments were carried out in perspex columns of 4 cm internal diameter and 20 cm long. The column was fitted with teflon end caps held with rubber rings. One end cap was fitted with a conical shape bottom to act as a distributor. The columns were packed with air-dried soil (collected in 1992) in small increments to establish uniform bulk density. Two layers (0.2 cm height) of acid washed sand were used to support the soil at each end of the column. The packed columns were slowly saturated with 8-10 L of distilled water.

Feed solutions, prepared in the desired pH and concentration range and stored in 20 L bottles, were pumped into the column using a piston pump, which provided a constant and reproducible flow (± 0.5%). Input concentration was measured before and after the experiment, while effluent samples were collected at designated times (5 min) using a fraction collector.

When the solute concentration in the effluent reached that of the influent, the column experiment was terminated, solution drained and the feed replaced with solute-free distilled water adjusted to pH 2. Then the desorption experiments were conducted, runs being stopped when all the adsorbed solute was recovered.

Bicomponent column studies were also carried out for the three chemical combinations. The procedure used was the same as that of single component studies.

3.4 Analysis

3.4.1 pH

The pH of the supernatant was measured using an Orion Research 701A/Digital Ionalyser. Samples for analysis were first centrifuged for 2-3 min and filtered through a 0.45 µm filter to remove any suspended soil particles before pH measurement.

3.4.2 Concentration measurement

All single solute experimental data were analyzed using a UV spectrophotometer and for bicomponent data HPLC was used to determine solute concentration. Initially the samples were analyzed using UV spectrophotometer and HPLC; the concentrations were found to be same.

3.4.2.1 UV

The concentrations of samples from washed soil experiments were measured using UV absorbance. A Varian 634S UV spectrophotometer with quartz cells with a 1 cm path length was used for analysis.

To determine concentrations, standard curves were prepared by measuring the UV absorbance in the concentration range of 5-100 mg/l for each compound. Calibration curves between absorbance and concentration were linear for all the compounds. The wavelengths for UV spectrophotometer analysis of various compounds are listed in Table 3.2.

3.4.2.2 HPLC

The samples from bicomponent mixtures were analyzed using HPLC. The equipment consisted of a Waters 6000A pump, a Tracor 970A variable wavelength detector (used at 230 nm) and a Dupont Instruments Column compartment. The integrator used was a Hewlett-Packard 3373B integrator with a Sekonic SS-250F chart recorder (1 mv, 150 mm/h). A Zorbax CN column, 200 mm x 4.6 mm was used for the analysis.

The mobile phase used for these columns was made by adding 450 ml of acetonitrile-210 and 35 ml of tetrahydrofuran to 0.1 M sodium dihydrogen orthophosphate. The mixture was made to 2 L with deionized water. The pH was adjusted to 3.2 using concentrated phosphoric acid. Acetonitrile was recycled into the completely mixed solvent reservoir to avoid wastage. This allowed the same mobile phase to be used for extended periods.

To accurately determine the bicomponent mixture, standards of known concentrations, in the range 10-50 mg/l, were injected and the peak areas recorded. Standard curves for each solute, based on the peak area, were prepared which allowed to concentration determination.

CHAPTER 4
EQUILIBRIUM ADSORPTION-DESORPTION

4.1 Introduction.

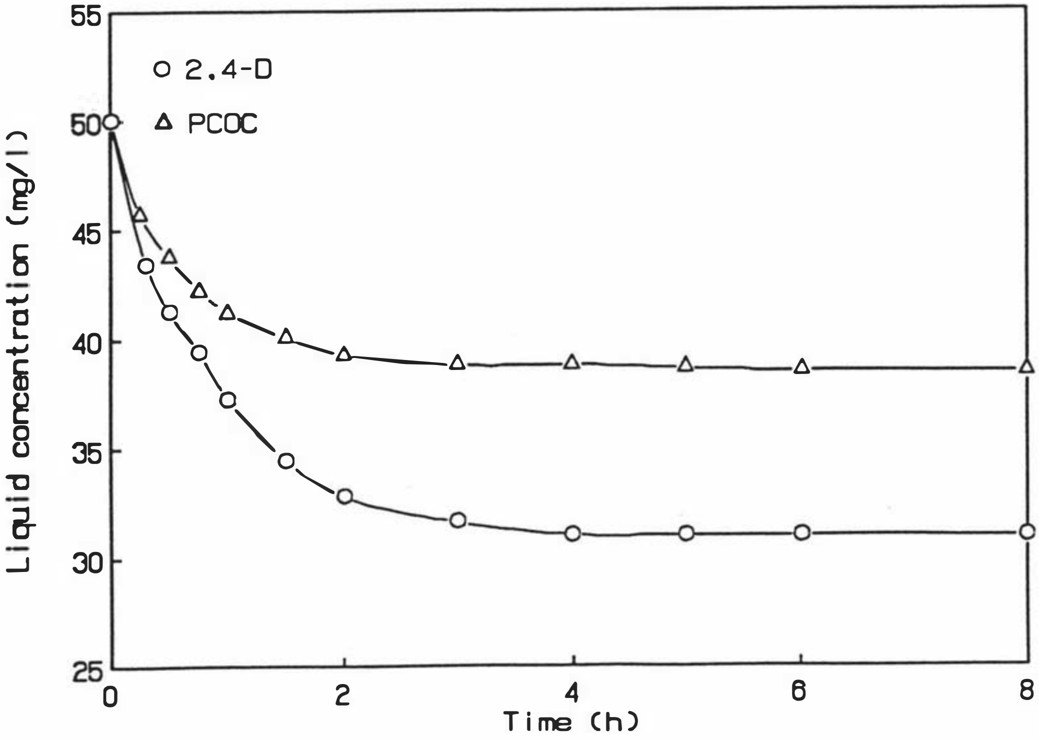
Equilibrium sorption plays a dominant role in the fate and transport of organic chemicals in soils, and is generally expressed in terms of isotherms. For any chemical, isotherm is dependent on the soil properties and environmental conditions. The information obtained from an isotherm gives a quantitative measure of the soil capacity to adsorb as well as desorb a given chemical.

The equilibrium adsorption/desorption of three phenoxyacetic acids and three chlorophenols in single and bi-component systems are examined in a volcanic soil to determine the sorption parameters and their relationships. In addition, the effects of pH, temperature and initial concentration on sorption were examined.

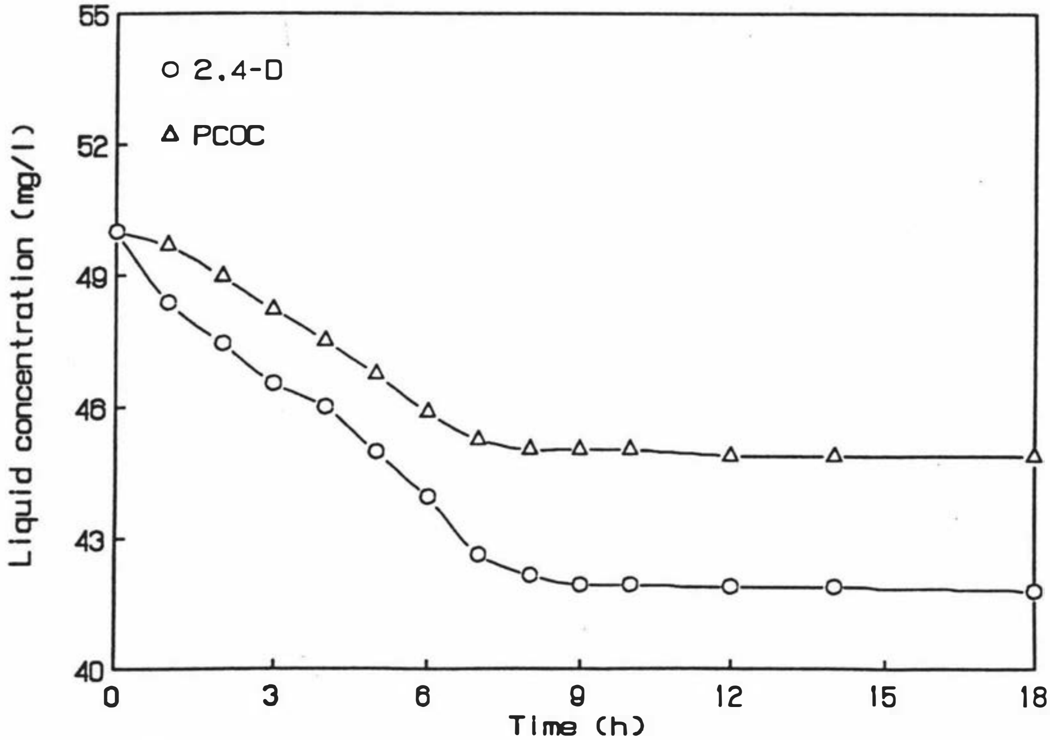
4.2 Preliminary studies

The contact time between the soil and chemical is an important parameter in an equilibrium adsorption study (Brusseau and Rao, 1989). Kan *et al.* (1994) report that the use of an inadequate contact time results in an underestimation of sorption capacity and leads to incorrect determination of isotherm parameters, determining sorption equilibrium time by taking 100 mg/l of solution with a known amount of soil in conical flasks and periodically measuring the decrease in solute concentration. Typical changes in liquid concentration with time for 2,4-D and PCOC are shown in Figure 4.1, which indicates that the equilibrium was reached in four hours. Based on these results, an equilibrium time of four hours was used for all single solute adsorption experiments.

The contact time for bicomponent equilibrium studies was also determined by the above procedure. Figure 4.2 shows results for a mixture of 2,4-D-PCOC and indicates that the time required to achieve equilibrium was 12 hours.



<u>Figure 4.1:</u> Equilibrium test for 2,4-D and PCOC in single component system (Temperature = 20°C, pH = 2, C_0 = 50 mg/l).



<u>Figure 4.2:</u> Equilibrium test for bicomponent mixture, 2,4-D-PCOC (Temperature = 20°C, pH = 2, C_0 = 50 mg/l).

4.3 Single component adsorption-desorption

4.3.1 Effect of pH

The effect of pH on adsorption of phenoxyacetic acids and chlorophenols was carried out to determine the range of pH values over which the positive adsorption takes place. This is shown in Figure 4.3 for 2,4-D, 2,4,5-T and MCPA. The figure shows that by increasing the solution pH the adsorption decreased for all three phenoxyacetic acids. In the present study, no adsorption of phenoxyacetic acids occurred near or slightly above the pK_a values of the respective compounds, this is because, as the pH is increased, the soil surface becomes negatively charged, therefore, the compounds are repulse from the soil and hence the adsorption decreases. The pH at which the adsorption was found to be zero is taken from Figure 4.3 is shown in Table 4.1.

Table 4.1 pH values below which positive adsorption of phenoxyacetic acids and chlorophenols take place.

Compound	pH	pK_a	Compound	pH	pK_a
Phenoxyacetic acid			Chlorophenol		
2,4-D	2.73	2.73	2,4-DCP	3.27	7.85
2,4,5-T	3.26	2.88	2,4,5-TCP	3.50	6.00
MCPA	3.52	3.05	PCOC	3.53	5.76

Phenoxyacetic acids are weak acids, compounds existing both in anionic and neutral forms in aqueous solutions. The relative amounts of each is determined by the acid equilibrium constant, K_a, and the aqueous solution pH. This equilibrium is expressed as:

$$HA_{(aq)} \rightleftharpoons H^{+}_{aq} + A^{-}_{aq}$$

The equilibrium constant, K_a, is expressed as,

$$K_a \equiv \frac{[H^+][A^-]}{[HA]} \qquad (4.1)$$

where [HA] is defined as the aqueous concentration of the neutral species; $[H^+]$ is the aqueous hydrogen ion concentration; and $[A^-]$ is the aqueous concentration of the anion

In addition, $pK_a = -\log_{10}K_a$ and $pH = -\log_{10}[H^+]$ which is expressed as,

$$\frac{[HA]}{[A^-]} = 10^{(pK_a - pH)} \tag{4.2}$$

which gives the ratio of the neutral species to the anion as a function of pH, and shows the increasing proportion of the anions at higher pHs resulting in higher adsorption of neutral form at low pH values. The trend of increasing sorption with decreasing pH suggests that the soil sorption of the neutral form of the weak acids is due to the organic matter of the soil. A large portion of the soil organic matter is in neutral form at pH 2 and, in addition, the hydrophobic neutral form of solute sorbs to the soil functional groups more than the anionic form (Fontaine *et al.,* 1991). Weber (1966) and Grover (1971) report the positive adsorption of phenoxyacetic acids below their respective pK_a values. The dependence of adsorption on pH is reported for other acid herbicides (Stougaard *et al.,* 1990; Fontaine *et al.,* 1991).

Figure 4.4 shows the effect of pH on the adsorption of 2,4-DCP, 2,4,5-TCP and PCOC; the pH values at which the adsorption was zero are shown in Table 4.1. The sorption of chlorophenols at low pH values by the soil is also due to the sorption of non-dissociated forms to the neutral organic matter (Hamaker and Thompson, 1972). Chlorophenols have pK_a values in the range 5-8, however no adsorption was observed beyond a pH of 3.5. As Bailey *et al.* (1968) report that the positive adsorption of chlorophenols occur when the pH is at least 1-2 units lower than the pK_a of the respective compounds. Similar trend was observed in this study. Schellenberg *et al.* (1984), Westall *et al.* (1985) and Lee *et al.* (1990) report the adsorption of chlorophenols onto soils and aquifer materials decrease with increasing solution pH.

From Table 4.1 it is clear that no adsorption of phenoxyacetic acids was observed at $pH=pK_a$, while for chlorophenols the adsorption was zero when pH is 2-3 units below the pK_a values. The cause for this discrepancy is not clear and more experimental work is needed to elucidate the reasons for the observed behaviour. The negligible or no adsorption of the anion form at pH value beyond 3.5 indicates relatively high mobility in soil solution, whereas the positive adsorption of the neutral form suggests, low mobility (Fontaine *et al.,* 1994). Hence, the transport of phenoxyacetic acids and chlorophenols depends on the proportion of anion versus neutral forms in soil

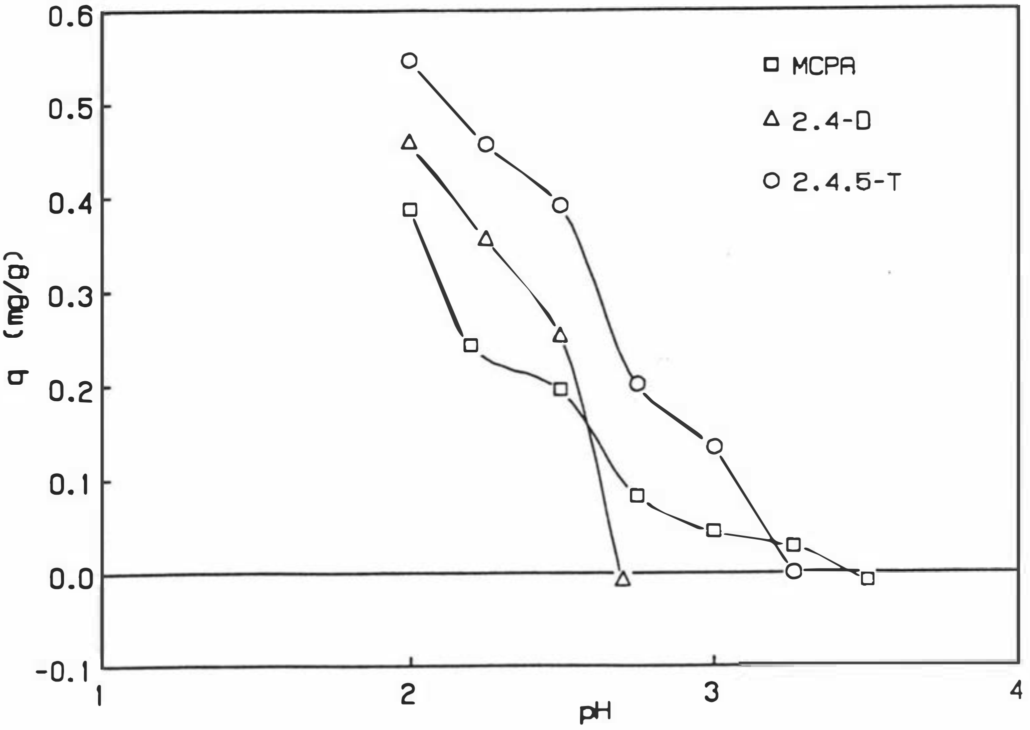


Figure 4.3: Effect of pH on adsorption of phenoxyacetic acids (C_0 = 50 mg/l, Temperature = 20°C).

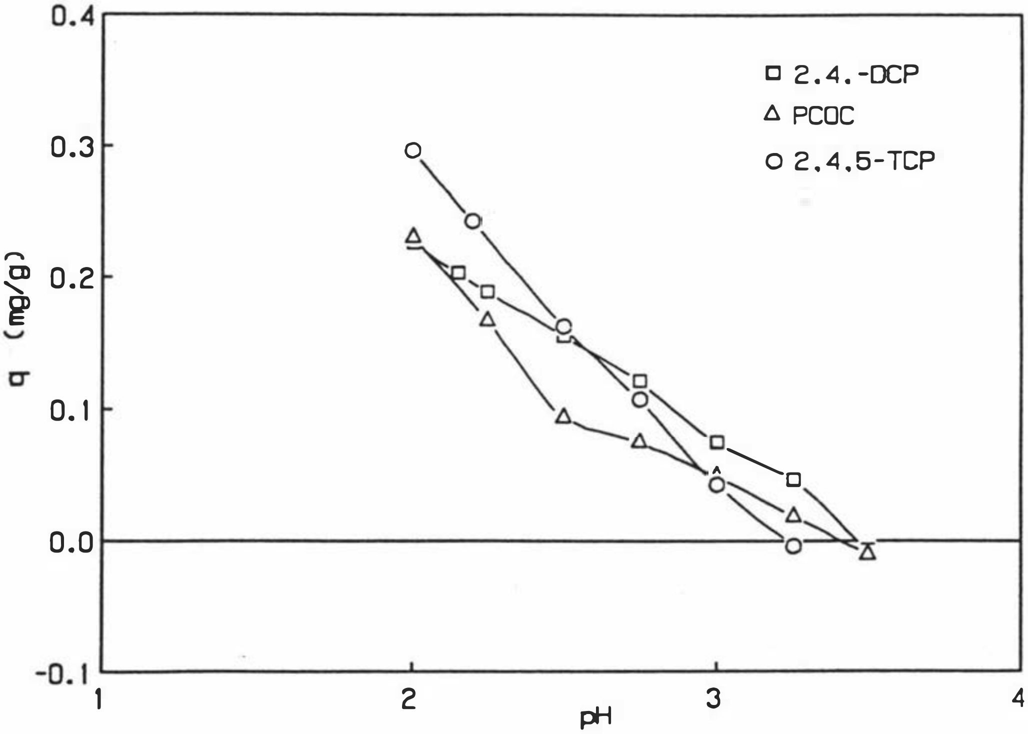


Figure 4.4: Effect of pH on adsorption of chlorophenols (C_0 = 50 mg/l, Temperature = 20°C).

4.3.2 Adsorption

In the adsorption experiments, the mass of solute which disappeared from the solution phase at the end of the adsorption equilibrium experiment was assumed to be adsorbed on soil:

$$q = (C_0 - C_e)\frac{V}{m} \tag{4.3}$$

where, q is the amount of solute adsorbed on the soil (mg/g), C_0 is the initial concentration of solute (mg/l), C_e is the solution-phase solute concentration at the end of the adsorption experiment (mg/l), V is the volume of solution (ml) and m is the mass of adsorbent (g).

Figures 4.5-4.10 show the plots of q *versus* C_e using the data obtained from adsorption experiments at 20°C and pH 2. In Section 2.3.7, where frequently used isotherm models were presented, only the Freundlich-type isotherm could describe the equilibrium sorption data satisfactorily compared to Langmuir, linear and IAST isotherm models. This was based on the r^2 values obtained for different models. The high correlation ($r^2 > 97\%$) indicates an excellent fit to the Freundlich adsorption equation. Accordingly, a Freundlich-type isotherm was used to describe the experimental data for all solutes. The Freundlich constants, K and 1/n were determined by nonlinear regression, are given in Table 4.2. The solid line in Figures 4.5-4.10 is the predicted profile using the Freundlich isotherm constants.

The 1/n values for both phenoxyacetic acids and chlorophenols are in the range 0.72-1.0. A $1/n < 1$ indicates a nonlinear isotherm, where the marginal adsorption energy of a chemical decreases with increasing surface concentration (Brusseau and Rao, 1989; Weber *et al.*, 1991). The isotherm nonlinearity could be attributed to varying adsorption energies and sorption involving site-specific mechanisms for phenoxyacetic acids and chlorophenols (Brusseau and Rao, 1989; Kan *et al.*, 1994). Similar 1/n values for organic chemicals were reported in a variety of soils by Hamaker and Thompson (1972), Calvet (1980), Schellenberg *et al.* (1984), Boyd *et al.* (1989) and Farrell and Reinhard (1994a).

The surface area covered by the solute at the end of the adsorption equilibrium was determined using the relationship (Farrell and Reinhard, 1994a):

$$S - q_{\max}N_{av}A_m \tag{4.4}$$

where, A_m is the area per molecule, N_A is the Avogadro's number and q_{max} is the amount adsorbed and expressed in moles of solute per unit weight of adsorbent. The surface coverage for phenoxyacetic acids and chlorophenols determined from the above equation are given in Table 4.2. The results show that the range of total surface coverage is 2.1-4.4% of the surface area indicating that the solutes may be adsorbed only to specific sites in soil (Hamaker and Thompson, 1972). Adsorption increased in the order 2,4,5-T > MCPA > 2,4-D > 2,4,5-TCP > PCOC > 2,4-DCP, and the results indicate that the sorption capacity for phenoxyacetic acids is higher compared to chlorophenols.

The surface coverage calculations were based on the effective surface area available for the solutes to diffuse into the pores greater than average molecular diameter of 45 A. Even though the Freundlich isotherm is generally used for multilayer adsorption, and only 2.1-4.4 % of surface coverage was observed, the equilibrium data obtained in the present study could be best fitted to Freundlich isotherm model compared to the other single solute isotherm models. Therefore, all the data were fitted to the nonlinear Freundlich isotherm.

The second batch of soil, collected in 1992, was used mainly for column experiments. However, due to a small change in soil properties (organic matter and CEC), equilibrium experiments were conducted to ascertain any significant change in adsorption capacity. These experiments were conducted for phenoxyacetic acid (2,4-D) and chlorophenol (PCOC) at 20°C and pH 2. The adsorption data was described by a Freundlich isotherm, and the constants K and 1/n are given in Table 4.2. These values were within the error limits (Table 4.2) for those compounds obtained earlier. From these results, it was concluded that the change in the adsorption capacity was not significant.

Table 4.2 Adsorption isotherm parameters for phenoxyacetic acids and chlorophenols

Compound	K_{ads}	$1/n_{ads}$	r^2	% coverage
2,4-D	0.020 ± 0.003	0.75 ± 0.027	98.8	3.25
	0.021 ± 0.008	0.76 ± 0.030	97.1	4.14[a]
2,4,5-T	0.015 ± 0.003	0.90 ± 0.046	97.3	4.36
MCPA	0.028 ± 0.007	0.72 ± 0.051	98.4	4.28
2,4-DCP	0.004 ± 0.001	1.00 ± 0.047	98.8	2.11
2,4,5-TCP	0.016 ± 0.004	0.76 ± 0.040	97.4	2.66
PCOC	0.006 ± 0.002	0.93 ± 0.064	97.5	3.12
	0.006 ± 0.008	0.96 ± 0.068	96.5	3.69[a]

[a] Soil collected in 1992.

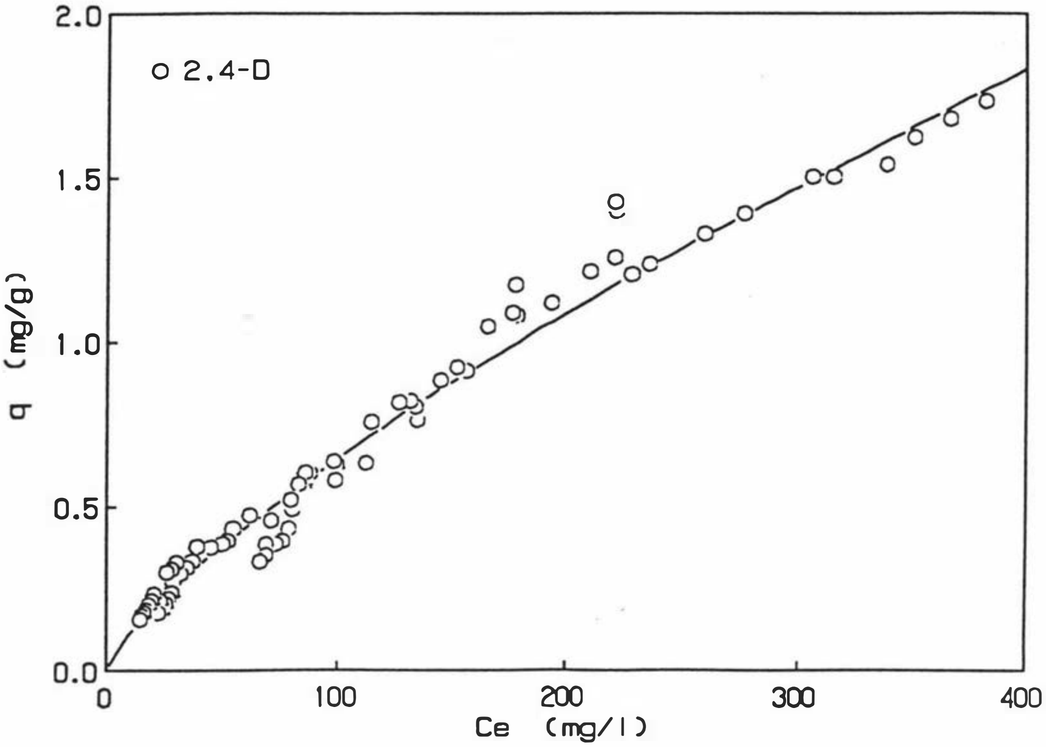


Figure 4.5: Adsorption isotherms of 2,4-D at 20°C and pH 2.

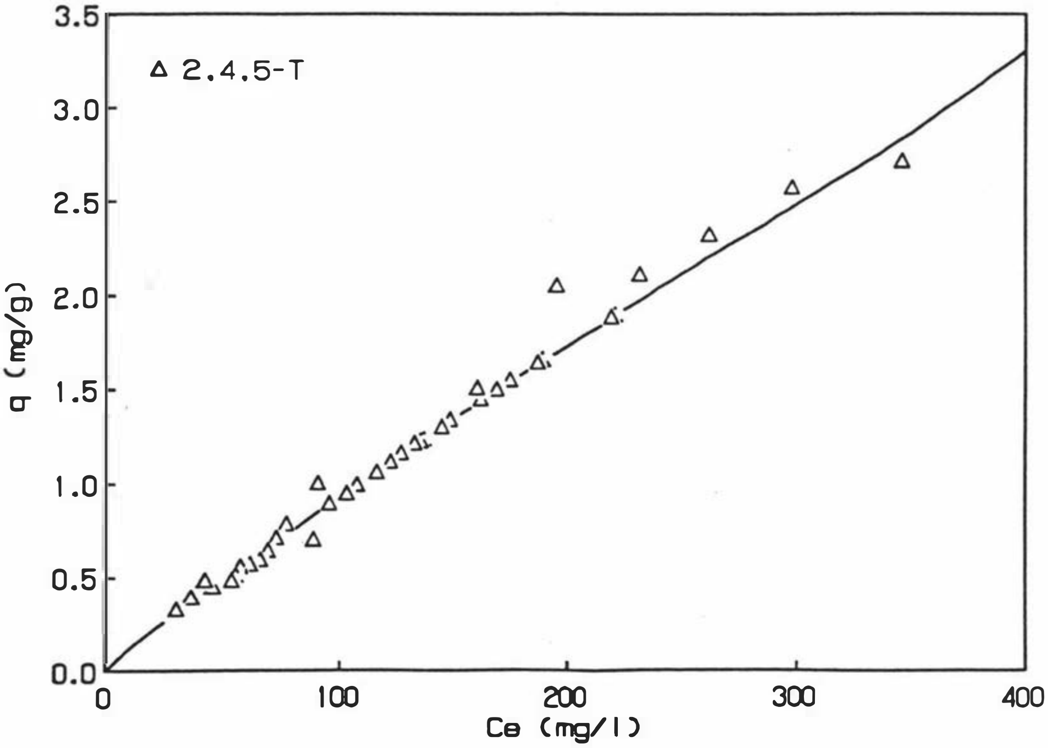


Figure 4.6: Adsorption isotherm of 2,4,5-T at 20°C and pH 2.

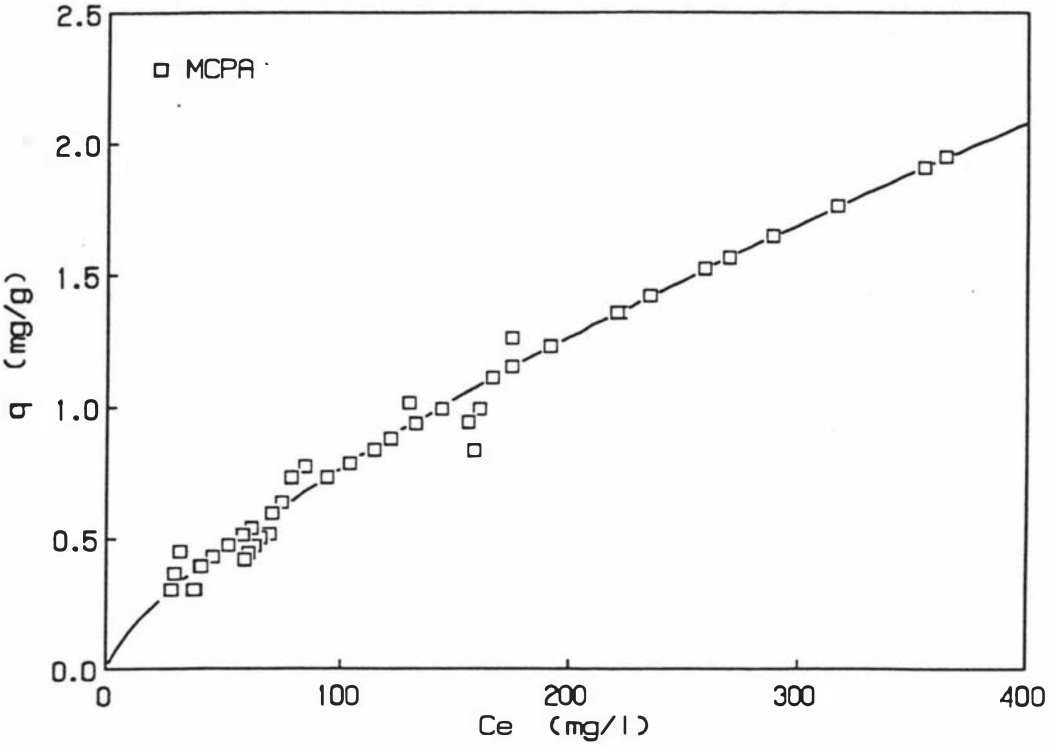


Figure 4.7: Adsorption isotherm of MCPA at 20°C and pH 2.

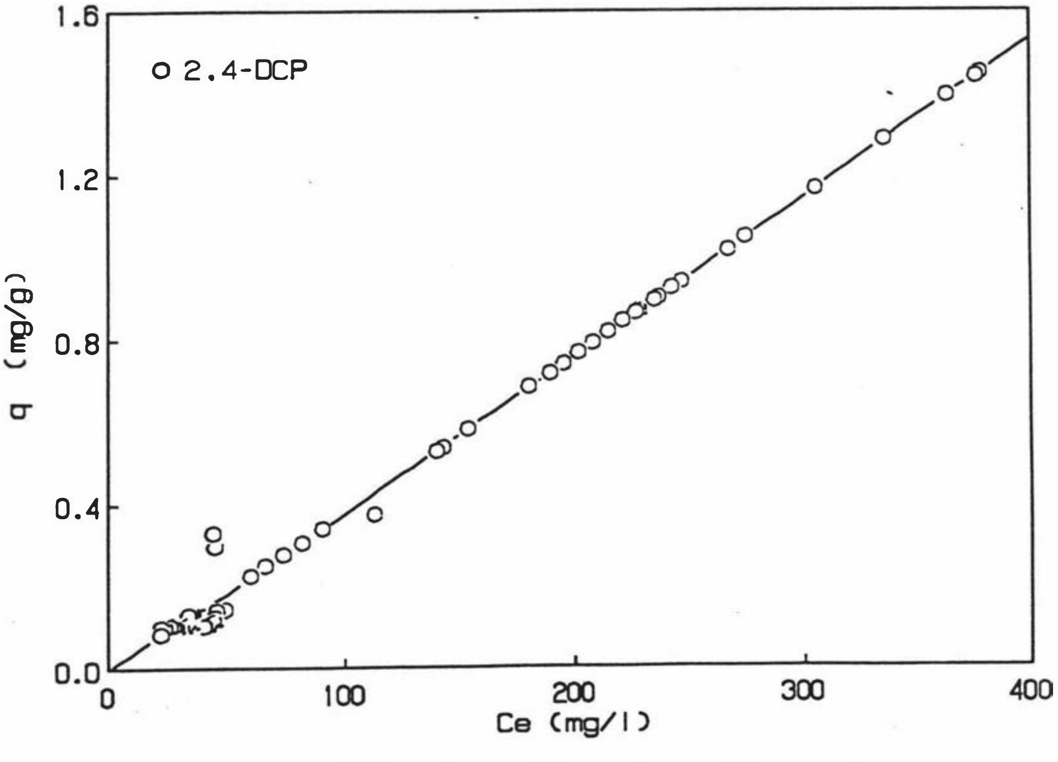


Figure 4.8: Adsorption isotherm of 2,4-DCP at 20°C and pH 2.

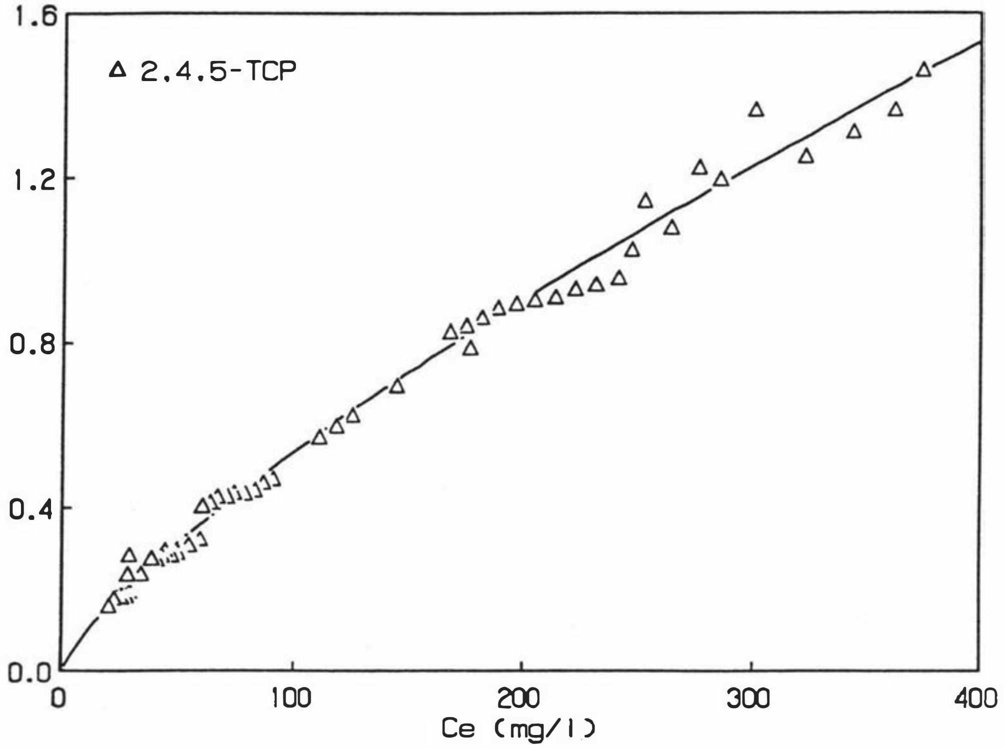


Figure 4.9: Adsorption isotherm of 2,4,5-TCP at 20°C and pH 2.

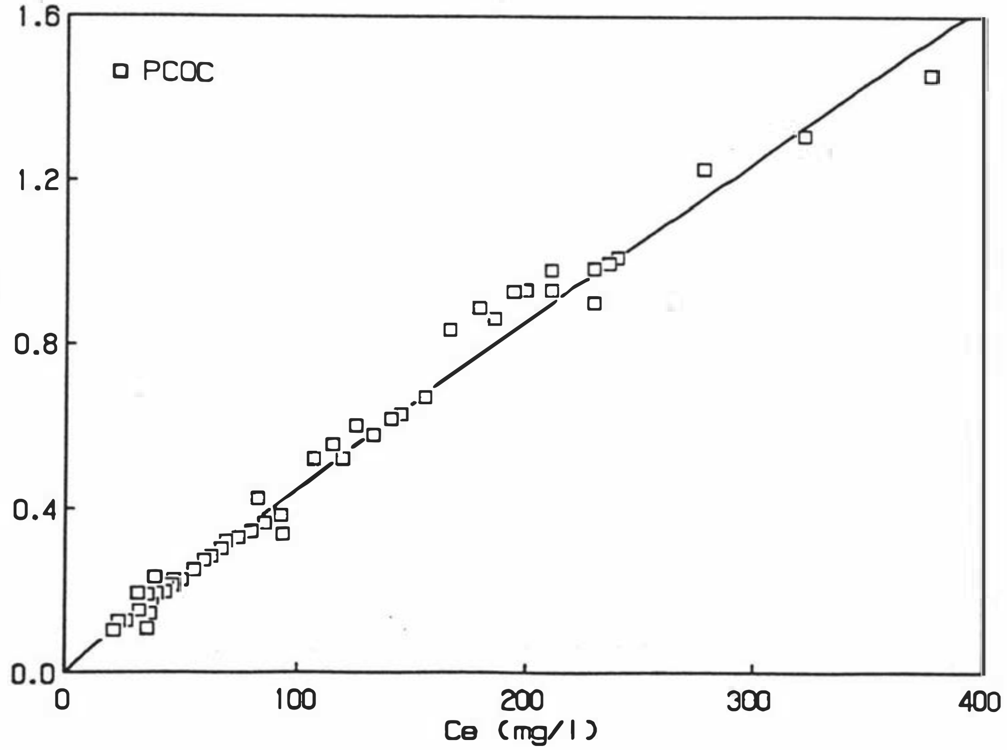


Figure 4.10: Adsorption isotherm of PCOC at 20°C and pH 2.

4.3.3 Effect of temperature

The effect of temperature on the adsorption of phenoxyacetic acids and chlorophenols is shown in Figures 4.11-4.16, respectively. The adsorption data was again described using a Freundlich-type isotherm, the constants K and 1/n determined from nonlinear regression at two temperatures are given in Tables 4.3. The solid lines in Figures 4.11-4.16 were predicted using Freundlich adsorption isotherm parameters at respective temperatures.

Increasing the temperature from 10 to 30°C resulted in a decrease in adsorption capacity for all the compounds investigated. The decrease in sorption of solute at higher temperatures is due to the increased solubility at higher temperatures; for example, the solubility of 2,4-D at 20°C is 400 mg/l and at 30°C it is 900 mg/l. Therefore, by increasing the temperature by 10°C the solubility increased by 2.5 times which resulted in reduced adsorption. An inverse relationship was observed between solubility and adsorption by many researchers (Calvet, 1980; Hassett and Banwart, 1989). In addition, the sorption reactions are exothermic in nature and an increase in temperature reduces the sorption (Hance, 1988).

The heat of adsorption (-ΔH) was calculated using Vant Hoff's equation (Hassett and Banwart, 1989);

$$\ln\frac{K_1}{K_2} = \frac{(-\Delta H)(T_1 - T_2)}{R_g T_1 T_2} \tag{4.5}$$

where, K_1 and K_2 are isotherm constants at temperatures T_1 and T_2, respectively, and R_g is the universal gas constant. The heat of adsorption values, determined from the above equation are listed in Table 4.3, and are higher for chlorophenols compared to phenoxyacetic acids. The (-ΔH) values obtained were similar in magnitude to those reported for adsorption of organic chemicals onto various soils (Hamaker and Thompson, 1972).

The estimated (-ΔH) values for phenoxyacetic acids and chlorophenols suggest that hydrogen bonding is the probable mechanism of adsorption (Table 2.1). In this mechanism, the carbonyl group of the undissociated phenoxyacetic acid interacts by forming a hydrogen bond with the water molecules attached to the soil exchange groups or to the ammonium groups present in the soil organic matter (Bailey *et al.*, 1968; Hermosin and Cornejo, 1993). The mechanism of phenoxyacetic acid adsorption is shown in Figure 4.17a.

The likely mechanism of adsorption of chlorophenols onto soil is shown in Figure 4.17b. Boyd (1982) suggests a hydrogen bond formation between the phenolic hydroxyl and H-bonding sites on organic matter. In this type of mechanism, the phenolic -OH acts as a proton acceptor (electron donor).

Table 4.3 Adsorption isotherm parameters for phenoxyacetic acids and chlorophenols - effect of temperature (pH = 2).

Compound	Temperature °C	K_{ads}	$1/n_{ads}$	r^2 (%)	-ΔH (kcal /mole)
2,4-D	10	0.029 ± 0.003	0.71 ± 0.019	98.5	4.72
	30	0.017 ± 0.001	0.78 ± 0.006	98.9	
2,4,5-T	10	0.019 ± 0.001	0.88 ± 0.010	98.6	4.66
	30	0.011 ± 0.001	0.94 ± 0.027	97.9	
MCPA	10	0.033 ± 0.001	0.70 ± 0.010	98.9	4.08
	30	0.020 ± 0.003	0.75 ± 0.031	98.6	
2,4-DCP	10	0.005 ± 0.001	0.96 ± 0.008	98.9	6.63
	30	0.002 ± 0.001	1.04 ± 0.009	98.9	
2,4,5-TCP	10	0.019 ± 0.002	0.74 ± 0.021	97.7	4.03
	30	0.012 ± 0.001	0.80 ± 0.012	98.9	
PCOC	10	0.009 ± 0.002	0.90 ± 0.024	98.9	7.30
	30	0.004 ± 0.001	0.97 ± 0.032	97.7	

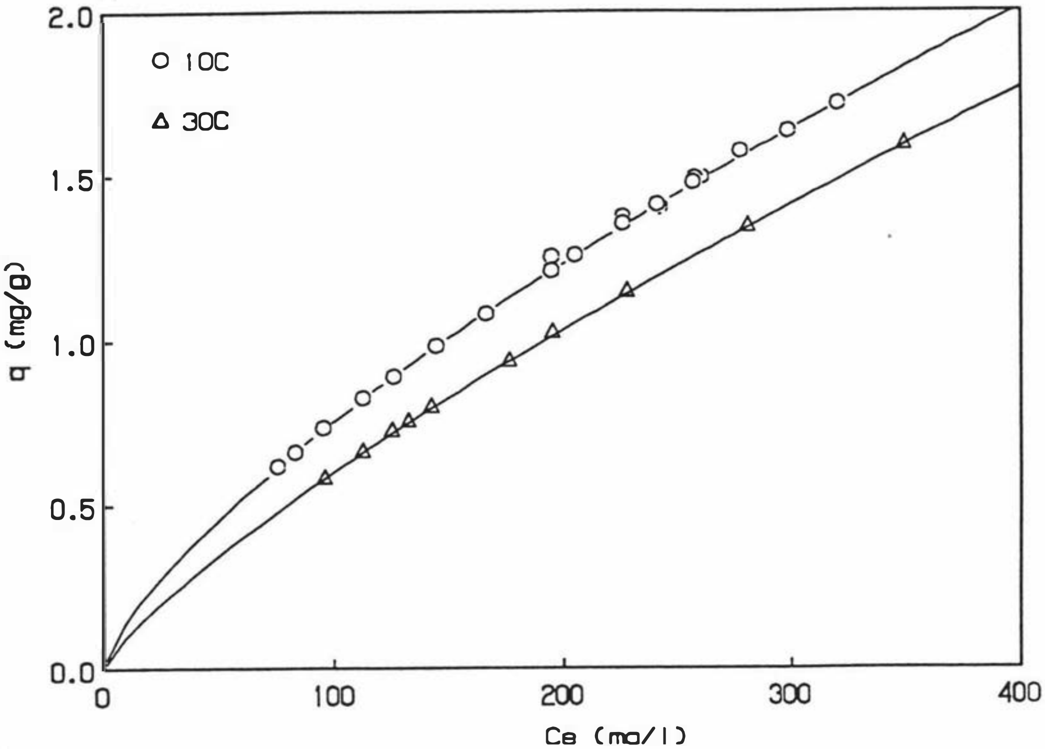


Figure 4.11: Effect of temperature on adsorption of 2,4-D at pH 2.

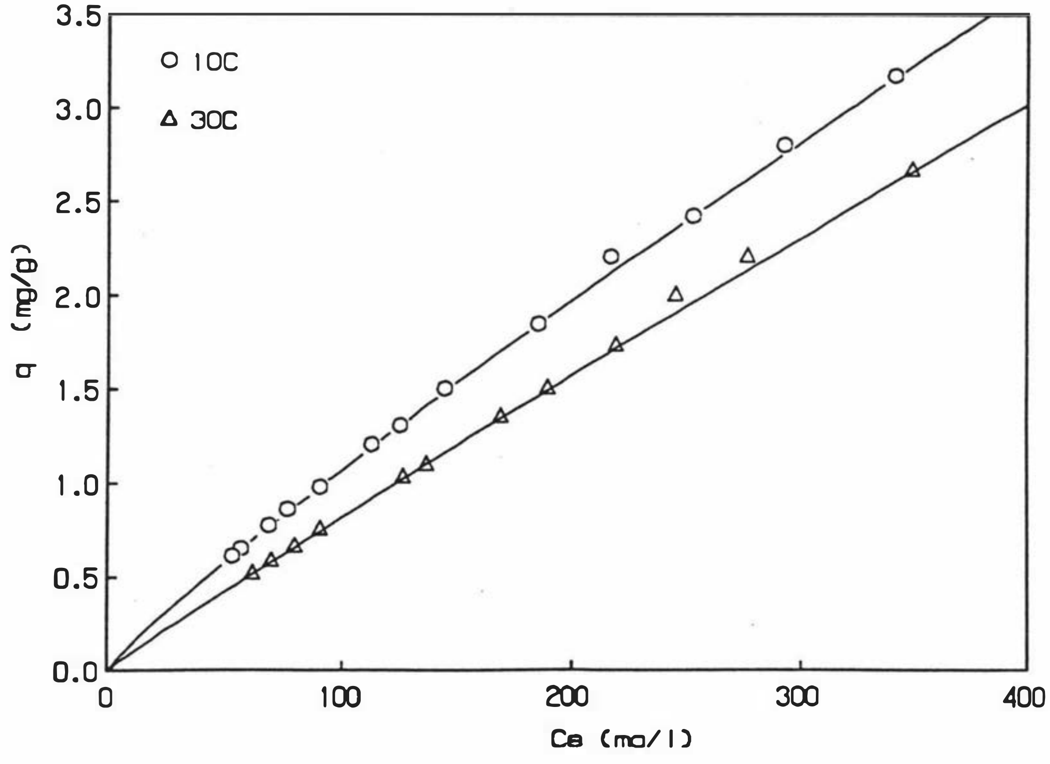


Figure 4.12: Effect of temperature on adsorption of 2,4,5-T at pH 2.

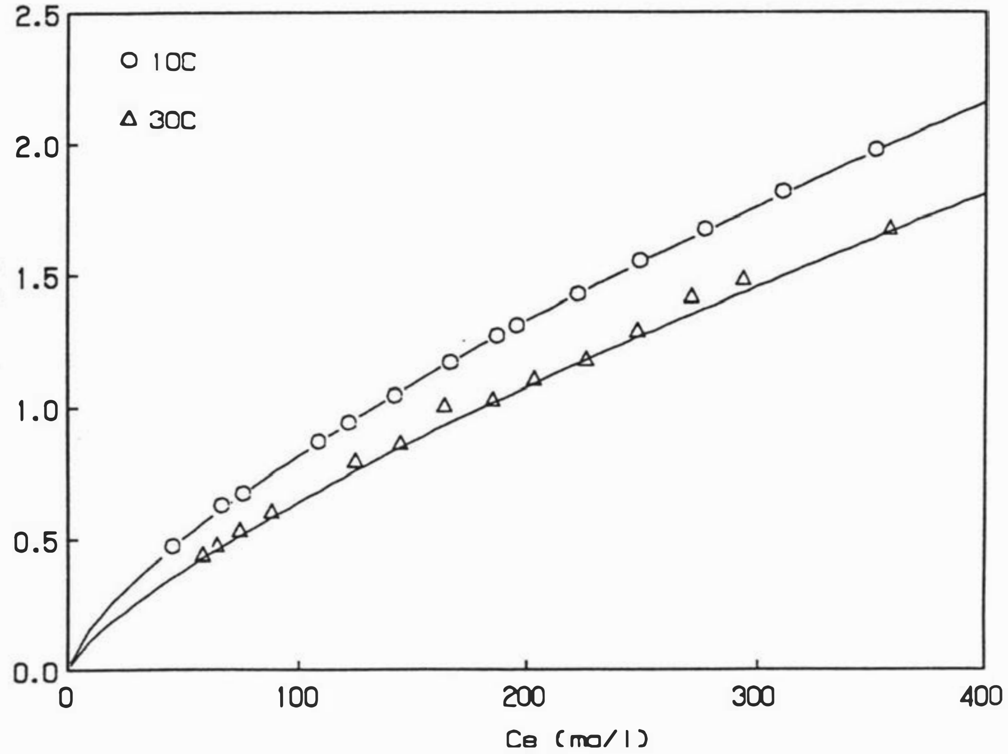


Figure 4.13: Effect of temperature on adsorption of MCPA at pH 2.

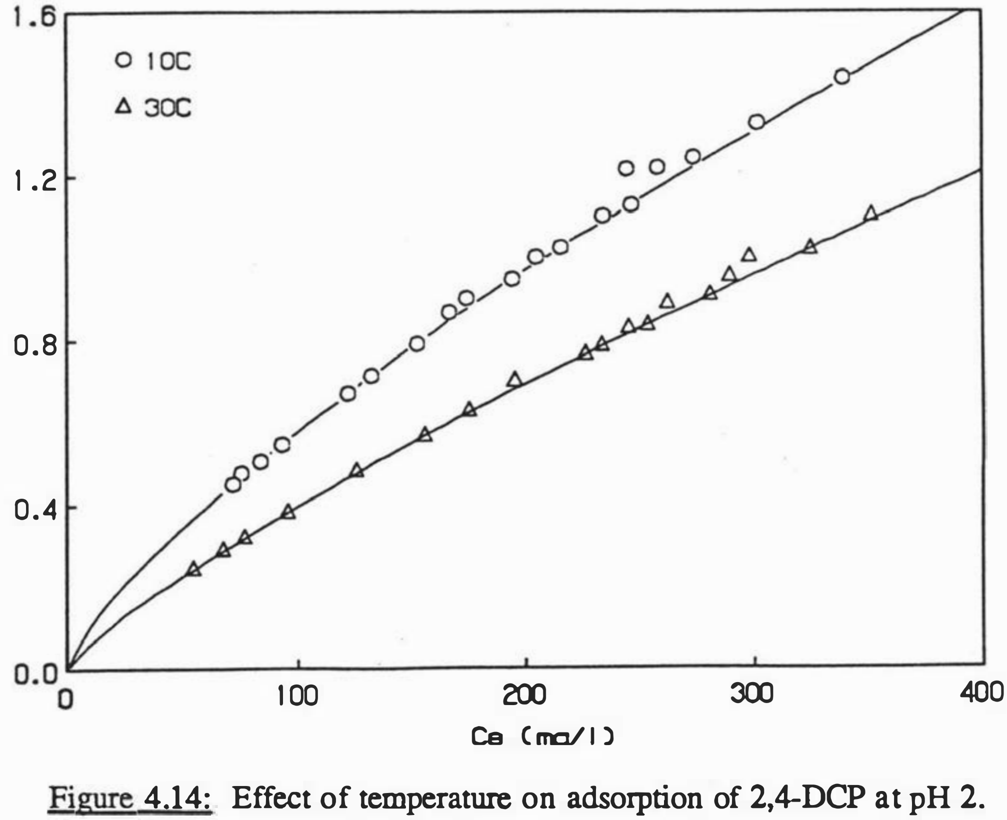


Figure 4.14: Effect of temperature on adsorption of 2,4-DCP at pH 2.

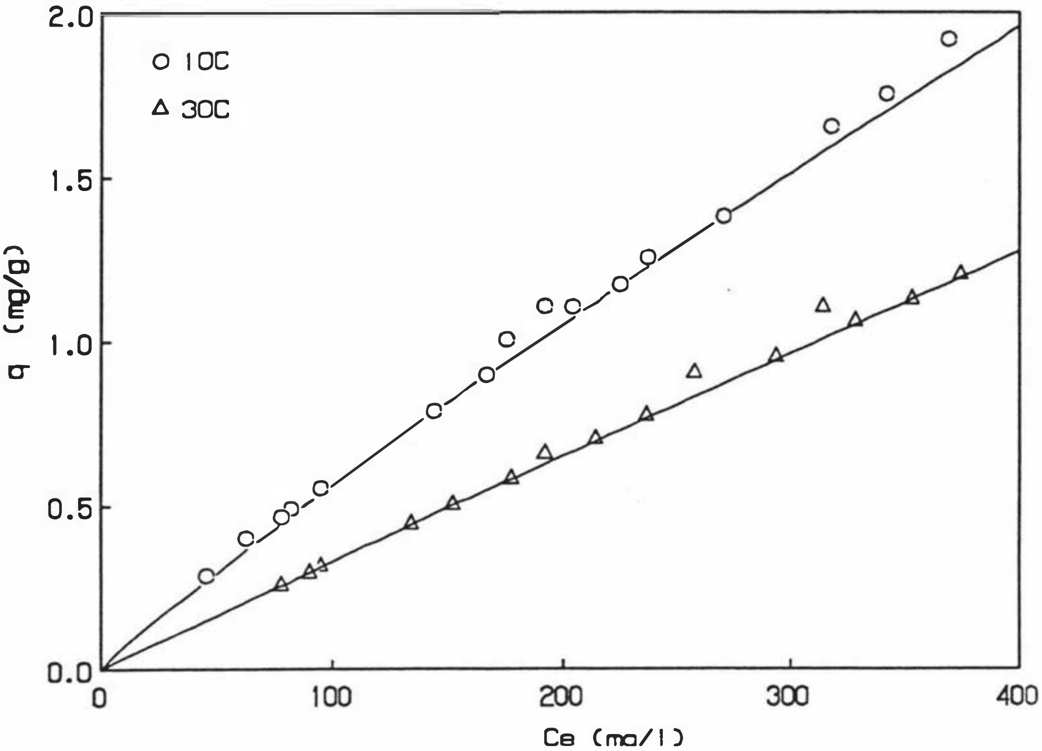


Figure 4.15: Effect of temperature on adsorption of 2,4,5-TCP at pH 2.

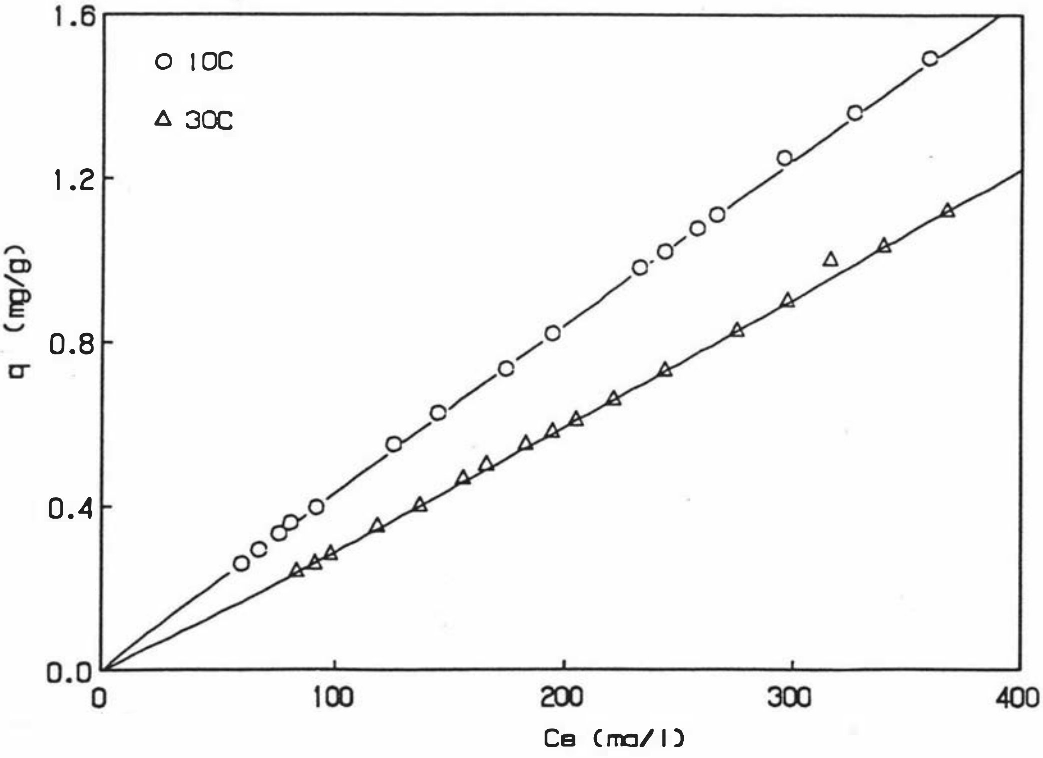


Figure 4.16: Effect of temperature on adsorption of PCOC at pH 2.

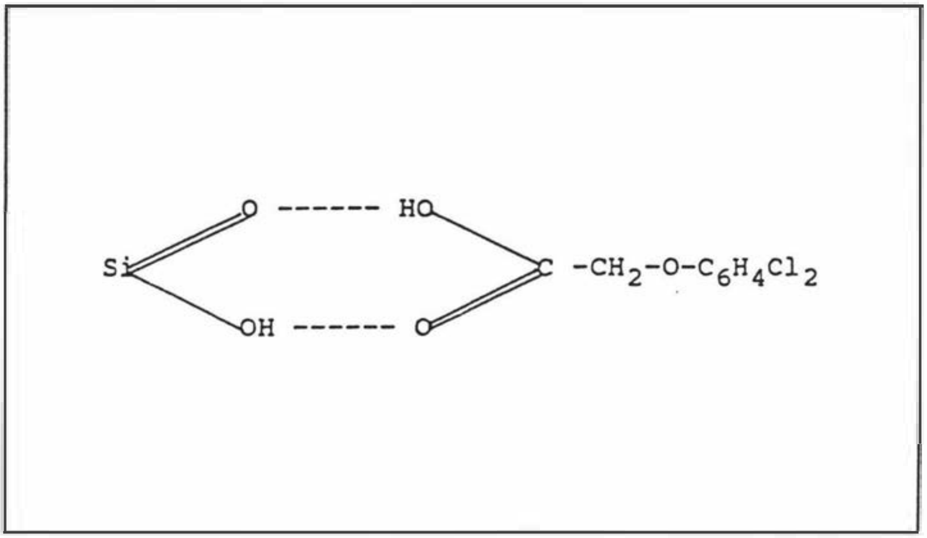


Figure 4.17a Mechanism of adsorption of phenoxyacetic acids (Bailey *et al.*, 1968; Hermosin and Cornejo, 1993).

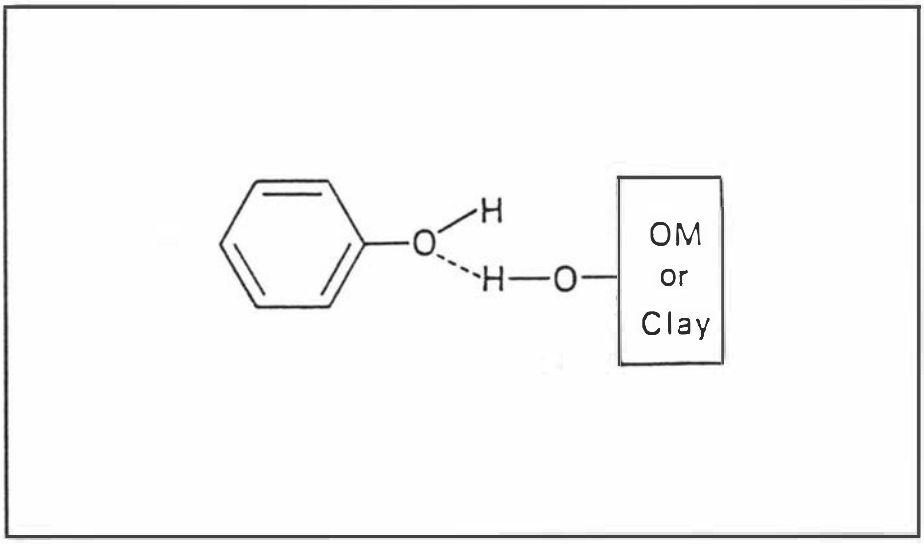


Figure 4.17b Mechanism of adsorption of chlorophenols (Boyd, 1982).

4.3.4 Desorption

The equilibrium desorption experiments, carried out for all compounds after the adsorption experiments, used the same soil-chemical mixture. The desorption equilibrium time for each step was 2 h, and for each dilution 20 ml of the supernate was replaced with solute free distilled water at pH 2. In each desorption step, the solution-phase concentration is the sum of the remaining solution-phase solute plus the solute that desorbed from the solid phase. Thus, the desorption from the soil during ith desorption step is expressed as,

$$\Delta q^{i}_{desorbed} = [C_i - C_{i-1}(1 - e)]\frac{V}{m} \tag{4.6}$$

where, $\Delta q^{i}_{desorbed}$ is changed in the solid-phase concentration (mg/g) during the ith desorption step; C_i and C_{i-1} are solution-phase solute concentrations at the end of the ith and (i-1)th desorption steps; and r is the fraction of the supernate replaced at each dilution, in this study, e = 0.2. At the first desorption step, C_{i-1} refers to the solution concentration at the end of adsorption experiment (C_e). In the following discussion, the percentage of solute desorbed is defined as the accumulated amount of solute desorbed from successive desorption steps, and expressed as,

$$\%\ solute\ desorbed\ (experimental) = \frac{\sum_{i=1}^{n} \Delta q^{i}_{desorbed}}{q_{max}} \times 100\% \tag{4.7}$$

where, n is the total number of desorption steps.

The adsorption and desorption isotherms at 20°C for phenoxyacetic acids and chlorophenols are shown in Figures 4.18-4.23, respectively. Isotherms were obtained from three adsorption equilibrium points as shown in figures. The desorption data were also fitted to a Freundlich-type equation, and the desorption parameters determined for each isotherm using nonlinear regression. Table 4.5 gives the Freundlich K_{des} and $1/n_{des}$ values for each desorption isotherm of phenoxyacetic acids and chlorophenols. The solid line in each figure was predicted using Freundlich isotherm parameters for adsorption and desorption. O indicates q_{max} where desorption is initiated.

Table 4.4 Desorption isotherm parameters for phenoxyacetic acids and chlorophenols, q_{max} is the amount adsorbed in the soil before desorption.

Chemical	q_{max} (mg/g)	K_{des}	$1/n_{des}$	r^2 (%)	K_{des} (Eq 4.9)
2,4-D					
1	0.44	0.10 ± 0.02	0.35 ± 0.06	95.5	0.11
2	0.92	0.30 ± 0.05	0.21 ± 0.04	93.9	0.32
3	1.34	0.53 ± 0.07	0.16 ± 0.06	96.7	0.56
2,4,5-T					
1	0.49	0.09 ± 0.01	0.43 ± 0.01	99.8	0.09
2	0.91	0.21 ± 0.01	0.32 ± 0.02	99.5	0.21
3	1.84	0.63 ± 0.03	0.20 ± 0.01	99.6	0.64
MCPA					
1	0.49	0.12 ± 0.02	0.36 ± 0.06	94.8	0.12
2	0.91	0.23 ± 0.03	0.28 ± 0.02	97.8	0.23
3	1.34	0.39 ± 0.06	0.23 ± 0.04	95.1	0.39
2,4-DCP					
1	0.38	0.11 ± 0.02	0.27 ± 0.04	94.8	0.11
2	0.94	0.12 ± 0.01	0.37 ± 0.02	99.3	0.12
3	1.19	0.23 ± 0.05	0.45 ± 0.04	96.6	0.22
2,4,5-TCP					
1	0.35	0.19 ± 0.04	0.15 ± 0.04	93.0	0.19
2	0.61	0.24 ± 0.04	0.20 ± 0.04	90.9	0.24
3	1.20	0.26 ± 0.06	0.24 ± 0.08	92.0	0.30
PCOC					
1	0.33	0.08 ± 0.03	0.32 ± 0.08	91.5	0.09
2	0.72	0.12 ± 0.03	0.36 ± 0.06	96.7	0.11
3	0.99	0.12 ± 0.02	0.39 ± 0.04	98.4	0.12

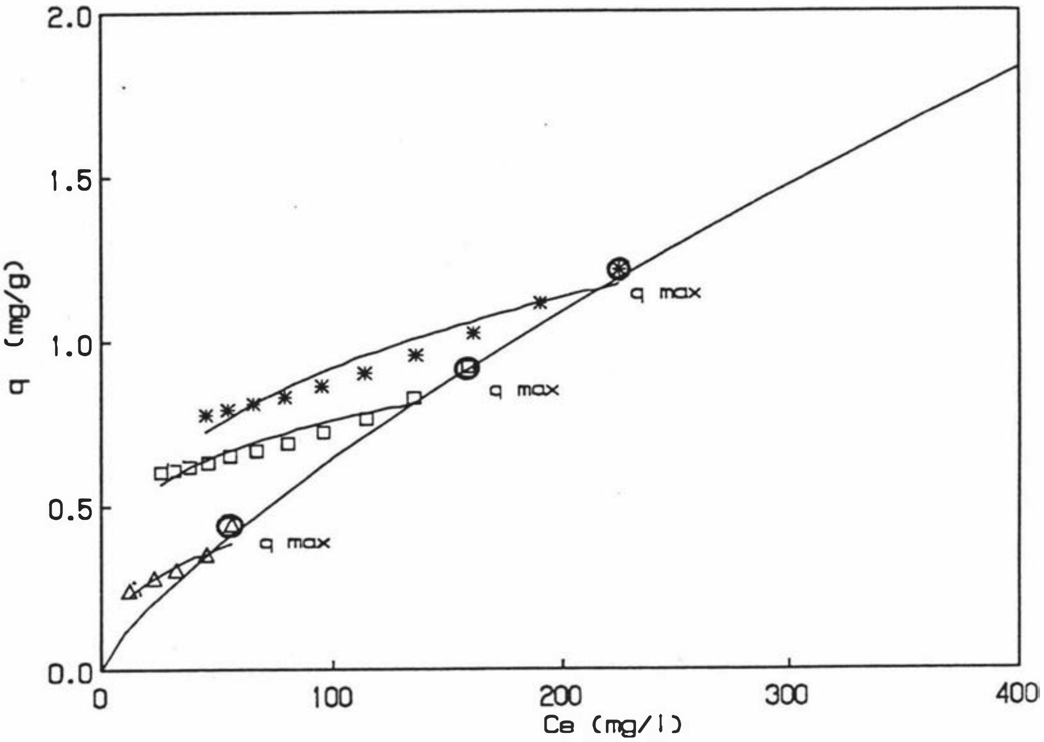


Figure 4.18: Desorption isotherms of 2,4-D at 20°C and pH 2.

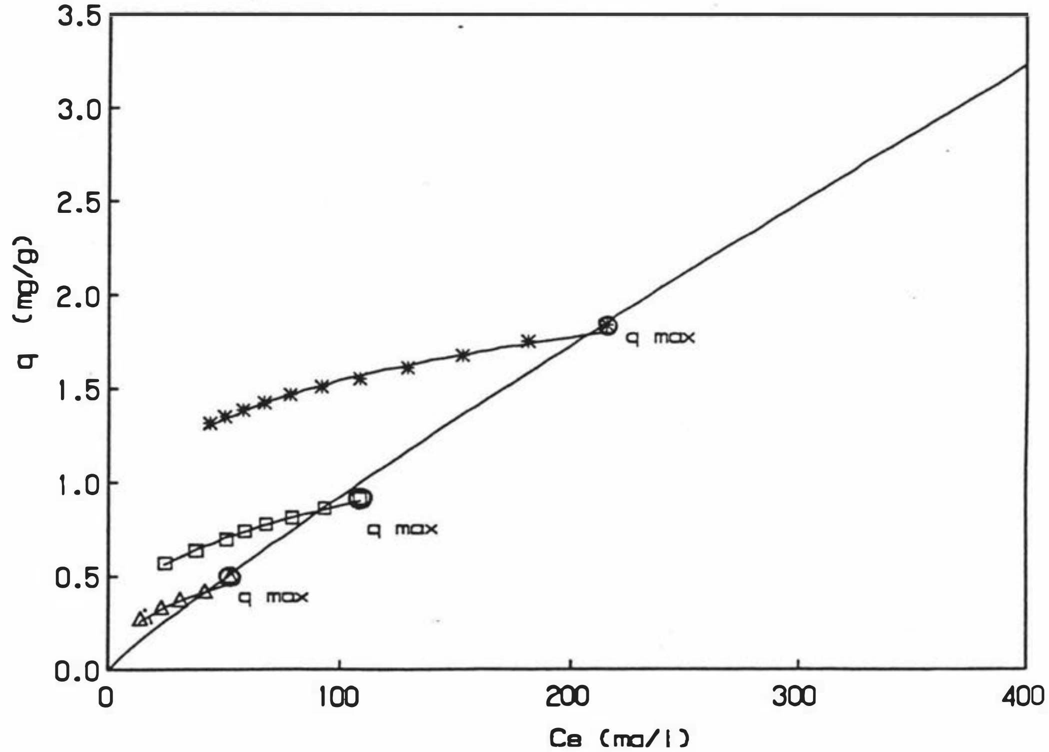


Figure 4.19: Desorption isotherms of 2,4,5-T at 20°C and pH 2.

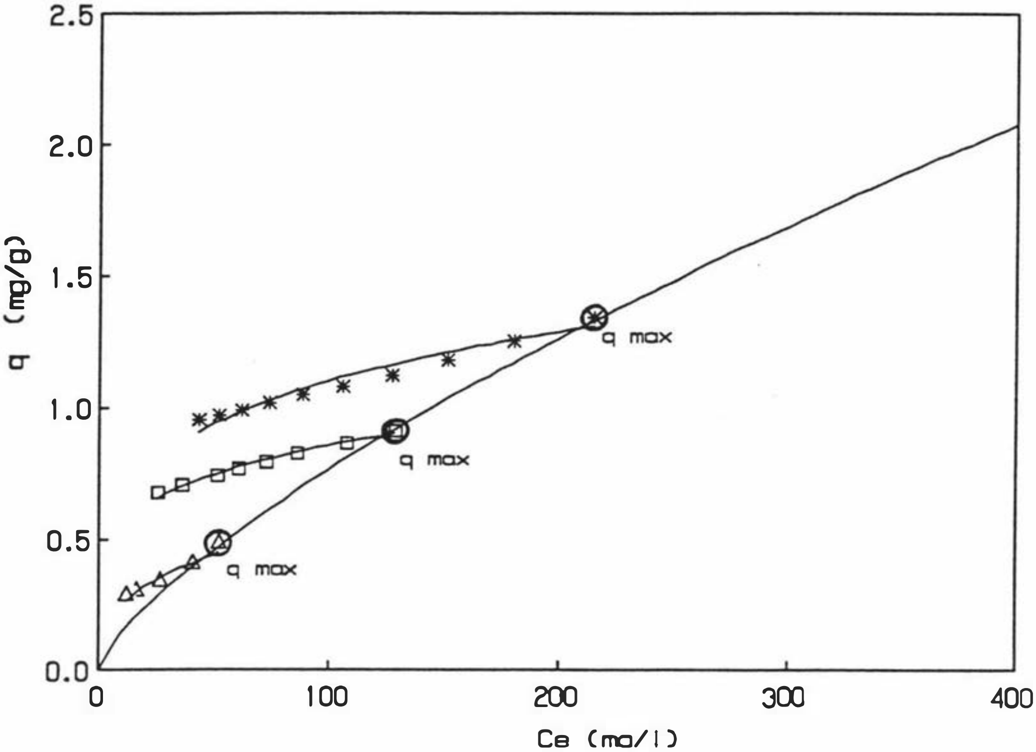


Figure 4.20: Desorption isotherms of MCPA at 20°C and pH 2.

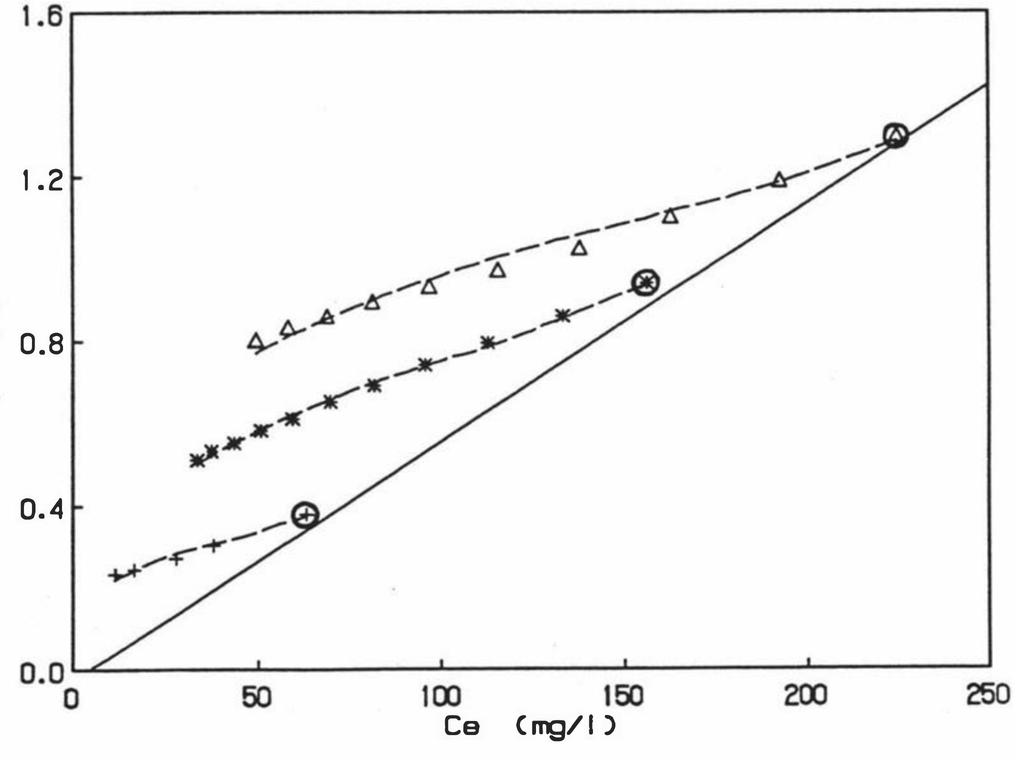


Figure 4.21: Desorption isotherms of 2,4-DCP at 20°C and pH 2.

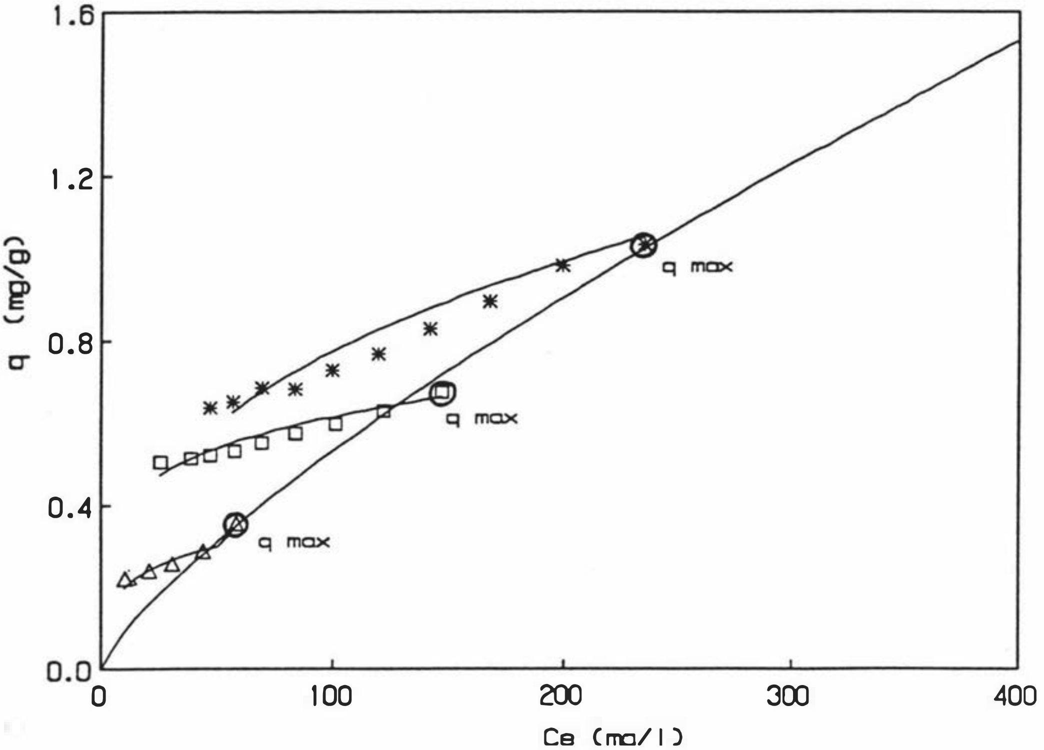


Figure 4.22: Desorption isotherms of 2,4,5-TCP at 20°C and pH 2.

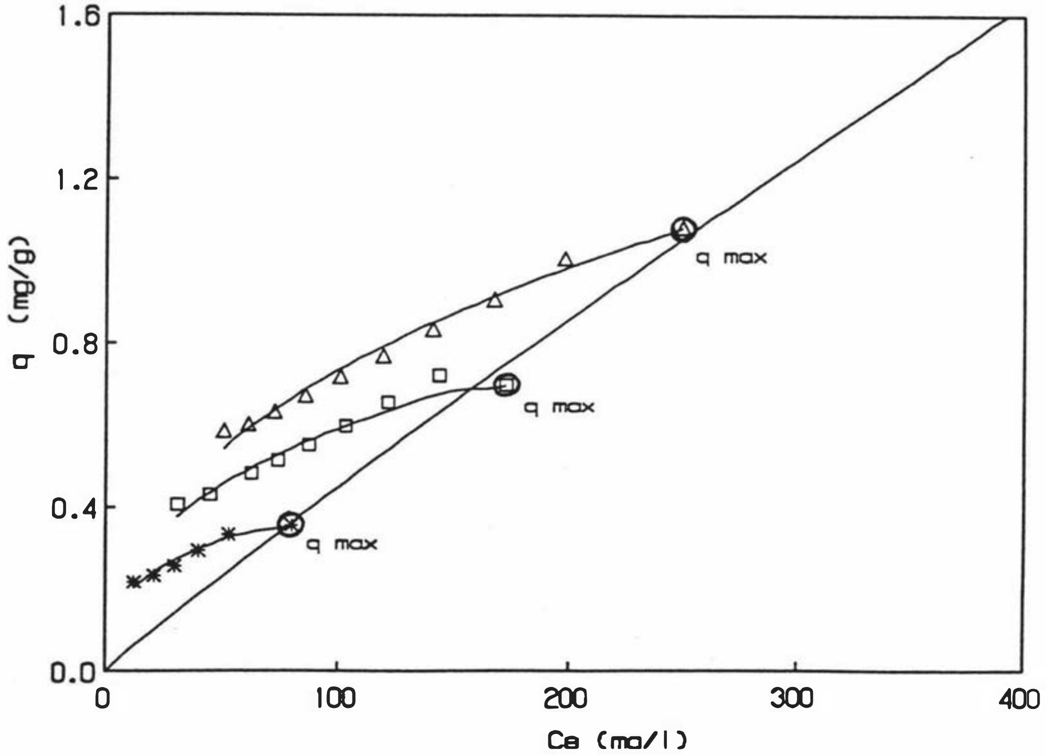


Figure 4.23: Desorption isotherms of PCOC at 20°C and pH 2.

The desorption coefficient, K_{des} found here has a higher value than the adsorption constant, K_{ads} (Table 4.2), also the equilibrium aqueous concentration is lower in the desorption experiments at the same adsorbed concentration (q_{max}) in soil.

The desorption path followed the solid line that is clearly different from the adsorption, which is generally attributed to hysteresis (Swanson and Dutt, 1973; Van Genuchten *et al.,* 1974 and Kan *et al.,* 1994). In the present study , 28-53 %of the adsorbed values were desorbed experimentally in ten steps. As discussed in section 3.3.2 (Chapter 3) each time only 20 ml of supernatant was removed and shaken to achieve equilibrium, resulting in a small concentration gradient for the solute to desorb. Further desorption steps could yield higher percentage recovery. However, the adsorption and desorption paths are clearly different indicating some hysteresis, but a definite conclusion could not be reached from the study.

Van Genuchten *et al.* (1974) and O'Connor *et al.* (1980) have also observed this difference for the desorption of 2,4,5-T in Glendale clay loam and attributed this discrepancy to hysteresis. Similar observations were made by Pignatello (1990) with the desorption of nine low molecular weight halogenated alkanes, and by Pavlostathis and Jaglal (1991) with the desorption of trichloroethylene from contaminated soils. Kan *et al.* (1994) also observed hysteresis in adsorption/desorption reactions for various organic chemicals in soils and sediments.

Many researchers suggest that the use of successive desorption steps could lead to serious calculation errors if nonsettling particles are present in the experiments (Gschwend and Wu, 1985; Kan *et al.,* 1994). In this study, after desorption equilibrium, 5 ml of supernatant was removed, filtered through 0.45μm and centrifuged at 6000 rpm. No soil particles were observed in the filter or at the bottom of the sampling tube. This implies that nonsettling particles were not removing the solute from the solution. If a significant amount of nonsettling particles were present, and these particles adsorbed solute as is generally suggested, this would mean that the actual amount of *nondesorbing* solute would be larger than reported, i.e., the desorption curves in Figures 4.18-4.23 would tend to be horizontal. However, the desorption curves in the figures do not prove the presence of irreversible adsorption or of hysteresis (Kan *et al.,* 1994).

Van Genuchten *et al.* (1974) describes a procedure to calculate desorption isotherm parameters using adsorption constants. This is established by equating the adsorption and desorption isotherm equations at the starting point of desorption, expressed as,

$$q_{max} = K_{ads} C^{\frac{1}{n_{ads}}} = K_{des} C^{\frac{1}{n_{des}}} \tag{4.8}$$

The above equation is rearranged as,

$$K_{des} = K_{ads}^{\frac{1}{\alpha}} q_{max}^{\frac{\alpha - 1}{\alpha}} \tag{4.9}$$

where, $\alpha = (1/n_{ads})/(1/n_{des})$. The parameter α, in the present study, is linearly related to the amount adsorbed (q_{max}) as,

$$\alpha = b_1 + b_2 q_{max} \tag{4.10}$$

where, b_1 and b_2 are empirical constants. Table 4.5 gives the values of b_1 and b_2 for phenoxyacetic acids and chlorophenols. Figure 4.24 shows the relationship between α and q_{max} for 2,4-D and PCOC. It is interesting to observe that the slope of the plot was positive for phenoxyacetic acids and negative for chlorophenols, because, for phenoxyacetic acids $1/n_{des}$ decreased with q_{max}, whereas for chlorophenols $1/n_{des}$ increased with q_{max}. However, the observed difference in the slopes could not be explained with the limited experimental data obtained in the present study. Swanson and Dutt (1973) and Van Genuchten *et al.* (1974) also report the dependence of α on q_{max}.

Table 4.5 Empirical constants b_1 and b_2 in Equation 4.10

Phenoxyacetic acid	b_1	b_2	Chlorophenol	b_1	b_2
2,4-D	0.87	2.87	2,4-DCP	4.47	-1.90
2,4,5-T	1.21	1.78	2,4,5-TCP	7.07	-4.23
MCPA	1.40	1.21	PCOC	3.24	-0.87

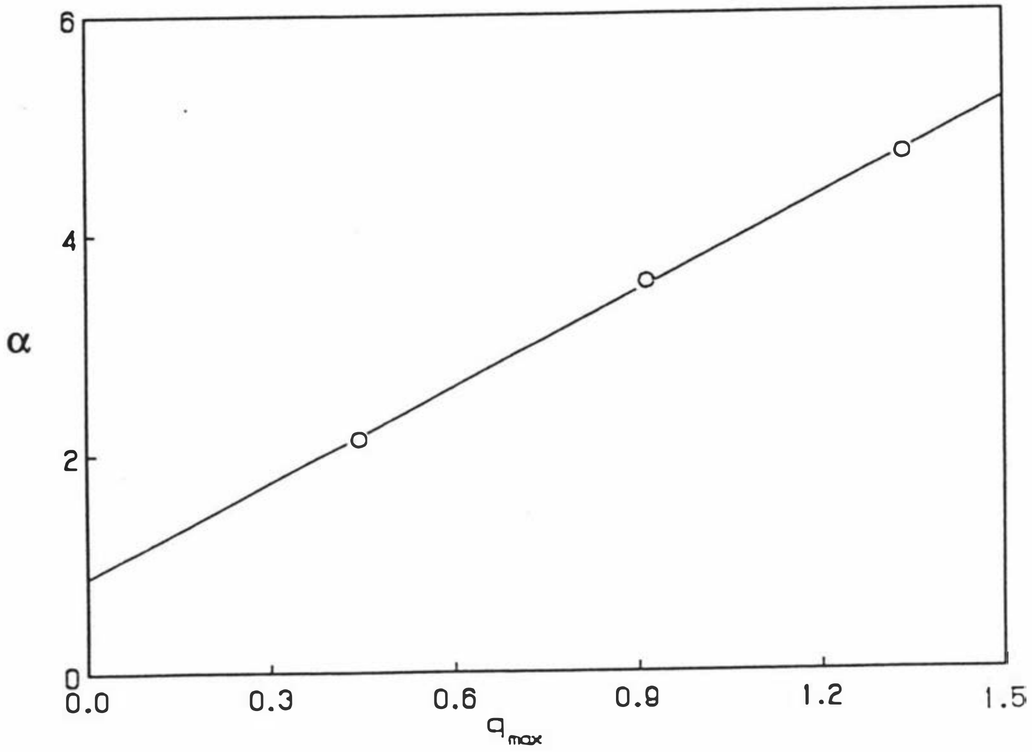


Figure 4.24a: A plot showing the relationship between α and q_{max} for 2,4-D.

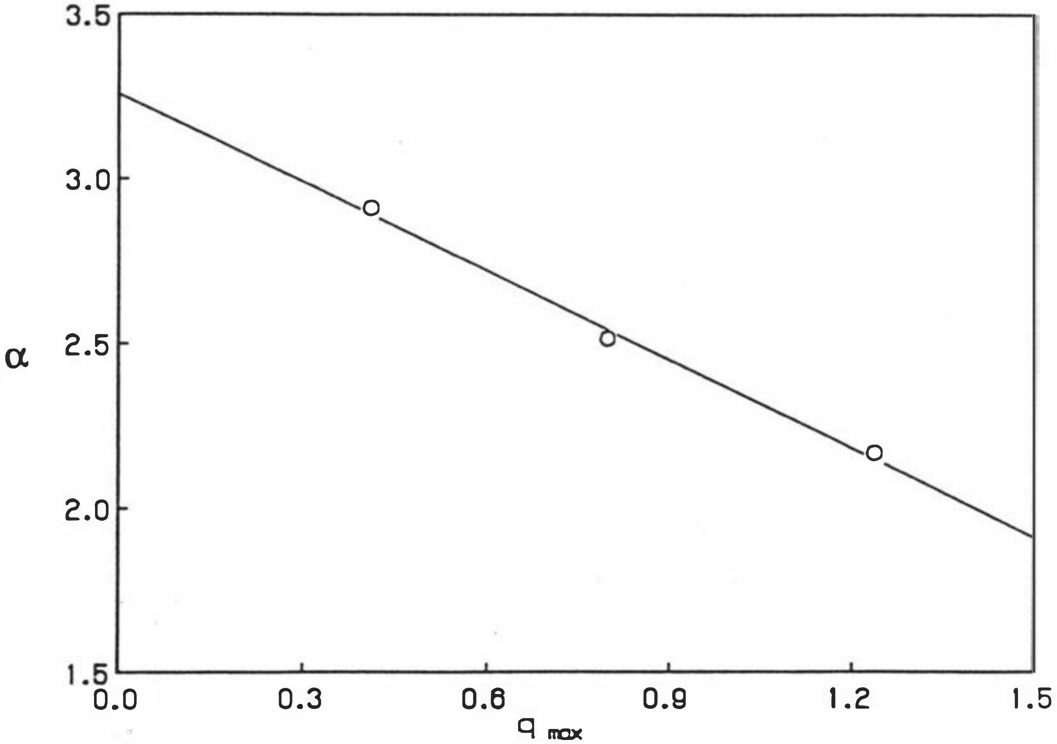


Figure 4.24b: A plot showing the relationship between α and q_{max} for PCOC.

The percentage of each chemical desorbed after ten desorption steps is given in Table 4.6. The ease of desorption of phenoxyacetic acids is in the order of 2,4-D > MCPA > 2,4,5-T. In case of chlorophenol desorption, the order was PCOC > 2,4,5-TCP > 2,4-DCP. The results indicate that chlorophenols desorbed more readily than phenoxyacetic acids.

Table 4.6 Percentage of phenoxyacetic acids and chlorophenols desorbed from soil

Chemical	q_{max}	q_{re}	% desorbed	Chemical	q_{max}	q_{re}	% desorbed
2,4-D	1.34	0.78	41.84	2,4-DCP	1.43	0.80	44.37
2,4,5-T	1.84	1.32	28.57	2,4,5-TCP	1.23	0.64	48.04
MCPA	1.45	0.95	34.28	PCOC	1.24	0.58	53.07

4.4 Bicomponent adsorption-desorption

Several multicomponent adsorption isotherms have been proposed in literature (Randtke and Prausnitz, 1972; Fritz *et al.*, 1981; Sheindorf *et al.*, 1981; Crittenden *et al.*, 1985) to describe the uptake of solutes that individually follow the Freundlich isotherm. For example, a multicomponent adsorption isotherm based on IAST, developed by Radtke and Prausnitz (1972), was used by other researchers to predict competitive adsorption in organic chemicals onto soils and sediments (Weber *et al.*, 1991; McGinley *et al.*, 1993).

The comparison of competitive sorption isotherms is based on theoretical derivations, on convenience of application and on successful prediction. Of the three bicomponent isotherms presented earlier, no solute-solute interaction parameters are required for IAST and Langmuir, and one for the multicomponent Freundlich isotherm (Sheindorf's model), which may be estimated from single component data. The IAST and Langmuir models, derived from basic principles, are limited to low concentrations (Sheintuch and Rebhun, 1988). The Freundlich-type isotherm proposed by Sheindorf *et al.* is also derived with the same assumptions of exponential distribution of energies. The competition coefficients could be determined experimentally or can be estimated depending on the proximity of adsorption properties of the two solutes. The multicomponent Freundlich-type isotherm presents a good compromise of convenience and accuracy. Its derivation enables extension to many soluble systems while the experimental information required to determine the competition coefficient is minimal. This isotherm predicted the uptake of solutes at even higher concentrations (Sheindorf *et al.*, 1981; Sheintuch and Rebhun, 1988).

The multicomponent Freundlich-type isotherm model proposed by Sheindorf *et al.* (1981) was employed, as IAST and modified IAST isotherms could not describe the bicomponent experimental data at high solute concentrations (Appendix 2). This model applied to analyze the adsorption and desorption experimental data of 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC. The competitive sorption coefficients were determined, and their dependence on the initial solute concentration examined.

4.4.1 Model

Sheindorf *et al.* (1981, 1982) propose the Freundlich-type multicomponent adsorption isotherm model based on single component parameters for describing the competitive adsorption. The model is based on the assumption that each component follows a Freundlich-type isotherm in pure component system and the influence of other solutes is accounted for by a competition coefficient. The model equations are expressed as,

$$q_1 = K_1\, C_1\, (C_1 + a_{12}\, C_2)^{\frac{1}{n_1} - 1} \tag{4.11}$$

$$q_2 = K_2\, C_2\, (C_2 + a_{21}\, C_1)^{\frac{1}{n_2} - 1} \tag{4.12}$$

where, K_1 & $1/n_1$ and K_2 & $1/n_2$ are the single component Freundlich isotherm parameters for components 1 and 2, respectively. The parameter a_{12} represents the competition coefficient of component 1 in presence of component 2, a_{21} is the competition coefficient of component 2 in presence of component 1. The competition coefficients can be determined from the bicomponent adsorption experiments by linearizing the Equations 4.11 and 4.12 as,

$$\frac{C_1}{C_2} = \frac{1}{C_2}\beta_1 - a_{12} \tag{4.13}$$

$$\frac{C_2}{C_1} = \frac{1}{C_1}\beta_2 - a_{21} \tag{4.14}$$

where,

$$\beta_1 = \left(\frac{K_1 C_1}{q_1}\right)^{\frac{1}{(1 - \frac{1}{n_1})}} \tag{4.15a}$$

$$\beta_2 = \left(\frac{K_2 C_2}{q_2}\right)^{\frac{1}{1 - \frac{1}{n_2}}} \tag{4.15b}$$

The intercept of plots C_1/C_2 *versus* β_1/C_2 is the competition coefficient, a_{12}, the competition coefficient, a_{21} is obtained from the intercept of plots C_2/C_1 against β_2/C_1.

4.4.2 Adsorption competition coefficients

The bicomponent equilibrium experimental data for the 2,4-D-MCPA system were analyzed using Equations 4.13 and 4.14. A plot of $C_{2,4\text{-}D}/C_{MCPA}$ *versus* $\beta_{2,4\text{-}D}/C_{MCPA}$ is shown in Figure 4.25a, the intercept of this line is the competition coefficient for 2,4-D in presence of MCPA, ($a_{2,4\text{-}D\text{-}MCPA}$). Similarly, $a_{MCPA\text{-}2,4\text{-}D}$, was determined as the intercept from plots $C_{MCPA}/C_{2,4\text{-}D}$ *versus* $\beta_{MCPA}/C_{2,4\text{-}D}$, (Figure 4.25b); values of $a_{2,4\text{-}D\text{-}MCPA}$ and $a_{MCPA\text{-}2,4\text{-}D}$, determined for various initial solute concentrations, are listed in Table 4.7. The competition coefficients, $a_{2,4\text{-}D\text{-}PCOC}$, $a_{PCOC\text{-}2,4\text{-}D}$, $a_{MCPA\text{-}PCOC}$ and $a_{PCOC\text{-}MCPA}$ were also determined using the above procedure, the values of competition coefficients for various initial concentrations are given in Table 4.7.

Table 4.7 Adsorption competition coefficients

2,4-D	MCPA	$a_{2,4\text{-D-MCPA}}$	$a_{\text{MCPA-2,4-D}}$
49.82	50.03	0.07*	0.32*
50.23	252.18	0.17	0.85
51.00	399.83	0.24	1.48
101.5	100.56	0.14	0.65
248.6	49.90	0.23	1.08
251.3	249.12	0.36	1.70
254.8	396.22	0.43	2.13
399.2	52.00	0.34	1.64
404.2	250.09	0.45	2.01
401.3	403.23	0.70	3.27

* shown in Figure 4.23

Table 4.7(a)

2,4-D	PCOC	$a_{2,4\text{-D-PCOC}}$	$a_{\text{PCOC-2,4-D}}$
48.86	51.23	0.07	0.36
52.34	250.75	0.27	0.94
52.29	402.75	0.41	2.04
100.7	102.45	0.17	0.65
250.7	50.00	0.07	1.13
252.2	247.56	0.26	1.87
253.2	399.75	0.35	2.35
402.2	46.45	0.12	0.46
403.1	254.75	0.25	2.25
400.9	401.22	0.40	3.60

Table 4.7(b)

MCPA	PCOC	$a_{MCPA\text{-}PCOC}$	$a_{PCOC=MCPA}$
51.23	49.75	0.08	0.25
50.12	251.77	0.14	0.63
52.76	401.75	0.21	0.93
102.3	101.34	0.12	0.63
252.2	52.19	0.31	0.90
252.1	248.75	0.38	1.28
255.3	400.00	0.38	1.68
397.6	49.87	0.31	1.33
403.2	254.36	0.45	1.63
395.3	402.24	0.63	2.62

From Table 4.7, it is interesting to note that the competition coefficients are dependent on the initial concentration of solutes. For example, at an initial concentration of 50 mg/l of 2,4-D and of 50 mg/l of MCPA, the $a_{2,4\text{-}D\text{-}MCPA}$ value was 0.071, increasing the MCPA concentration to 250 mg/l, but keeping 2,4-D at 50 mg/l; $a_{2,4\text{-}D\text{-}MCPA}$ increase to 0.166 and a further increase in MCPA to 400 mg/l, increased the $a_{2,4\text{-}D\text{-}MCPA}$ to 0.240. A plot of $a_{2,4\text{-}D\text{-}MCPA}$ against MCPA concentration, shown in Figure 4.26a, indicated a linear dependence of the competition coefficients with the initial solute concentration, while $a_{MCPA\text{-}2,4\text{-}D}$ increased linearly with an increase in 2,4-D initial concentration (Figure 4.26b). This variation in competition coefficients with initial concentration was correlated as,

$$a_{i\,j} = p_i C_{i,0} + p_j C_{j,0} \tag{4.16}$$

where, p_i and p_j are empirical constants, $C_{i,0}$ and $C_{j,0}$ are the initial solute concentrations of components i and j. The constants, p_i and p_j, determined by a nonlinear regression are given in Table 4.8.

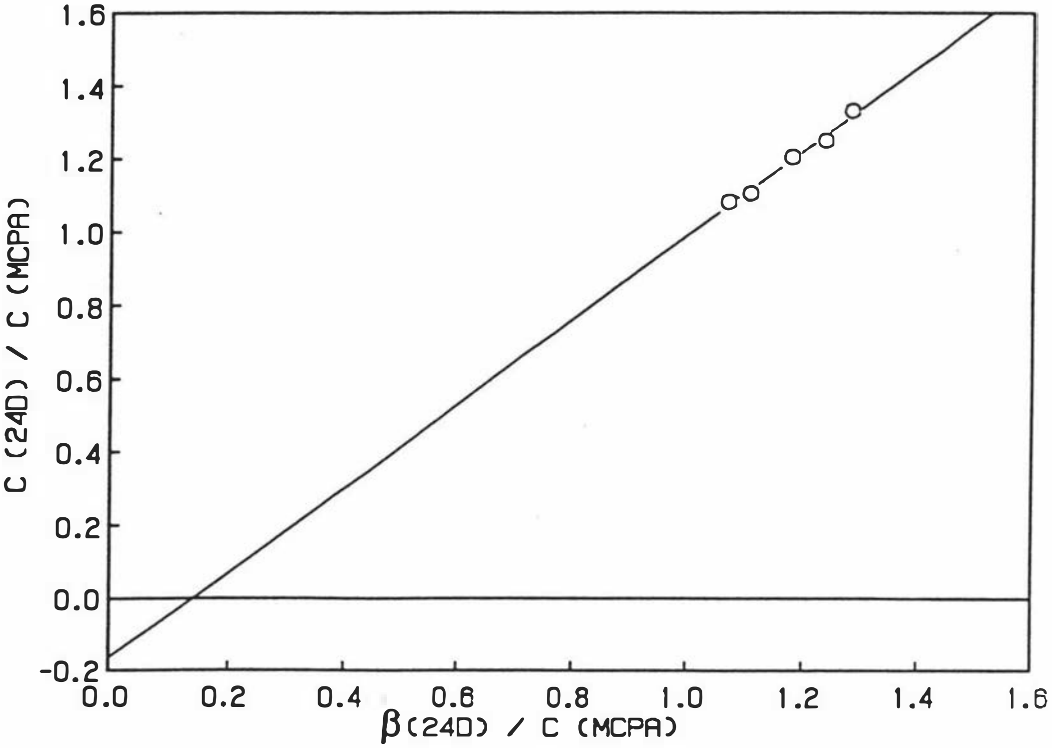


Figure 4.25a: Adsorption competition coefficient, $a_{2,4\text{-}D\text{-}MCPA}$ for 2,4-D-MCPA bicomponent mixture (C_0 = 50 mg/l each).

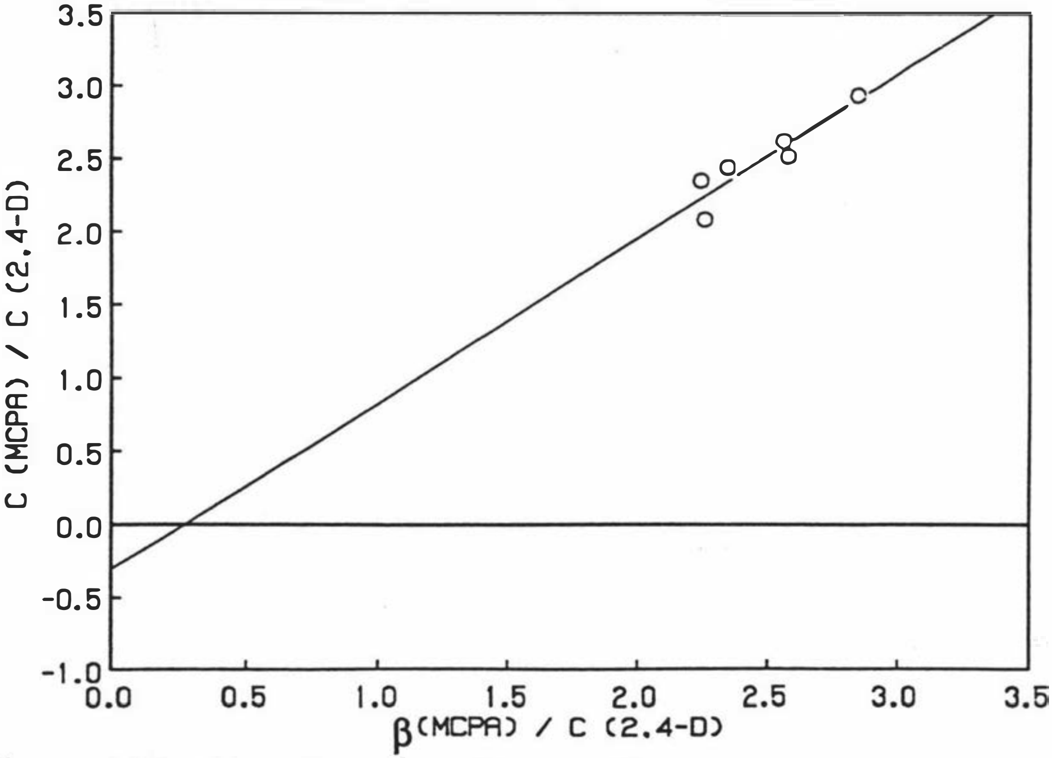


Figure 4.25b Adsorption competition coefficient, $a_{MCPA\text{-}2,4\text{-}D}$ for 2,4-D-MCPA bicomponent mixture (C_0 = 50 mg/l each).

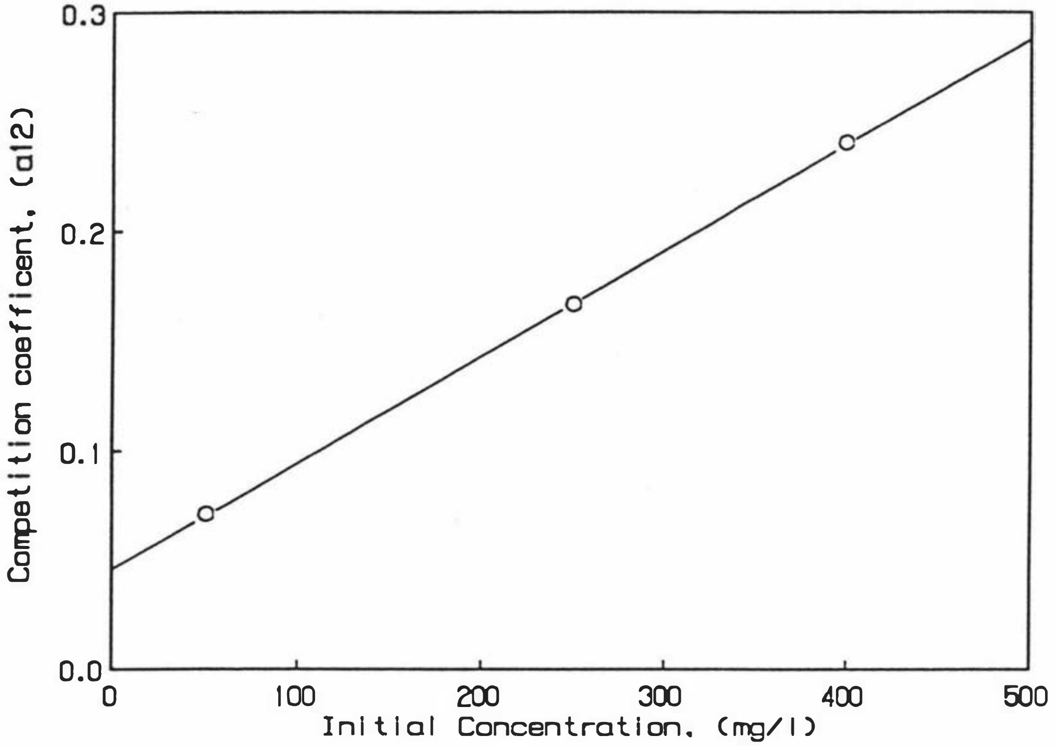


Figure 4.26a A plot showing the dependence of competition coefficient, $a_{2,4\text{-D-MCPA}}$ on initial concentration.

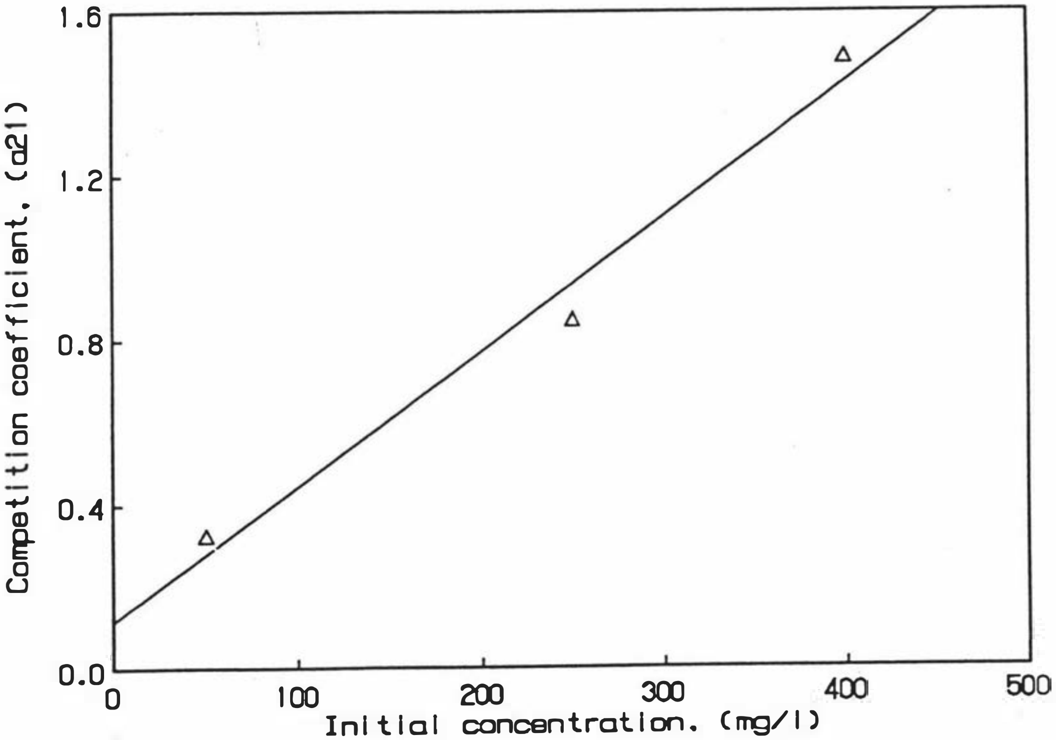


Figure 4.26b A plot showing the dependence of competition coefficient, $a_{\text{MCPA-2,4-D}}$ on initial concentration.

Table 4.8 Values of p_i and p_j in Equation 4.16

Competition coefficient	$p_i x 10^3$	$p_j x 10^3$	r^2 (%)
$a_{2,4\text{-}D\text{-}MCPA}$	0.86	0.59	93.5
$a_{MCPA\text{-}2,4\text{-}D}$	3.73	3.28	94.5
$a_{2,4\text{-}D\text{-}PCOC}$	0.09	0.94	92.9
$a_{PCOC\text{-}2,4\text{-}D}$	1.77	5.40	91.8
$a_{MCPA\text{-}PCOC}$	0.91	0.47	93.0
$a_{PCOC\text{-}MCPA}$	3.24	2.25	93.2

4.4.3 Adsorption isotherms

The competitive adsorption isotherms for 2,4-D and MCPA are predicted using Equation 4.11 and 4.12 in combination with Equation 4.27. Figure 4.27 compares the predicted and experimental data for 2,4-D and MCPA in presence of each other at two initial concentrations.

Lower equilibrium concentrations of MCPA were observed when 2,4-D was present at lower concentrations and as the concentration of 2,4-D increased, it competed more effectively for sorption in the presence of MCPA. As shown in Figure 4.27, an increase in the concentration of 2,4-D from 50 to 400 mg/l resulted in a decrease in the sorption of MCPA.

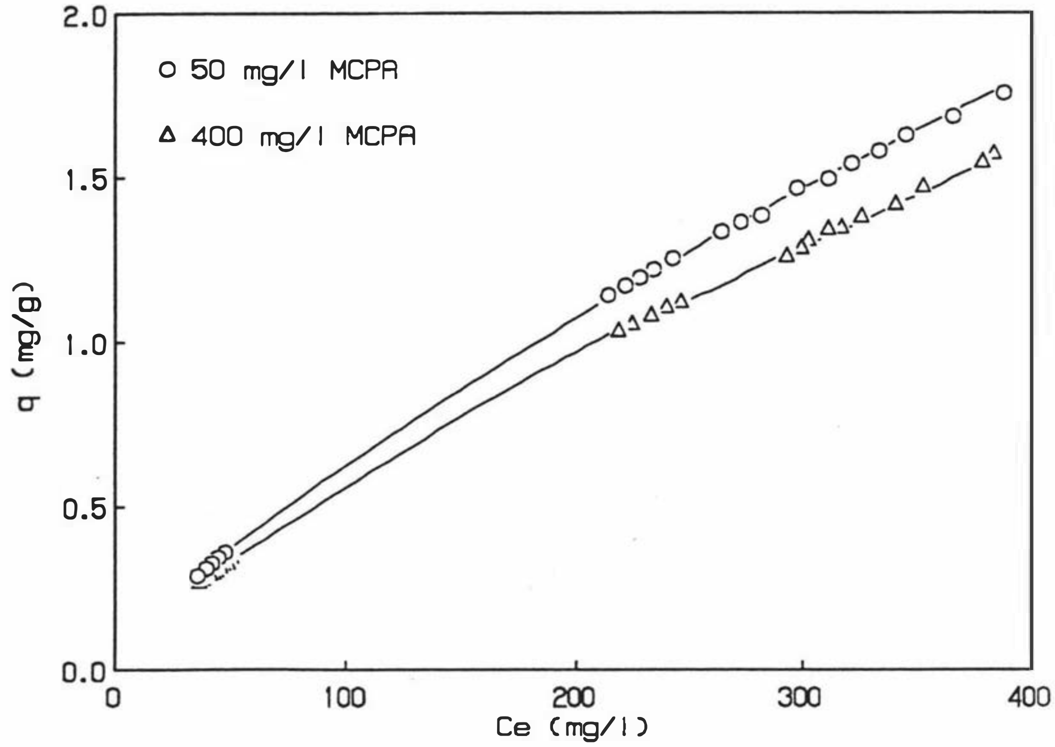


Figure 4.27a: Bicomponent adsorption isotherms of 2,4-D in the presence of MCPA.

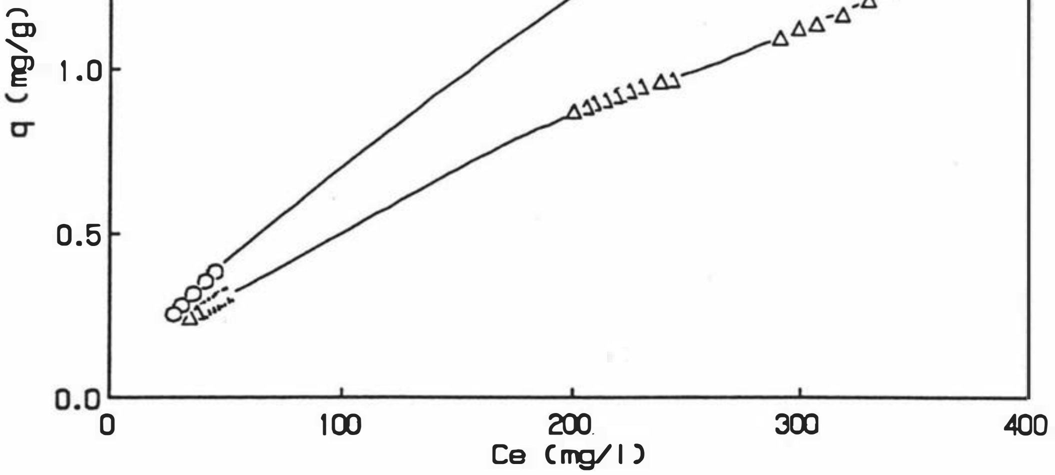


Figure 4.27b: Bicomponent adsorption isotherms of MCPA in the presence of 2,4-D.

From these results, it is also clear that 2,4-D adsorption capacity decreased as the concentration of MCPA increased from 50 to 400 mg/l. For example, for a mixture of 400 mg/l each of 2,4-D and MCPA, the total amount of 2,4-D adsorbed was 1.63 mg/g compared to 1.83 mg/g when no MCPA was present, a corresponding drop of 11%. The adsorption capacity of MCPA in presence of 2,4-D, on the other hand, decreased by 31%.

The predicted and observed isotherms for 2,4-D-PCOC and MCPA-PCOC bicomponent mixtures are shown in Figures 4.28 and 4.29, respectively. The adsorption capacities of MCPA and 2,4-D in the presence of PCOC decreased by 8 and 11%, respectively, the adsorption capacity of PCOC, in the presence of 2,4-D, decreased by 10%, and by 8% in the presence of MCPA for an initial concentration of 400 mg/l of each.

Competitive sorption effects in volcanic soil are most likely attributable to the same soil components related to the nonlinearity of the sorption isotherms. Sorption on the heterogeneous surfaces of organic matter is likely to be competitive because of variations in sorption energies and limitations in particular types of sites (Brusseau and Rao, 1989).

While there is an indication that the sorption in the bisolute system is reduced, particularly at high concentrations, limitations in acquiring precise sorption data at low concentrations makes it difficult to discern any significant difference between bisolute and single solute isotherm data. Competitive sorption is clearly not evident at low concentrations for all the solutes examined.

Bicomponent experiments have demonstrated that competition occurs between the solutes when adsorbing onto soil. The extent of competition reflects the sorption strength of the individual solutes, which is inversely proportional to aqueous solubility of the compounds. These equilibrium experiments suggest that solute competition within mixtures may enhance the mobility of the solutes in soil.

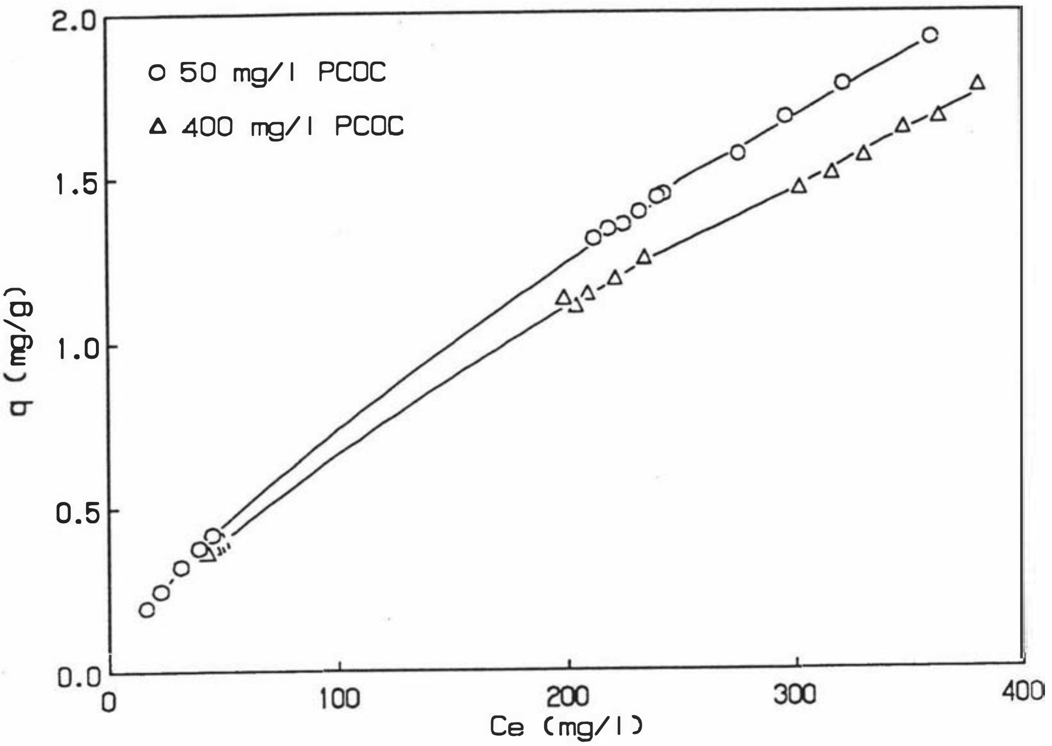


Figure 4.28a: Bicomponent adsorption isotherms of 2,4-D in the presence of PCOC.

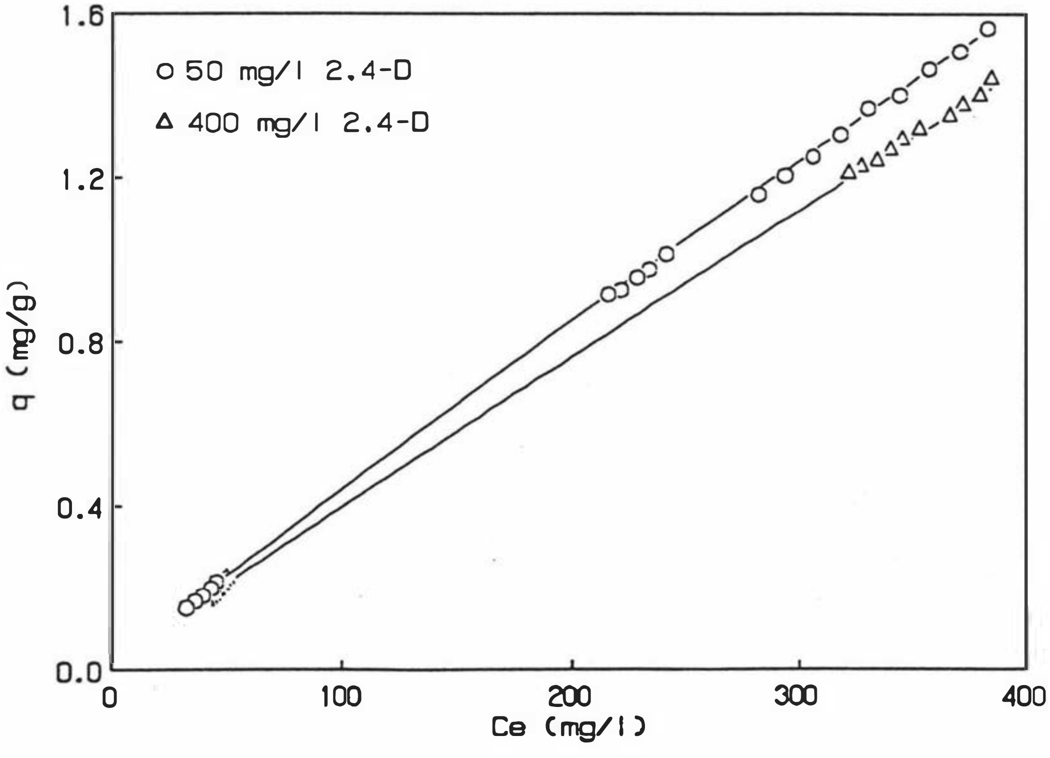


Figure 4.28b: Bicomponent adsorption isotherms of PCOC in the presence of 2,4-D.

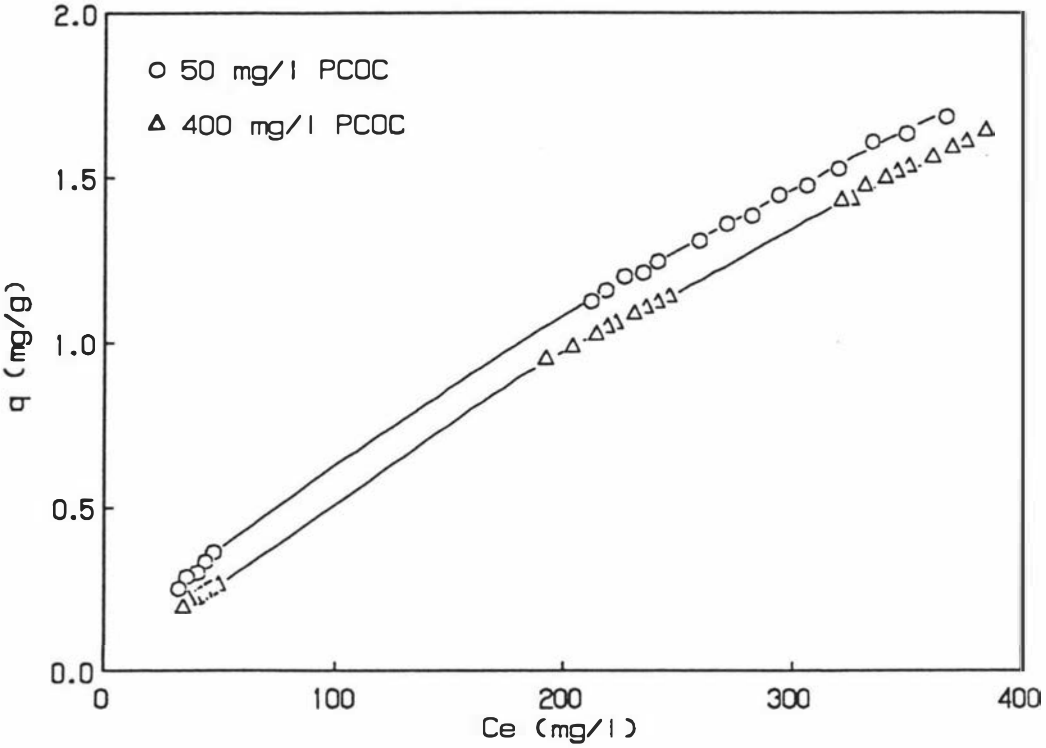


Figure 4.29a: Bicomponent adsorption isotherms of MCPA in the presence of PCOC.

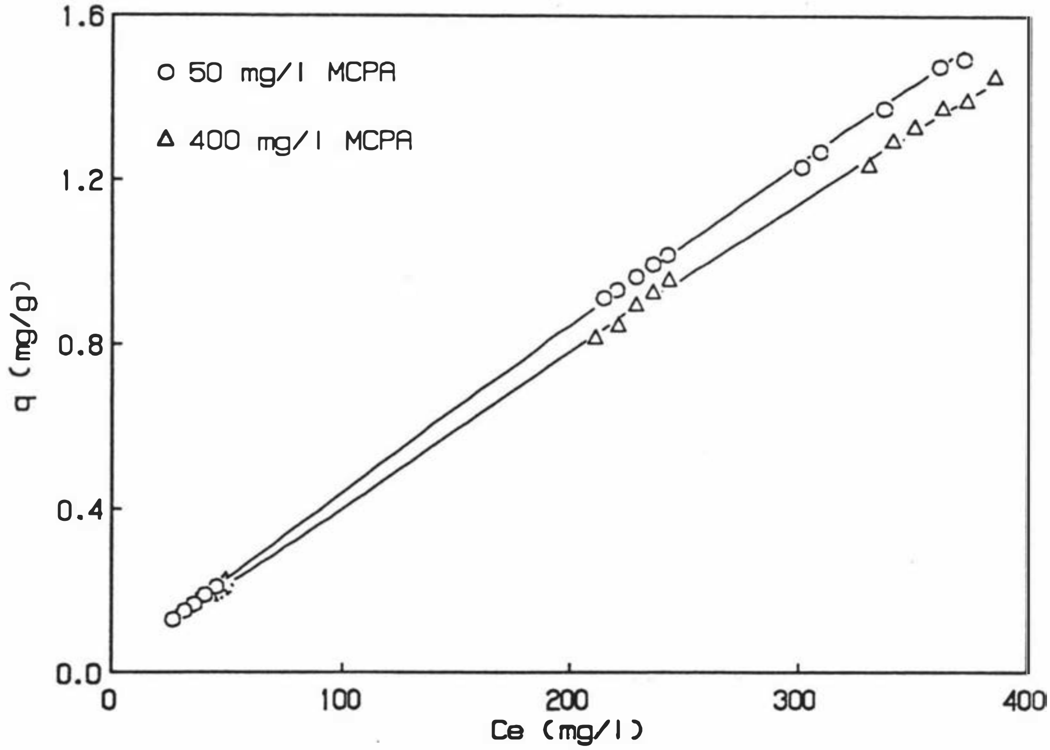


Figure 4.29b: Bicomponent adsorption isotherms of PCOC in the presence of MCPA.

4.4.4 Desorption isotherms

The desorption experiments were carried out immediately after the adsorption experiments, using the same soil-solution mixture. Equations 4.11 and 4.12 were used to predict the desorption isotherms by replacing the single component adsorption parameters with the corresponding desorption parameters. The desorption isotherm is expressed as,

$$q_i = K_{des,i} C_i (C_i + d_{ij} C_j)^{\frac{1}{n_i} - 1} \tag{4.17}$$

where, $d_{i,j}$ is the desorption competition coefficient. The single component desorption parameters were calculated using the procedure given in section 4.3.4. The steps involved are,

Step 1: The Freundlich desorption constant $1/n_{des}$ was determined using Equation 4.10, for a given q_{max}.

Step 2: Using this $1/n_{des}$ value, K_{des} were calculated from Equation 4.9 and are given in Table 4.9.

Table 4.9 The calculated K_{des} and $1/n_{des}$ values ($C_{0,1} = C_{0,2} = 50$ mg/l).

Bicomponent Mixture	K_{des}	$1/n_{des}$
2,4-D-MCPA		
2,4-D	0.08	0.39
MCPA	0.10	0.38
2,4-D-PCOC		
2,4-D	0.08	0.39
PCOC	0.07	0.30
MCPA-PCOC		
MCPA	0.10	0.38
PCOC	0.07	0.31

Step 3: The competition coefficient was determined by plotting C_i/C_j *versus* β_i/C_j, as described in section 4.4.2. Table 4.10 gives the desorption coefficients (d_{ij}) at various initial concentrations and q_{max} values.

Table 4.10 Desorption competition coefficients

$C_{0,1}$ (mg/l)	$C_{0,2}$ (mg/l)	$q_{max,1}$ (mg/g)	$q_{max,2}$ (mg/g)	$d_{i,j}$	$d_{j,i}$
2,4-D	**MCPA**				
49.82	50.03	0.36	0.38	0.11	0.16
101.5	100.56	0.60	0.61	0.19	0.31
251.3	249.12	1.14	1.05	0.52	0.86
401.3	403.23	1.67	1.38	0.88	1.24
2,4-D	**PCOC**				
48.86	51.23	0.36	0.21	0.08	0.06
100.7	102.45	0.59	0.41	0.19	0.15
252.2	247.56	1.19	0.95	0.38	0.57
400.9	401.22	1.66	1.44	0.52	0.87
MCPA	**PCOC**				
51.23	49.75	0.45	0.20	0.14	0.10
102.3	101.34	0.68	0.42	0.30	0.21
252.1	248.75	1.32	0.96	0.66	0.62
395.3	402.24	1.87	1.48	1.11	1.03

An examination of Table 4.10 indicate that d_{ij} values varied linearly with q_{max}. An empirical relation of the form,

$$d_{i,j} = s_i q_{max,i} + s_j q_{max,j} \tag{4.18}$$

was used to correlate d_{ij} with q_{max} values. In Equation 4.18, s_i and s_j are empirical constants and $q_{max,i}$ and $q_{max,j}$ are the amounts adsorbed, the subscripts i and j refer to component 1 and 2, respectively. The values of s_i and s_j obtained from a nonlinear regression analysis for each bicomponent mixture are listed in Table 4.11.

Table 4.11 Values of s_i and s_j in Equation 4.18

Competition coefficient	s_i	s_j	r^2 (%)
$d_{2,4\text{-D-MCPA}}$	1.36	-1.00	90.5
$d_{\text{MCPA-2,4-D}}$	1.64	-1.09	93.4
$d_{2,4\text{-D-PCOC}}$	0.21	0.12	91.2
$d_{\text{PCOC-2,4-D}}$	-0.80	1.53	95.5
$d_{\text{MCPA-PCOC}}$	0.20	0.41	93.7
$d_{\text{PCOC-MCPA}}$	-0.10	0.95	91.8

The competitive desorption isotherms for 2,4-D and MCPA are shown in Figure 4.30, which shows a good agreement between the model prediction and experimental data. The results reveal that, after five stages of desorption, 30% of 2,4-D and 27 % of MCPA of the initially adsorbed amounts could be desorbed.

The bicomponent desorption isotherms of 2,4-D-PCOC and MCPA-PCOC mixtures are shown in Figures 4.31 and 4.32, respectively. The amount of each solute desorbed in a bicomponent mixture are given in Table 4.12. The table indicates that both 2,4-D and MCPA desorbed to a greater extent in the presence of PCOC than in a pure component system. On the other hand, PCOC desorbed more readily in the presence of MCPA than in the presence of 2,4-D. The percentage of each chemical desorbed in presence of the other is shown in Figure 4.33.

In bicomponent desorption experiments 20 ml of supernatant was removed and the amount of solute desorbed was estimated following the same procedure that was used for single solute experiments. Again, the concentration gradient was too small to achieve complete desorption and more number of stages could achieve complete desorption.

In the studies conducted by Pignatello (1990), the pollutants were in contact with the soil for many years, which was probably sufficient to allow the pollutants to contact times were of the magnitude of hours, yet the compounds are difficult to desorb. One possibility is that the solutes are somehow irreversibly bound to the soil. According to Kan *et al.* (1994), a pollutant can be irreversibly bound, without any chemical reaction, if some physical alteration of the soil takes place. Such physical alterations could include configuration changes to organic matter as a consequence of change of pH or coagulation of the mineral or organic soil particles. However, it is not possible to determine the structure of the soil to detect any matrix rearrangement has conclusively occurred or not.

Table 4.12 Percentage of each chemical desorbed in a bicomponent mixture

Chemical	Percentage desorbed in presence of		
	2,4-D	MCPA	PCOC
2,4,-D	41.84*	29.88	40.25
MCPA	26.55	34.28*	52.00
PCOC	42.22	73.00	53.07*

* Corresponding single solute desorption

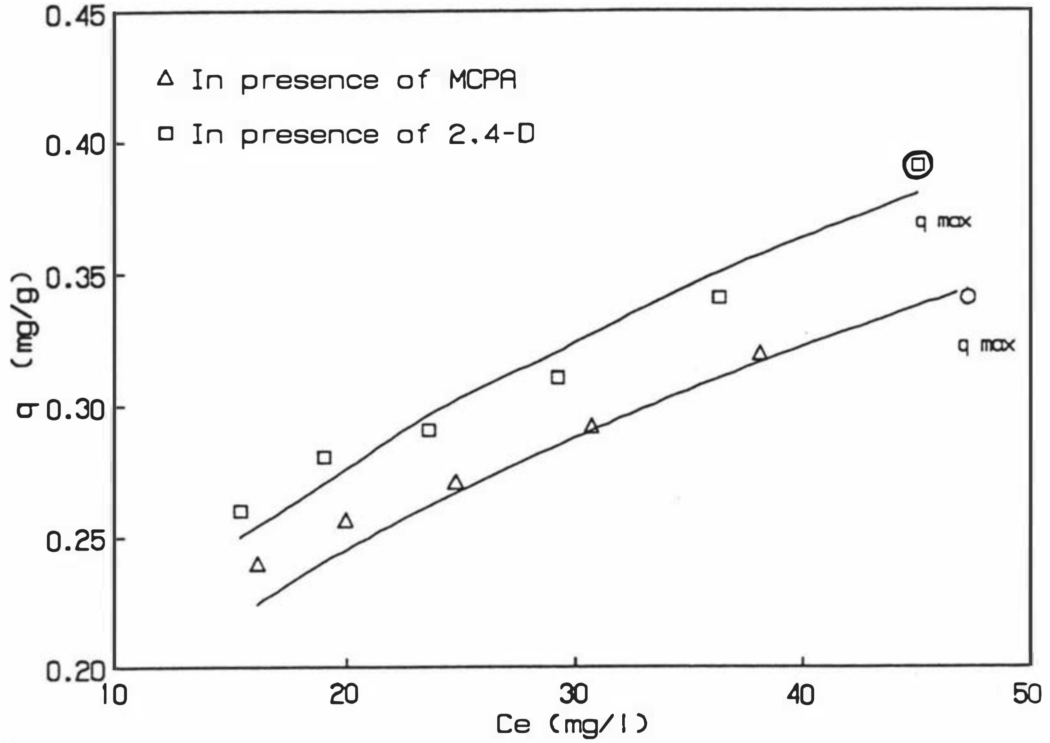


Figure 4.30: Bicomponent desorption isotherms for 2,4-D-MCPA. The solid lines were predicted using Equation 4.17. O indicates q_{1max} where desorption is initiated.

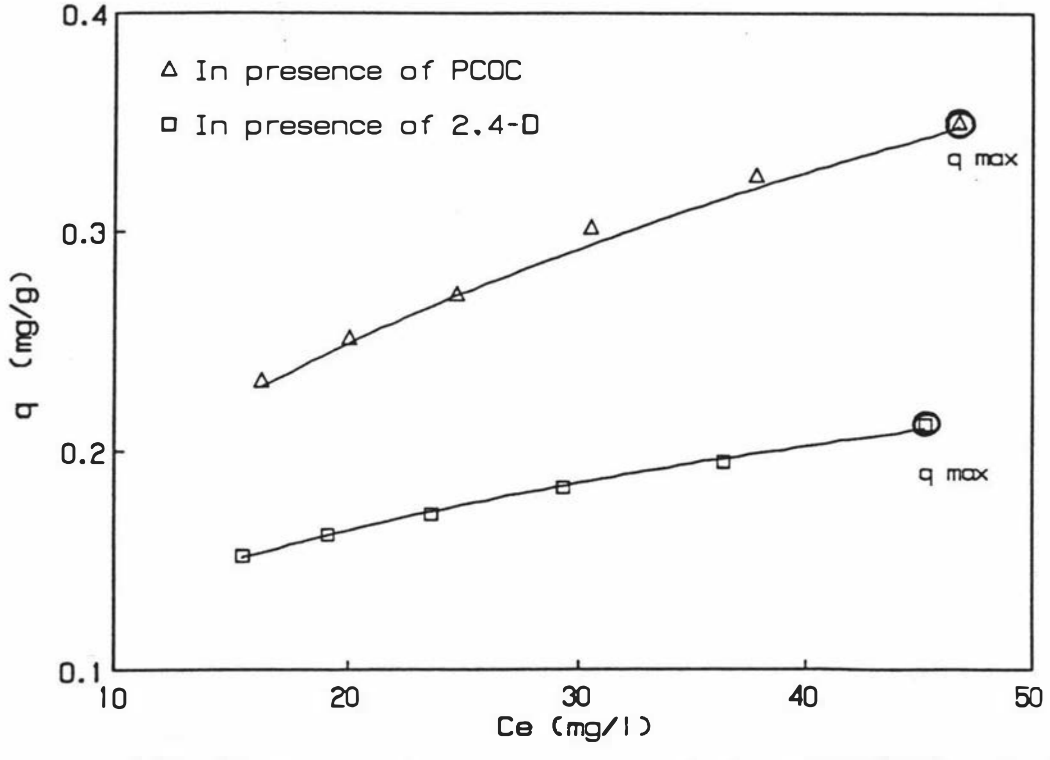


Figure 4.31: Bicomponent desorption isotherms for 2,4-D-PCOC. The solid lines were predicted using Equation 4.17. O indicates q_{1max} where desorption is initiated.

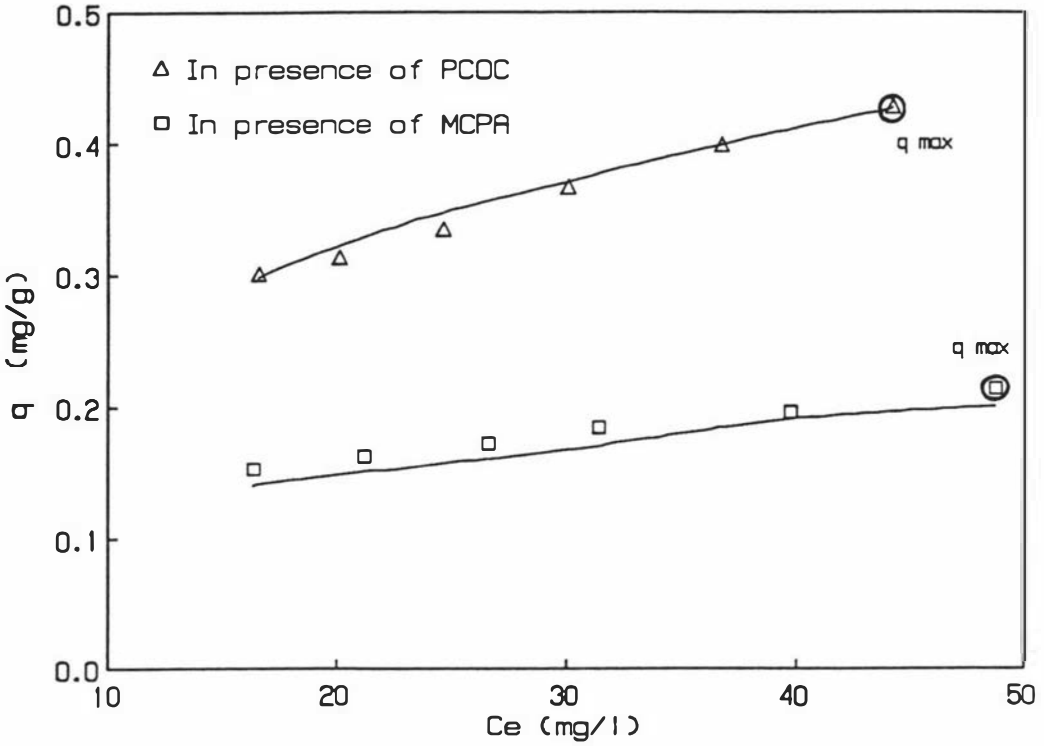


Figure 4.32: Bicomponent desorption isotherms for MCPA-PCOC. The solid lines were predicted using Equation 4.17. O indicates q_{max} where desorption is initiated.

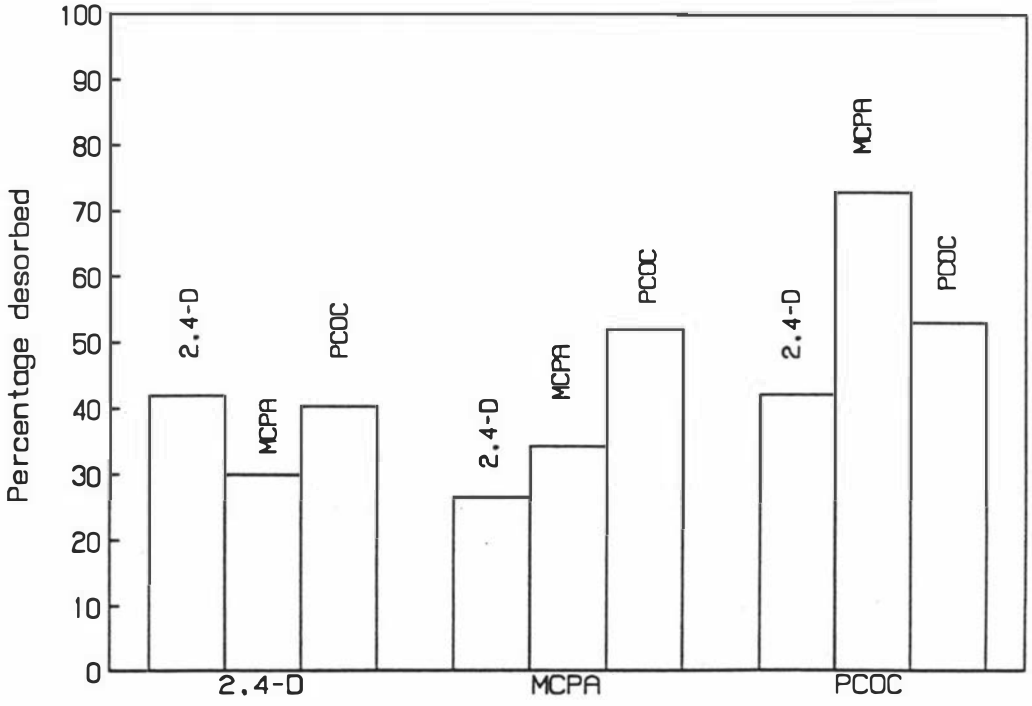


Figure 4.33: Percentage of each chemical desorbed in a bicomponent system.

CHAPTER 5
ADSORPTION-DESORPTION KINETICS

5.1 Introduction

For better understanding and prediction of organic chemical fate and transport, accurate models are required not only for estimating the extent of sorption at equilibrium, but also for estimating the rate at which solute sorb, to and desorb from the soil. Detailed laboratory investigations have revealed that adsorption and desorption of organic compounds from soils and sediments occur over a broad time scale ranging from instantaneous to weeks and months (Grathwohl and Reinhard, 1993). Understanding the mechanism of sorption and desorption is important for selecting the clean-up methods.

The adsorption kinetics of organic chemicals were examined by several authors. Khan (1973) investigated the kinetics of 2,4-D onto humic acid and reports that the intraparticle diffusion was the rate limiting process. The sorption of hydrophobic organic chemicals onto natural sediments and soils indicate that a single effective diffusivity parameter could be used to quantify the sorption kinetics (Wu and Gschwend, 1986). Ball and Roberts (1991), Overcash *et al.* (1991), Zhang and Sparks (1993) report the sorption kinetics of organic contaminants in soils and sediments.

There are only a few studies reported on desorption kinetics of organic chemicals in soils (Voice and Weber, 1983). Pavlostathis and Jaglal (1991) observed desorption of trichloroethylene from a contaminated soil was very slow; however, no quantitative determination of the diffusion coefficient was attempted. Brusseau *et al.* (1991), Overcash *et al.* (1991), Pavlostathis and Mathavan (1992), Connaugton *et al.* (1993) and Farrell and Reinhard (1994b) report the desorption of organic solutes from contaminated soils and sediments. In all these studies, a two-phase pattern of desorption from soils was observed, i.e., an initial fast stage (in hours) and a subsequent longer slow phase (in days). The second stage was attributed to slow solute diffusion from internal sorption sites. The rate of desorption was strongly correlated to the residence time of the solute in the soil.

In this chapter, the kinetics of adsorption and desorption of three phenoxyacetic acids and three chlorophenols in soil are examined, and film-mass transfer and surface diffusion coefficients for sorption and desorption are estimated using a surface diffusion model. In addition, the sorption kinetics of bicomponent systems are investigated.

5.2 Homogeneous surface diffusion model (HSDM)

The transport mechanisms in a soil particle are assumed to occur by means of a pore or a surface diffusion mechanism as shown in Figure 5.1. In the surface diffusion mechanism, the transport of solutes occur in an adsorbed state, molecules migrating along the surface to an available adjacent adsorption site, the molecule having enough energy to leave the site it is presently occupying. Further examination of the two possible mass transfer mechanisms shows that surface diffusion flux is many times greater than the pore diffusion flux for strongly adsorbed species (Crittenden, 1976; Hand *et al.*, 1983). In the model developed, the contribution of pore diffusion to the adsorbate transport was assumed to be negligible. The reasons for this assumption are given in Appendix 3.

The surface diffusion mechanism-incorporated model, referred to as the homogeneous surface diffusion model or HSDM, is based on the following assumptions:

- adsorbent particles are homogeneous;
- surface diffusive flux can be described by Fick's law;
- an equilibrium isotherm relates the liquid and solid phase concentrations;
- the mass transfer between the liquid and solid phases occurs by film-diffusion; and
- surface diffusion is the predominant intraparticle mass transfer mechanism and is independent of solute concentration.

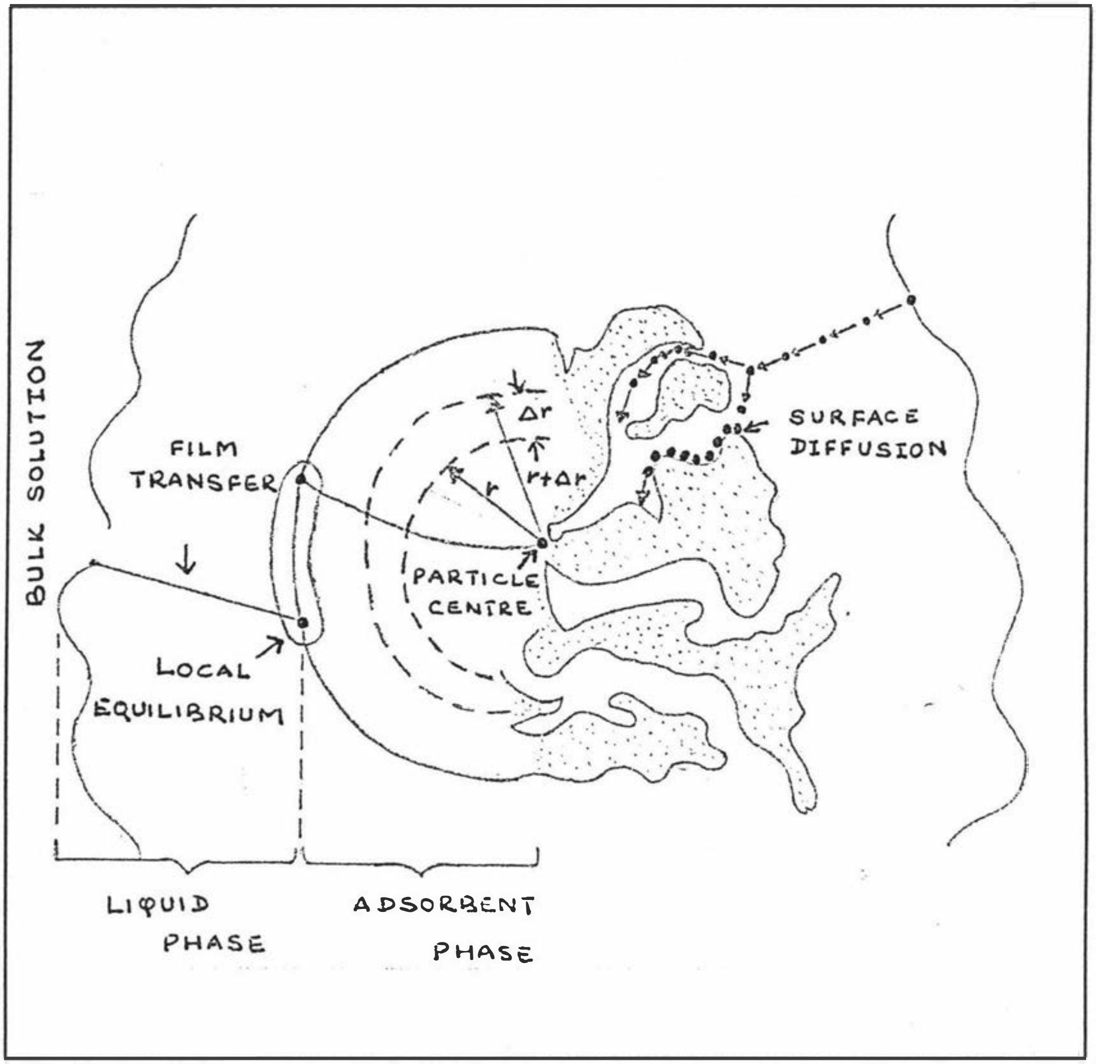


Figure 5.1: Mass transport mechanisms in a homogeneous surface diffusion model

The surface diffusion mechanism incorporating the above assumptions was used by Hand *et al.* (1983) for the kinetic data of phenols and chlorophenols in a batch reactor. Similarly, Bhaskar and Bhamidimarri (1992) used a surface diffusion model for 2,4-D adsorption onto activated carbon. Several other researchers used the model to evaluate the surface diffusion coefficients for a variety of organic solutes (Crittenden and Weber, 1978; Fritz *et al.*, 1981; Wu and Gschwend, 1986).

The mass balance equations for HSDM are expressed as (Hand *et al.*, 1983; Bhaskar and Bhamidimarri, 1992):

Adsorber

$$V \frac{dC}{dt} = k_l \, A \, (C - C_s) \tag{5.1}$$

where, k_l is the film-mass transfer coefficient.

Particle

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial q}{\partial r}) \tag{5.2}$$

where, D_s is the surface diffusion coefficient.

The coupling equation at the liquid-solid interface is expressed as,

$$\rho_p D_s A \frac{\partial q}{\partial r} = k_f A (C - C_s) \tag{5.3}$$

where, C and C_s are the bulk and interface concentrations, respectively.

The initial and boundary conditions governing Equation 5.1 and 5.2 are,

$$t = 0 \; ; \quad q = 0 \; ; \quad C = C_0 \tag{5.4}$$

$$r = 0 \; ; \quad \frac{\partial q}{\partial r} = 0 \tag{5.5}$$

$$r = R\ ; \quad q = q_s \tag{5.6}$$

The derivation of the above mass balance equations is shown in Appendix 4.

An instantaneous equilibrium at the solid-liquid interface is assumed and is expressed by the Freundlich-type isotherm (Equation 2.2) as,

$$q_s = K\ C_s^{1/n} \tag{2.2}$$

Equations 5.1-5.6 and Equation 2.2 contain two independent variables, time *t*, and radial position, *r* and three dependent variables, adsorbent-phase concentration, *q*; bulk liquid phase concentration, C; and liquid phase concentration at the exterior surface of the adsorbent, C_s.

Equations 5.1-5.6 are converted to dimensionless form using the following:

$$Y = \frac{C}{C_0}; \quad u = \frac{q}{q_0}; \quad X = \frac{r}{R}; \quad \tau = \frac{D_s t}{R^2} \tag{5.7}$$

$$B = \frac{(k_f A/V)}{(D_s/R^2)}\ ; \quad F = \frac{VC_0}{Wq_0} \tag{5.8}$$

Substituting the above nondimensional variables and parameters, Equations 5.1-5.6 become:

$$\frac{dY}{d\tau} = B(Y - Y_s) \tag{5.9}$$

$$\frac{\partial u}{\partial \tau} = \frac{1}{X^2}\frac{\partial}{\partial X}(X^2\frac{\partial u}{\partial X}) \tag{5.10}$$

$$\frac{\partial u}{\partial X}_{|X=1} = \frac{BF}{3}(Y - Y_s) \tag{5.11}$$

$$X = 0 \; ; \quad \frac{\partial u}{\partial X} = 0 \tag{5.12}$$

$$X = 1 \; ; \quad u = u_s \tag{5.13}$$

$$\tau = 0 \; ; \quad u = 0 \, , \quad Y = 1 \tag{5.14}$$

$$u_s = Y_s^{1/n} \tag{5.15}$$

where, B is the ratio of film diffusion time to surface diffusion time, F is the separation factor and W = (ρ_p AR/3) is the weight of the adsorbent. The dimensionless model Equations 5.9-5.14, along with the Freundlich isotherm (Equation 5.15), were solved using a combination of orthogonal collocation (with six points), fourth order Runge-Kutta and Newton-Raphson (for nonlinearity) techniques.

5.3 Results and discussion

The results obtained from kinetic experiments for single and bi-solute system are presented in following sections. A solute concentration of 100 mg/l was used for all experiments. Experiments were conducted at pH 2 in a constant temperature room at 20±1°C as described in section 3.3.3.

5.3.1 Film-mass transfer coefficients

Preliminary experiments were carried out to find the critical basket speed above which the k_l remains relatively constant. Four runs were conducted at different basket speeds ranging from 100-600 rpm for two representative compounds. Figure 5.2 and 5.3 show the plots of liquid concentration for 2,4-D and PCOC *versus* time for various speeds. The k_l is measured directly from the initial 20-45 seconds of the uptake data when intraparticle diffusional resistance is assumed to be negligible (Peel *et al.*, 1981; Brusseau and Rao, 1989). The k_l, which is proportional to the initial slope (k_lA/V) of the plot, was determined using this procedure; the values obtained are given in Table 5.1. The surface diffusion coefficient value determined at each rpm using HSDM is also shown in Table 5.1. It can be seen from Table 5.1 that there was a significant change in k_l value as the basket speed increased from 100 to 600 rpm, although the change in D_s is insignificant over this range. Hence, all further experiments were carried out at 250 rpm.

Hand *et al.* (1983) report the importance of minimizing k_l because better estimates of D_s are obtained when the data only reflects intraparticle mass transfer resistance. However, in the experimental method chosen in this study, the k_l was not eliminated even at higher agitation speeds; in addition, measurement problems were encountered at higher rpm values. To balance the accuracy of measurement and better estimation of D_s the experiments were conducted at 250 rpm. In addition, Miller and Pedit (1992) report that k_l is not an important factor in determining the rate of sorption. That is, D_s is sufficiently small that internal particle diffusion is the rate-determining step.

Table 5.1 Effect of agitation on k_l and D_s

Compound	rpm	$k_l x10^3$ cm/s	$D_s x10^7$ cm^2/s
2,4-D	100	3.65 ± 0.10	1.80
	250	5.32 ± 0.31	1.89
	400	6.84 ± 0.44	1.93
	600	6.99 ± 0.56	2.01
PCOC	100	2.13 ± 0.26	1.48
	250	3.81 ± 0.48	1.57
	400	3.85 ± 0.43	1.59
	600	4.15 ± 0.57	1.61

Figures 5.4-5.9 show the plots of ln C *versus t* for the first minute of the uptake rate data at 250 rpm for phenoxyacetic acids and chlorophenols, respectively. The figures show that the film-mass transfer controls the adsorption during the initial 20-45 seconds of adsorption and that the deviation from the straight line, thereafter, is assumed due to the development of intraparticle diffusional resistance (Bhaskar and Bhamidimarri, 1992). The k_l values for each compound obtained from the initial slope of the plot are given in Table 5.2.

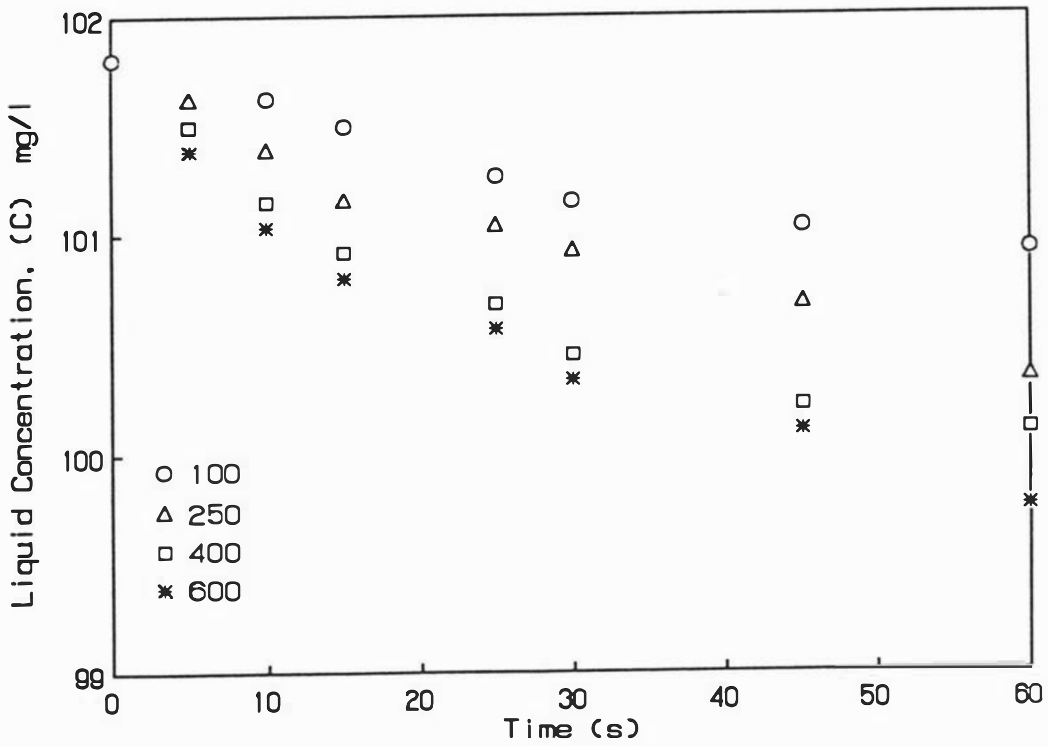


Figure 5.2: Effect of stirrer speed on film-mass transfer coefficient, k_l for 2,4-D.

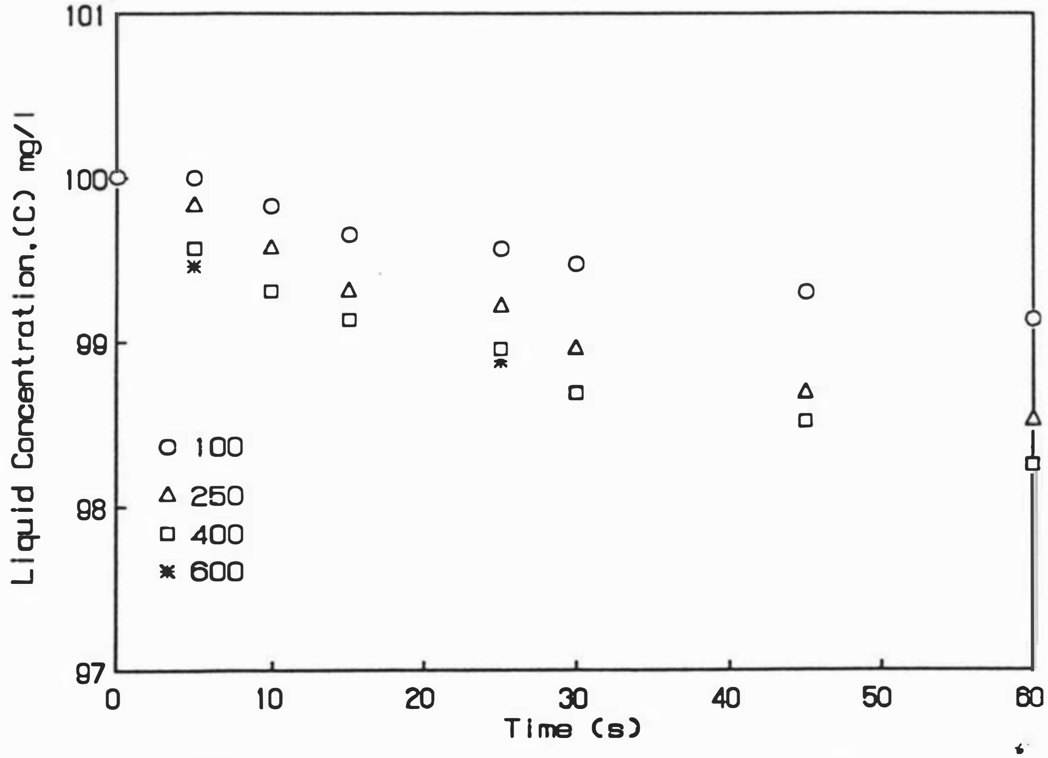


Figure 5.3: Effect of stirrer speed on film-mass transfer coefficient, k_l for PCOC.

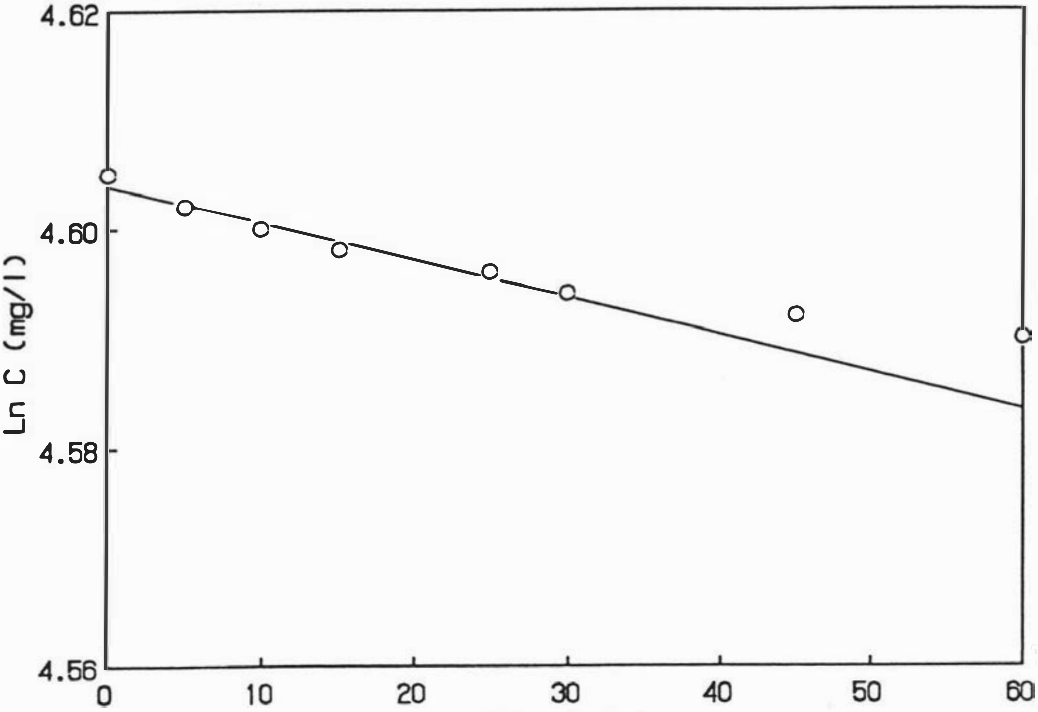


Figure 5.4: Determination of k_1 from initial uptake rate data for 2,4-D.

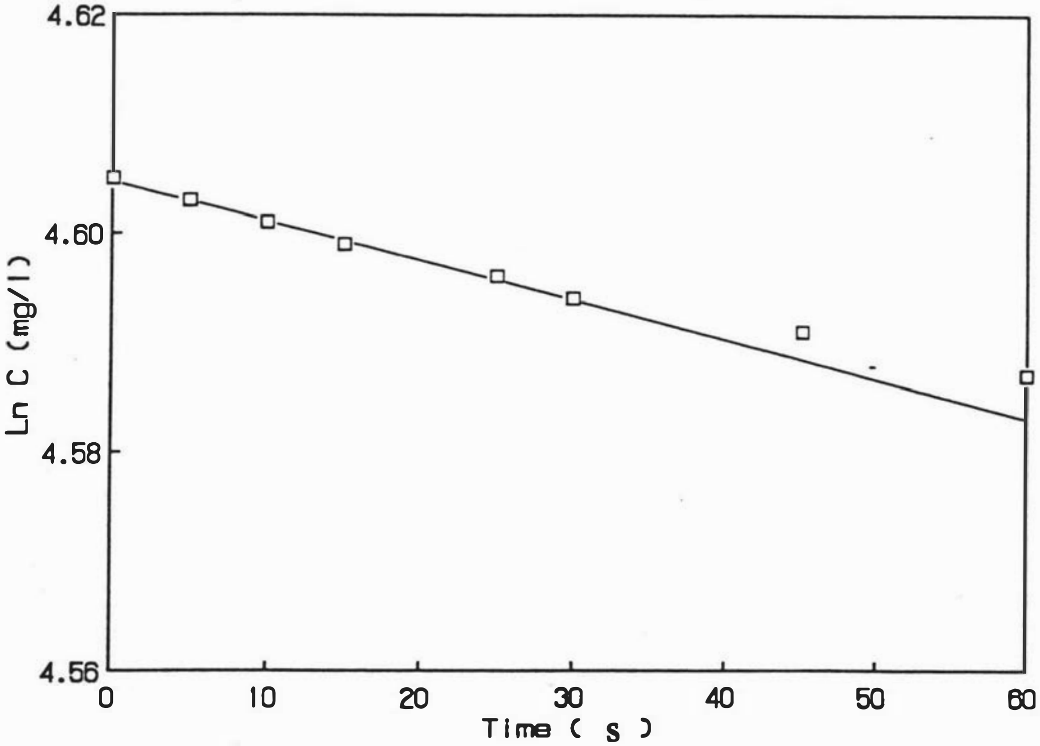


Figure 5.5: Determination of k_1 from initial uptake rate data for 2,4,5-T.

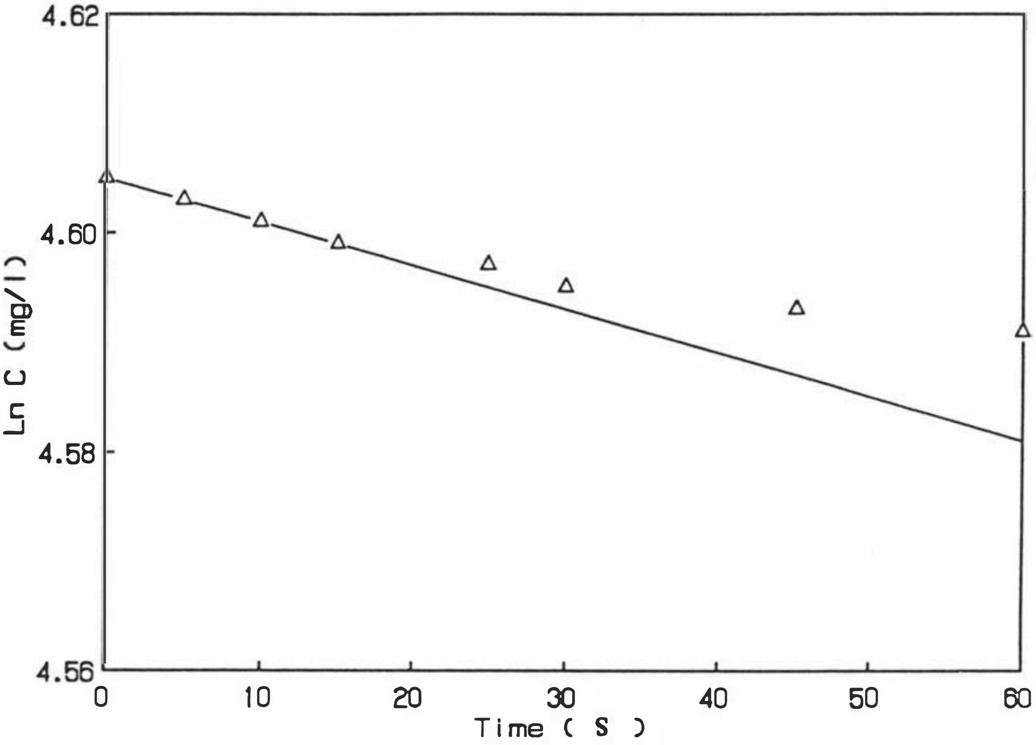


Figure 5.6: Determination of k_1 from initial uptake rate data for MCPA.

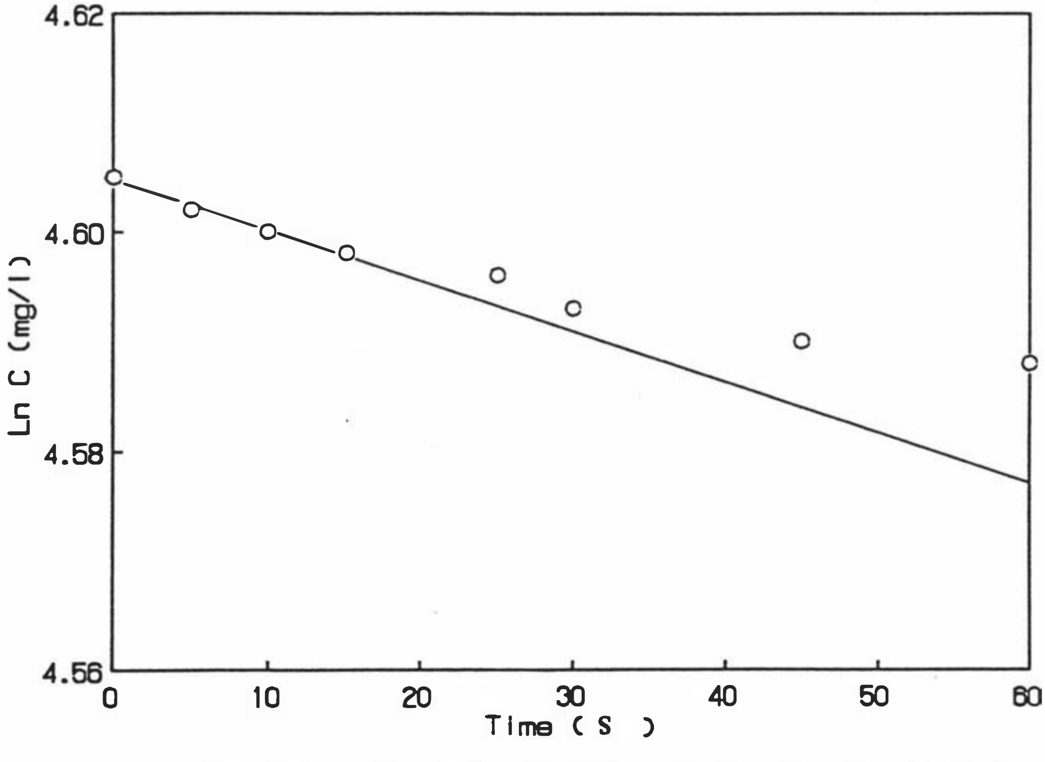


Figure 5.7: Determination of k_1 from initial uptake rate data for 2,4-DCP.

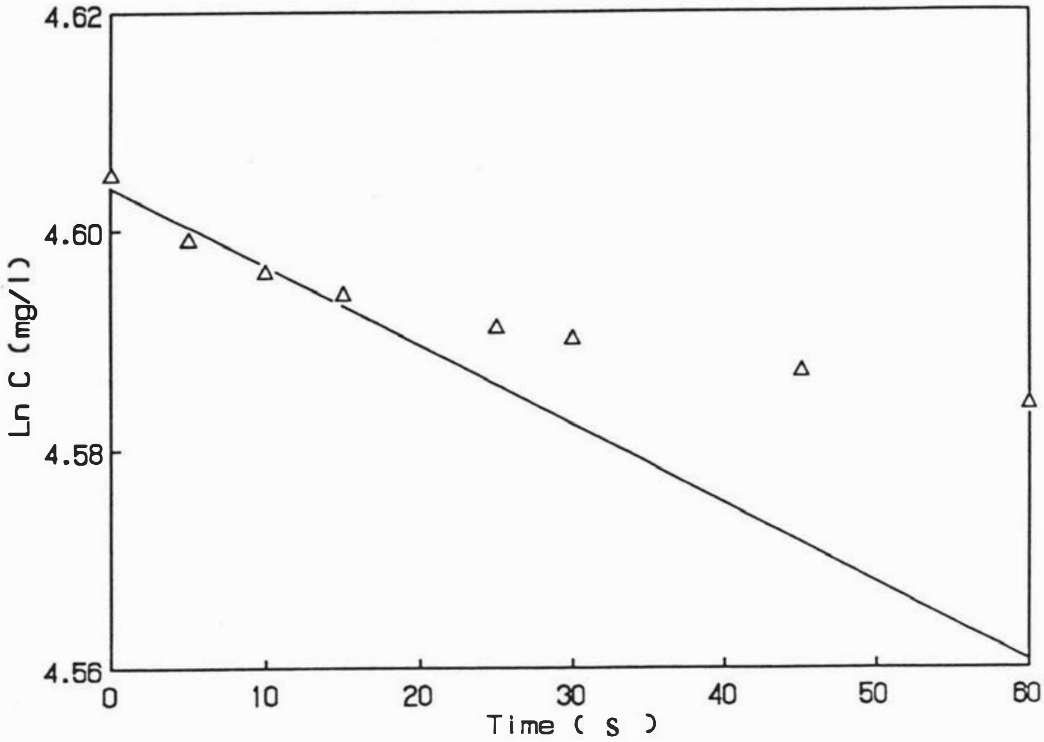


Figure 5.8: Determination of k_1 from initial uptake rate data for 2,4,5-TCP.

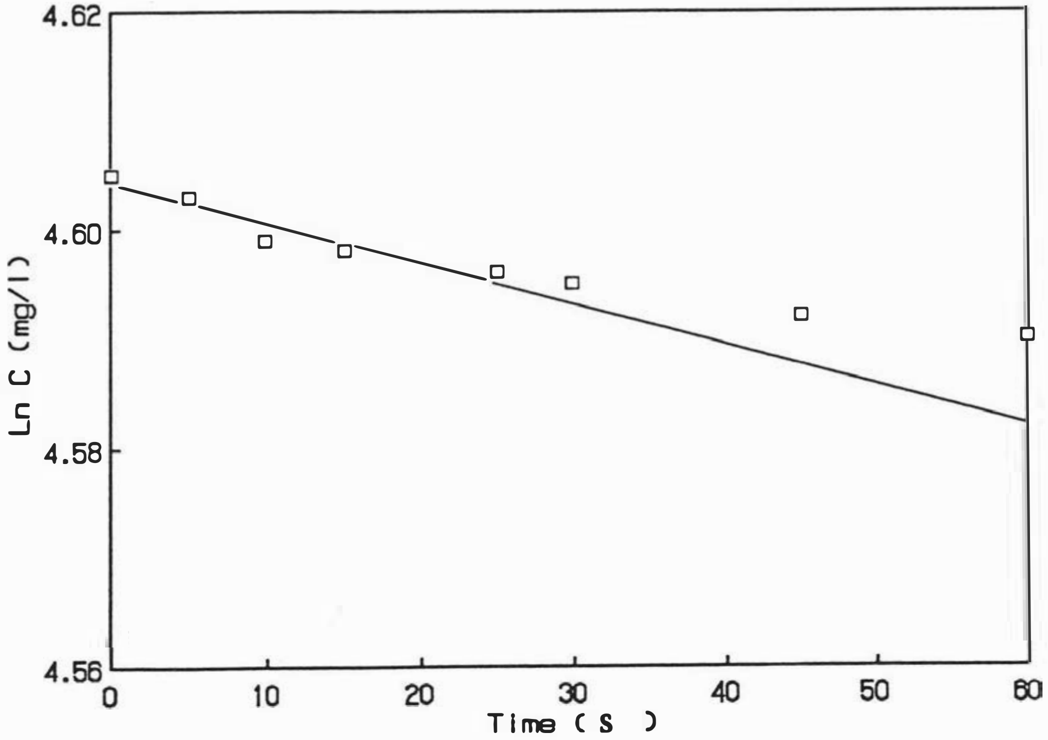


Figure 5.9: Determination of k_1 from initial uptake rate data for PCOC.

5.3.2 Single component adsorption

The experimental data of phenoxyacetic acids and chlorophenols are plotted in Figures 5.10 and 5.11, respectively, along with the model solution. The input parameters used for the HSDM are listed in Table 5.2.

The adsorption surface diffusion coefficients were determined by matching the experimental data with the numerical solution of model Equations 5.9-5.15. Since the Freundlich sorption constants were known, and the parameter F could be calculated from the experimental conditions, the model solution was best fitted to the kinetic data by varying the parameter, B. The adsorption surface diffusion coefficients calculated from the non-dimensional parameter B are given in Table 5.2.

Table 5.2 Single component adsorption batch kinetic data (250 rpm, pH = 2).

Compound	C (mg/l)	F	B	BF/3	k_lx10^3 (cm/s)	$D_{s,ads}$x10^7 (cm^2/s)
2,4-D	93.5	15.50	4.84	25	5.17 ± 0.31	1.89
2,4,5-T	91.0	10.78	9.74	35	5.61 ± 0.10	1.29
MCPA	91.3	13.06	6.89	30	6.23 ± 0.20	1.30
2,4-DCP	94.2	18.52	8.15	50	4.77 ± 0.31	2.19
2,4,5-TCP	92.4	12.51	11.99	50	7.47 ± 0.76	1.68
PCOC	93.7	14.84	11.12	55	3.34 ± 0.48	1.57

The boundary condition at the solid-liquid interface (Equation 5.11) contains the dimensionless parameter, (BF/3), called Biot number representing the ratio of the film-mass transfer to the surface diffusion. According to Fritz *et al.* (1981), Hand *et al.* (1983), Smith (1991), when (BF/3) << 1, external film-mass transfer resistance is the rate controlling step, whereas for (BF/3) > 100, surface diffusion is the rate controlling mechanism. Values of (BF/3) between 1 and 100 indicate that both the film-mass transfer and surface diffusion are rate controlling processes (Crittenden *et al.*, 1980; Sontheimer *et al.*, 1985). The Biot numbers obtained in this study clearly indicate that both film-mass transfer and surface diffusion are significant for the adsorption of phenoxyacetic acids and chlorophenols.

5.3.3 Single component desorption

The desorption experiments were performed immediately after adsorption. The desorption experimental data for phenoxyacetic acids and chlorophenols are shown in Figures 5.12 and 5.13, respectively.

The desorption surface diffusion coefficients were also obtained by matching the batch kinetic data with the numerical solution of Equations 5.9-5.15. The input parameters for the model are listed in Table 5.3. The Freundlich parameters, K_{des} and $1/n_{des}$ were estimated, based on q_{max} values as described in section 4.5.4. The separation factor was determined using the relation, $F = VC_0 / Wq_{max}$. Previous experimental work with similar soils found that k_l was an unimportant factor in determining the rate of sorption (Crittenden *et al.*, 1986 and Hutzler *et al.*, 1986). That is, D_s is sufficiently small that internal particle diffusion was the rate-determining step (Miller and Pedit, 1992). Based on this evidence the k_l was assumed to be the same for both adsorption and desorption. Since the bulk concentration in the desorption phase increases with time, the initial condition of the adsorber was appropriately changed. The model solution was obtained as, $C - C_0$ *versus* t for desorption rate data.

Table 5.3 Single component desorption batch kinetic data.

Compound	q_{max} (mg/g)	K_{des}	$1/n_{des}$	F	B	BF/3	$D_{s,des} \times 10^7$ (cm²/s)
2,4-D	0.44	0.105	0.35	9.08	8.21	25	1.67
2,4,5-T	0.60	0.120	0.39	6.89	13.87	32	1.36
MCPA	0.58	0.138	0.34	7.84	10.76	28	1.25
2,4-DCP	0.39	0.110	0.27	18.56	9.19	57	1.93
2,4,5-TCP	0.51	0.258	0.15	12.28	12.16	50	1.65
PCOC	0.42	0.099	0.32	14.52	10.62	51	1.63

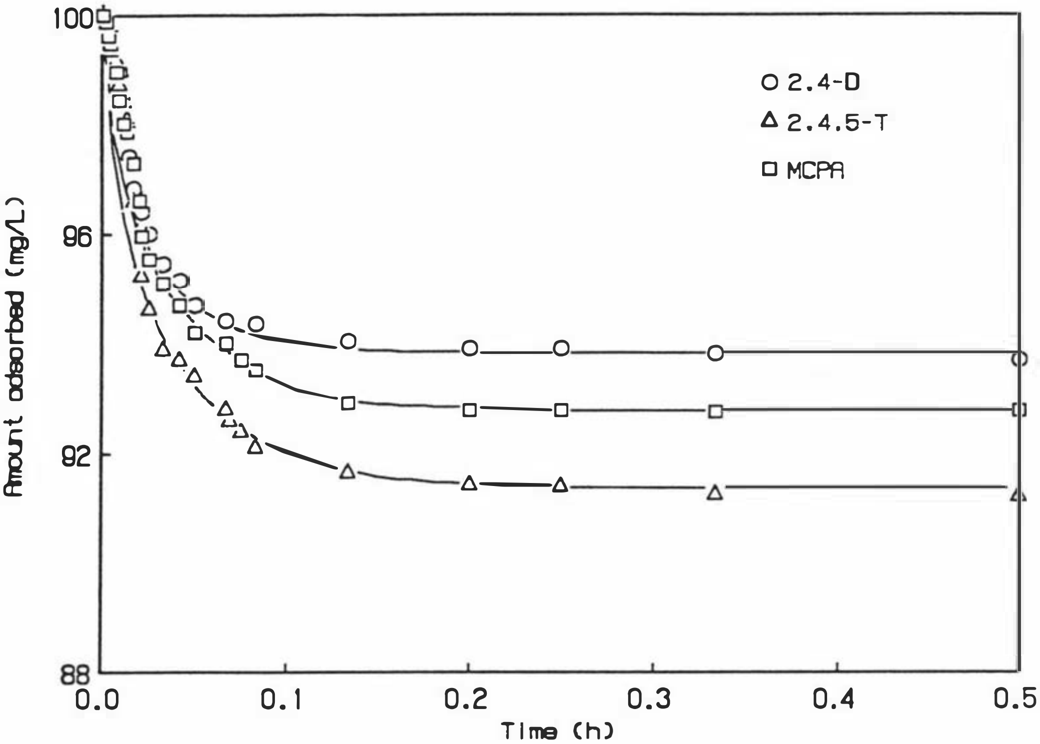


Figure 5.10: Experimental data and model fit for adsorption of phenoxyacetic acids in a batch reactor.

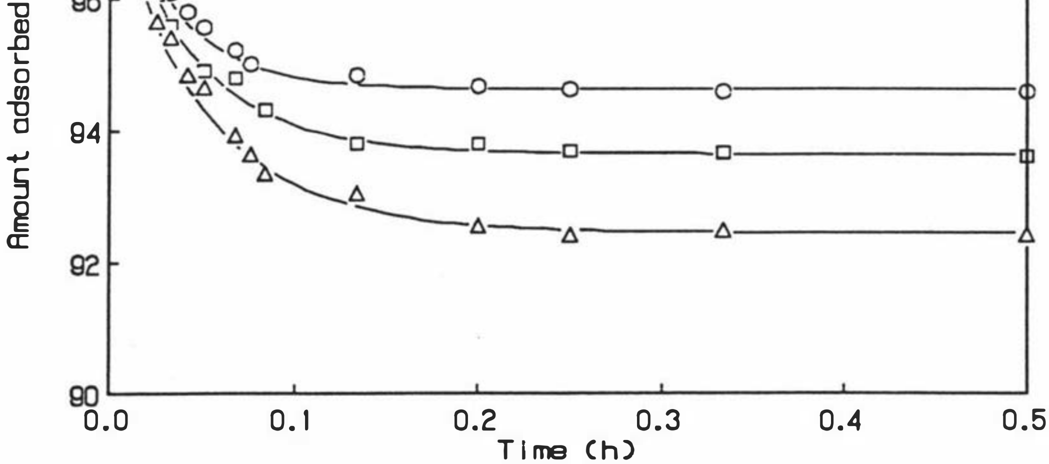


Figure 5.11: Experimental data and model fit for adsorption of chlrophenols in a batch reactor.

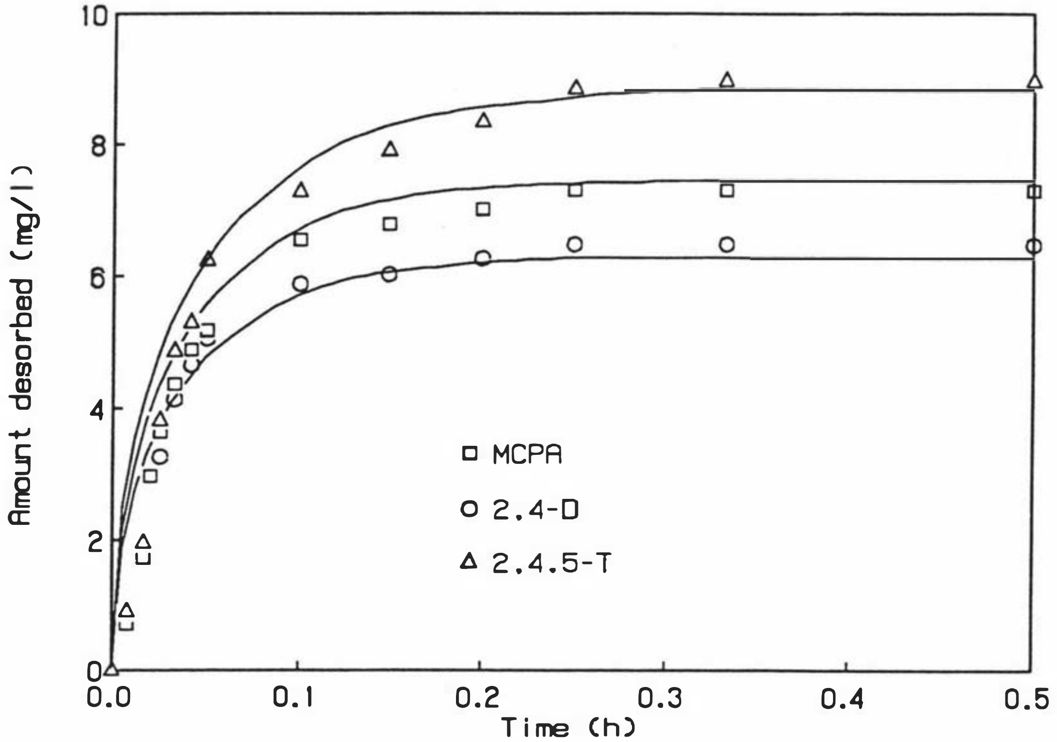


Figure 5.12: Experimental data and model fit for desorption of phenoxyacetic acids.

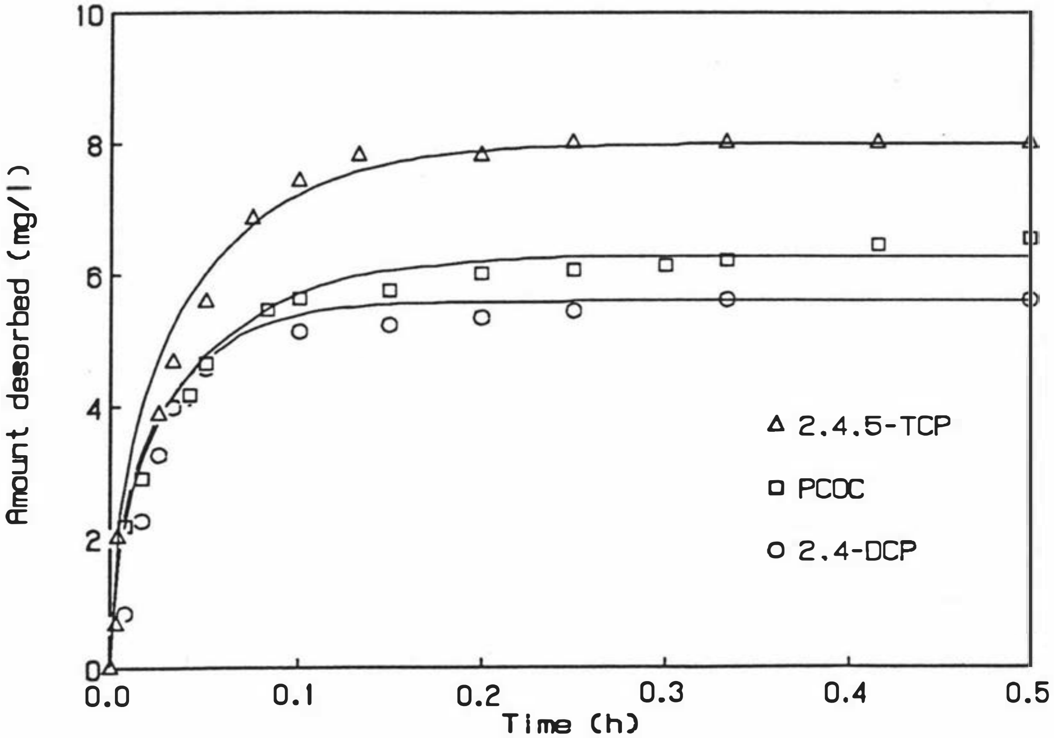


Figure 5.13: Experimental data and model fit for desorption of chlorophenols.

Figures 5.12 and 5.13 show the desorption experimental data and model fit for both phenoxyacetic acids and chlorophenols, where the Biot numbers were also in the range of 1-100 indicating that both film-mass transfer and surface diffusion are rate controlling mechanisms. The desorption surface diffusion coefficients obtained from the parameter, B, are given in Table 5.3. A comparison of $D_{s,ads}$ and $D_{s,des}$ values indicate that they are similar in order of magnitude, although $D_{s,des}$ values are slightly smaller than the corresponding $D_{s,ads}$ values.

Adsorption and desorption kinetics for all compounds were characterized by rapid initial uptake in the first minute, followed by a slower sorption rate; little change in solution concentration was observed after 30 min, showing a two-phase pattern. It has been well documented in literature that adsorption/desorption of many organic compounds follows a biphasic pattern (Pavlostathis and Mathavan, 1992). The second phase of sorption was observed to extend for several days/months, before final equilibrium was reached. Coates and Elzerman (1986) predicted equilibrium times of several years for PCBs in sediments based on desorption kinetics. In the present study, the high water to soil (100:1) ratio used allowed uniform mixing and adequate soil dispersion in baskets which caused shorter time periods for equilibrium compared to batch equilibrium studies (Brusseau and Rao, 1989). Stirring the suspension resulted in the breakup of the aggregates, which led to a smaller size of the agglomerates, exposing the adsorbed solutes to the bulk liquid. This resulted in enhanced desorption kinetics, where the rates of sorption and desorption were found to be similar (Miller and Pedit, 1992). Considering the nature of the experiments and the data fitting involved, rate parameter estimates are believed to be significantly more accurate than those typically obtained from short-term exposure through soil columns, and by other methods.

The results show several interesting features of sorption consistent with the intraparticle diffusion mechanism. Compounds with greater sorption capacities have slower diffusion rates in soil. This finding is important, because if local sorption equilibrium between molecules in bulk liquid, and those sorbed in the aggregates are always established, the compounds with higher adsorption capacities (e.g., 2,4,5-T > 2,4,-D) were predicted to penetrate the soil more slowly, since diffusive transport occurs primarily in the intraparticle mechanism. The observed inverse relationship between surface diffusion coefficient and sorption capacity agrees qualitatively with results of previous investigators (Wu and Gschwend 1986; Ball and Roberts, 1991). In addition, the compounds with higher molecular weight (e.g., 2,4,5-TCP > 2,4-DCP) penetrated slowly because of lower diffusivities (Satterfield, 1981). Therefore, the effects of sorption dominated the observed variation in diffusion coefficients for the different compounds. Measurable soil properties, including internal porosity, natural organic matter content, and internal surface area showed no correlation to the sorption kinetics.

The adsorption and desorption processes were found to be completely reversible because the majority of the adsorbed solute was recovered (> 90%). Also, the desorption processes has a similar time scale (Figures 5.11 and 5.13) as the adsorption process (Figures 5.10 and 5.12) for all the compounds examined. Both sorption and desorption processes were completed in eight hours for all compounds, which shows that the sorption process of phenoxyacetic acids and chlorophenols is reversible. Other laboratory studies, with freshly contaminated soil, have also reported little resistance to desorption (Connaughton *et al.,* 1993). Karickhoff and Morris (1985) studied the sorption kinetics for hydrophobic pollutants and report that the final portion of the sorbed material (10% on initial adsorbed mass) tend to desorb slowly, a two-resistance model is used to describe the desorption rate if the final slow rate was ignored.

From the analysis, it is clear that the model can be applied to a number of compounds by adjusting the D_s from easily measured sorption parameters. Therefore, by incorporating D_s in transport models it will certainly improve the capability to predict the fate of organic contaminants.

5.3.4 Bicomponent kinetics

The bicomponent kinetic experiments demonstrate the influence on rate of a particular solute in the presence of another competing solute. In chapter 4, competitive effects were observed in bicomponent systems; in this section, the relationships developed earlier for competitive sorption are used to predict the kinetics of three bicomponent mixtures.

Virtually all of the limited bicomponent kinetics studies reported in the literature, are concerned with the adsorption of organic chemicals onto activated carbon (Fritz *et al.*, 1981; Mathews and Su, 1983; Fettig and Sontheimer, 1987b). Mathews and Su (1983) investigated the bicomponent adsorption kinetics of phenol-naphthalene mixtures onto activated carbon, using the bicomponent HSDM, based on single component model equations and report that the adsorption rate was predicted satisfactorily. The measured surface diffusion coefficients were about 10% smaller than single component values.

Fettig and Sontheimer (1987a, b and c) report the bicomponent kinetic experiments for three mixtures of *p*-nitrophenol-*p*-nitrobenzoic acid, *p*-hydroxybenzoic acid-*p*-nitrophenol and *p*-nitrophenol-naphthalenedisulfonic acid. The bicomponent HSDM predicted the experimental profile of the more strongly adsorbed *p*-nitrobenzoic acid accurately, however, failed to predict the profile of the weakly adsorbed *p*-nitrophenol. Similar observations were made by the authors for the adsorption of *p*-hydroxybenzoic acid-*p*-nitrophenol and *p*-nitrophenol-naphthalenedisulfonic acid mixtures. The surface diffusivities obtained from the model fit were 1.5-5.0 times higher than the single component diffusivities. They conclude that the high bicomponent diffusivities may be due to the dependence of surface diffusivity on equilibrium capacity.

Recently, Kenneth *et al.* (1992) report the adsorption kinetics of phenol-*p*-chlorophenol and phenol-2,5-dichlorophenol onto XAD-4, a synthetic resin; the experimental data were modelled on a combination of pore and surface diffusion mechanisms, the smaller surface diffusion coefficients observed in bicomponent systems were attributed to the contribution of pore diffusion to the intraparticle transport.

In all the above studies, displacement effects were observed, i.e., the strongly adsorbed component displacing the weakly adsorbed one. These displacement effects were reported to be dependent on the initial concentrations of the components; however, the effects were found to reduce when the concentration ratio was low or high. Kenneth *et al.* (1992) conclude that for solutes having similar adsorptive behaviours, the surface diffusion mechanism predicts better than the pore diffusion mechanism.

In this section, the HSDM was applied to describe the adsorption and desorption kinetics of bicomponent mixtures based on the work of Fritz *et al.* (1981) and Fettig and Sontheimer (1987b).

5.3.4.1 Model equations

The single component equations presented in section 5.2 were extended to bicomponent systems. In addition to the assumptions listed above, the following simplifications were made:

- diffusional interactions between the solutes were assumed to be negligible, as the competitive effects are due to equilibrium adsorption and desorption phenomenon; and
- the film-mass transfer coefficient, k_l for each component is assumed to be the same as in a single component system. This was based on the experimental work of Fettig and Sontheimer (1987b), who observed that the k_l values in single and bicomponent systems essentially remain the same.

The HSDM equations for a bicomponent system are expressed as,

Adsorber

$$V\frac{dC_1}{dt} = k_{l,1}A(C_1 - C_{1,s}) \tag{5.16}$$

$$V\frac{dC_2}{dt} = k_{l,2}A(C_2 - C_{2,s}) \tag{5.17}$$

Particle

$$\frac{\partial q_1}{\partial t} = \frac{D_{s,1}}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial q_1}{\partial r}) \tag{5.18}$$

$$\frac{\partial q_2}{\partial t} = \frac{D_{s,2}}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial q_2}{\partial r}) \tag{5.19}$$

The coupling equations at the liquid-solid interface are expressed as:

$$\rho_p D_{s,1} A \frac{\partial q_1}{\partial r}\bigg|_{r=R} = k_{l,1} A (C_1 - C_{1,s}) \tag{5.20}$$

$$\rho_p D_{s,2} A \frac{\partial q_2}{\partial r}\bigg|_{r=R} = k_{l,2} A (C_2 - C_{2,s}) \tag{5.21}$$

The initial and boundary conditions are expressed as:

$$t = 0 \; ; \; C_1 = C_{1,0} \; , \; C_2 = C_{2,0} \; , \; q_1 = q_2 = 0 \tag{5.22}$$

$$r = 0 \; ; \; \frac{\partial q_1}{\partial r} = \frac{\partial q_2}{\partial r} = 0 \tag{5.23}$$

$$r = R \; ; \; q_1 = q_{1,s} \; ; \; q_2 = q_{2,s} \tag{5.24}$$

The nondimensional variables and parameters are expressed as:

$$u_1 = \frac{q_1}{q_{1,0}} \; ; \; u_2 = \frac{q_2}{q_{2,0}} \; ; \; Y_1 = \frac{C_1}{C_{1,0}} \; ; \; Y_2 = \frac{C_2}{C_{2,0}} \tag{5.25}$$

$$X = \frac{r}{R} \; ; \; \tau = \frac{D_{s,1} t}{R^2} \tag{5.26}$$

$$B_1 = \frac{(k_{l,1}A/V)}{(D_{s,1}/R^2)} \; ; \quad B_2 = \frac{(k_{l,2}A/V)}{(D_{s,2}/R^2)} \tag{5.27}$$

$$F_1 = \frac{VC_{1,0}}{Wq_{1,0}} \; ; \quad F_2 = \frac{VC_{2,0}}{Wq_{2,0}} \tag{5.28}$$

Equations 5.18-5.24 were converted to dimensionless form and expressed as:

$$\frac{dY_1}{d\tau} = B_1(Y_1 - Y_{1,s}) \tag{5.29}$$

$$\frac{dY_2}{d\tau} = \frac{D_{s,2}}{D_{s,1}} B_2(Y_2 - Y_{2,s}) \tag{5.30}$$

$$\frac{\partial u_1}{\partial \tau} = \frac{1}{X^2}\frac{\partial}{\partial X}\left(X^2\frac{\partial u_1}{\partial X}\right) \tag{5.31}$$

$$\frac{\partial u_2}{\partial \tau} = \frac{D_{s,2}}{D_{s,1}} \frac{1}{X^2}\frac{\partial}{\partial X}\left(X^2\frac{\partial u_2}{\partial X}\right) \tag{5.32}$$

$$\left.\frac{\partial u_1}{\partial X}\right|_{x=1} = \frac{B_1F_1}{3}(Y_1 - Y_{1,s}) \tag{5.33}$$

$$\left.\frac{\partial u_2}{\partial X}\right|_{x=1} = \frac{B_2F_2}{3}(Y_2 - Y_{2,s}) \tag{5.34}$$

$$\tau = 0 \; ; \; Y_1 = Y_2 = 1 \; ; \; u_1 = u_2 = 0 \tag{5.35}$$

$$X = 0 \; ; \; u_1 = u_2 = 0 \tag{5.36}$$

$$X = 1 \; ; \; u_1 = u_{1,s} \; , \; u_2 = u_{2,s} \tag{5.37}$$

where, B_1 and B_2 represent the ratios of film diffusion time to surface diffusion time, F_1 and F_2 are the separation factors for components 1 and 2, respectively. The liquid and solid phase concentrations are related by the competitive adsorption isotherm and expressed as:

$$q_{1,s} = K_1 C_{1,s}(C_{1,s} + a_{12}C_{2,s})^{\frac{1}{n_1} - 1} \tag{5.38}$$

$$q_{2,s} = K_2 C_{2,s}(C_{2,s} + a_{21}C_{1,s})^{\frac{1}{n_2} - 1} \tag{5.39}$$

or,

$$u_{1,s} = \frac{Y_{1,s}(Y_{1,s} + l_1 Y_{2,s})^{1/n_1 - 1}}{(1 + l_1)^{1/n_1 - 1}} \tag{5.40}$$

$$u_{2,s} = \frac{Y_{2,s}(Y_{2,s} + l_2 Y_{1,s})^{1/n_2 - 1}}{(1 + l_2)^{1/n_2 - 1}} \tag{5.41}$$

where, $l_1 = a_{12}\, C_{1,0}/C_{2,0}$ and $b_2 = l_{21}\, C_{2,0}/C_{1,0}$. Equations 5.29-5.37 in combination with Equations 5.40 and 5.41, were solved using orthogonal collocation, fourth order Runge-Kutta and Newton-Raphson techniques.

5.3.4.2 Bicomponent adsorption

The bicomponent adsorption runs were conducted for three mixtures, i.e., 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC for an initial concentration of 100 mg/l of each. The competition coefficient, $a_{i,j}$ for each component at 100 mg/l was determined using the relationship obtained in section 4.5.2. The separation factor, F, was estimated based on the bicomponent adsorption isotherms (Equations 5.38 and 5.39). The experimental conditions and model parameters for bicomponent systems are given in Table 5.4.

Figure 5.14 shows the experimental data and model solution of the competitive adsorption of the 2,4-D-MCPA mixture. The individual concentration profiles of both compounds were obtained by best fitting the model solution to the experimental data by varying the respective B values. The surface diffusion coefficients determined from B_1 and B_2 for 2,4-D and MCPA, 1.67×10^{-7} cm^2/s and 1.26×10^{-7} cm^2/s, respectively, indicate they were of the same order as the single solute surface diffusion coefficient values, although the actual values were slightly smaller in a bisolute system. This could be due to competitive effects. Figures 5.15 and 5.16 show the experimental and model fit for bisolute adsorption of 2,4-D-PCOC and MCPA-PCOC mixtures. The surface diffusion coefficients for each solute in the mixture are given in Table 5.4 and were found to be smaller (2,4-D-12%; MCPA-4% and PCOC-6%) than the respective single solute values. Kenneth *et al.* (1992) also report that the surface diffusion coefficients of the phenol-*p*-nitrophenol mixture onto XAD-4 were 15% smaller than those for the single solute system.

Table 5.4 Bicomponent adsorption batch kinetic data ($C_{1,0} = C_{2,0} = 100$ mg/l, 250 rpm, W = 20g, pH = 2).

Bicomponent mixture	C (mg/l)	$a_{i,j}$	F	BF/3	$D_{s,ads} \times 10^7$ (cm^2/s)	% change
2,4-D-MCPA						
2,4-D	89.10	0.15	8.03	22	1.67	11.6
MCPA	91.40	0.70	7.58	27	1.26	3.1
2,4-D-PCOC						
2,4-D	89.00	0.10	7.94	24	1.65	12.70
PCOC	93.60	0.72	11.56	45	1.49	5.10
MCPA-PCOC						
MCPA	88.08	0.14	6.77	32	1.25	3.85
PCOC	92.00	0.55	11.48	40	1.45	7.64

5.3.4.3 Bicomponent desorption

Bicomponent desorption rate experiments were conducted immediately after the adsorption experiments for the three mixtures. The desorption experimental data were also analyzed using the equations 5.29-5.37 in combination with 5.40 and 5.41, with respective desorption equilibrium parameters. The desorption isotherm parameters and separation factors were estimated based on the amount adsorbed (q_{max}) of each component. The desorption competition coefficient ($d_{i,j}$) values were determined using the empirical relationship developed in section 4.5.4. The k_l values for the desorption were assumed to be the same as in single solute adsorption studies. The values of input parameters required for the model solution are given in Table 5.5.

Table 5.5 Bicomponent desorption batch kinetic data.

Bicomponent mixture	q_{max} (mg/g)	K_{des}	$1/n_{des}$	$d_{i,j}$	F	BF/3	$D_{s,des}$x10^7 (cm^2/s)	% change
2,4-D-MCPA								
2,4-D	0.55	0.14	0.31	0.32	7.51	28	1.36	18.56
MCPA	0.43	0.10	0.38	0.43	5.40	33	1.20	4.0
2,4-D-PCOC								
2,4-D	0.55	0.14	0.31	0.16	7.51	26	1.67	-
PCOC	0.32	0.09	0.31	0.05	9.35	50	1.64	-
MCPA-PCOC								
MCPA	0.59	0.14	0.34	0.28	5.83	36	1.18	5.6
PCOC	0.40	0.09	0.32	0.32	13.22	45	1.33	18.40

The experimental data and model solution for the desorption of the 2,4-D-MCPA mixture, given in Figure 5.17, demonstrates that the model satisfactorily describes the desorption of each solute. The calculated $D_{s,des}$ values from parameters B_1 and B_2 are given in Table 5.5. The bisolute desorption surface diffusion coefficients were found to be smaller compared to the respective single solute desorption values.

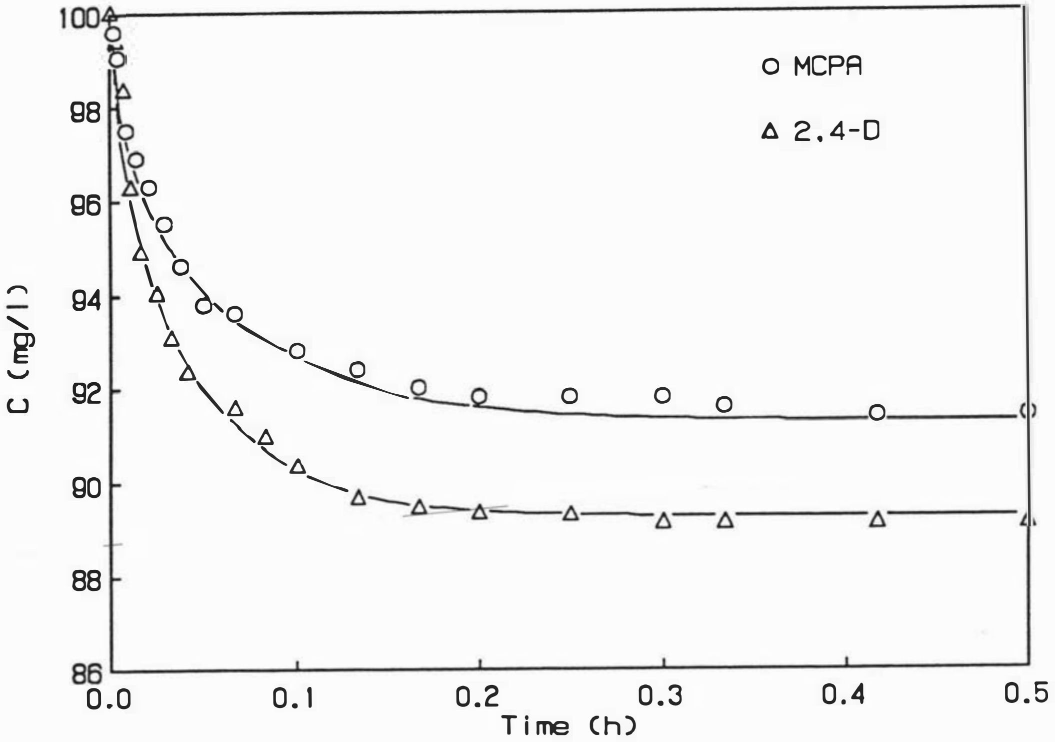


Figure 5.14: Bicomponent adsorption experimental data of 2,4-D-MCPA in a batch reactor. Solid lines show the model fit to the experimental data.

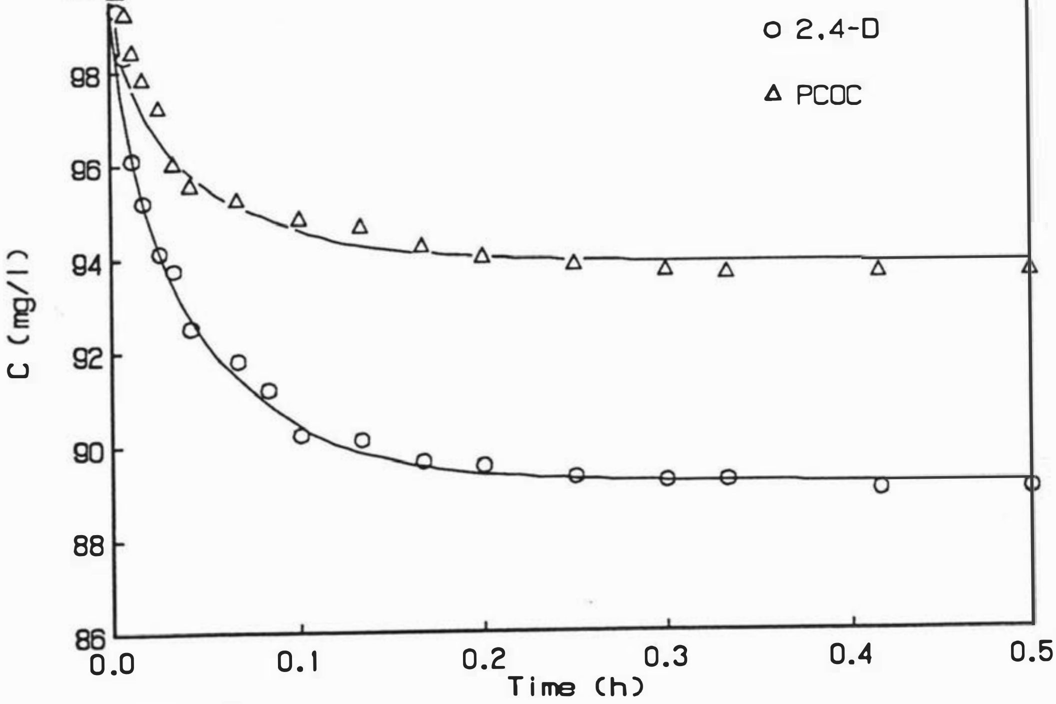


Figure 5.15: Bicomponent adsorption experimental data of 2,4-D-PCOC in a batch reactor. Solid lines show the model fit to the experimental data..

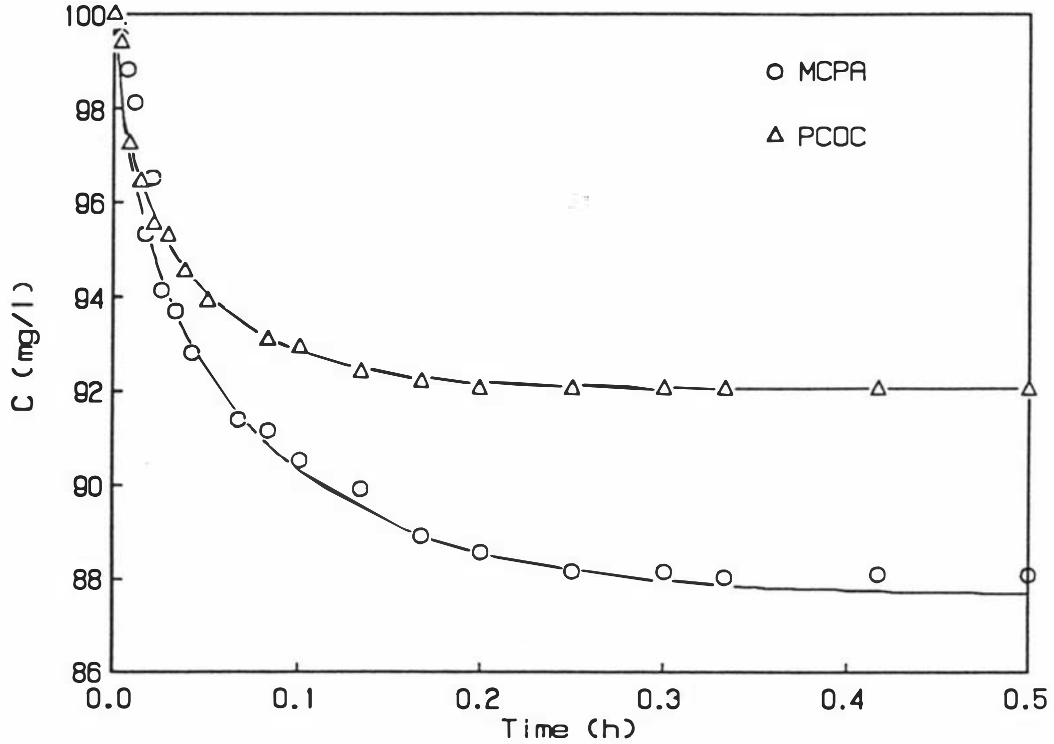


Figure 5.16: Bicomponent adsorption experimental data of MCPA-PCOC in a batch reactor. Solid lines show the model fit to the experimental data.

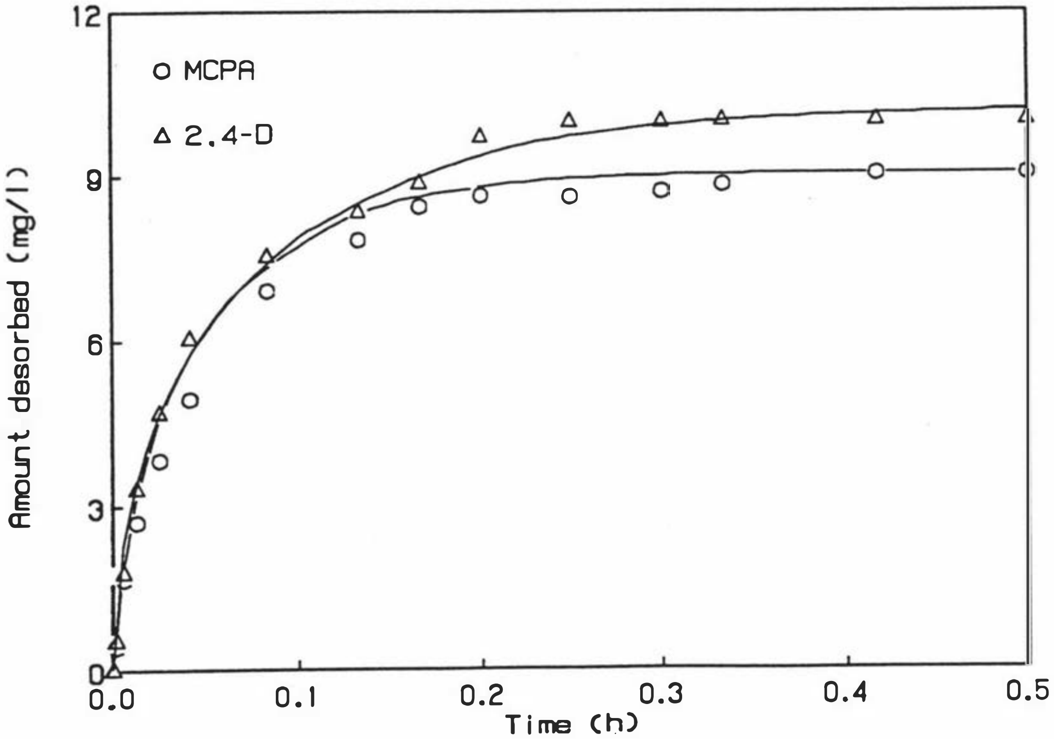


Figure 5.17: Bicomponent desorption kinetic data for 2,4-D-MCPA. Solid lines show model fit to the experimental data.

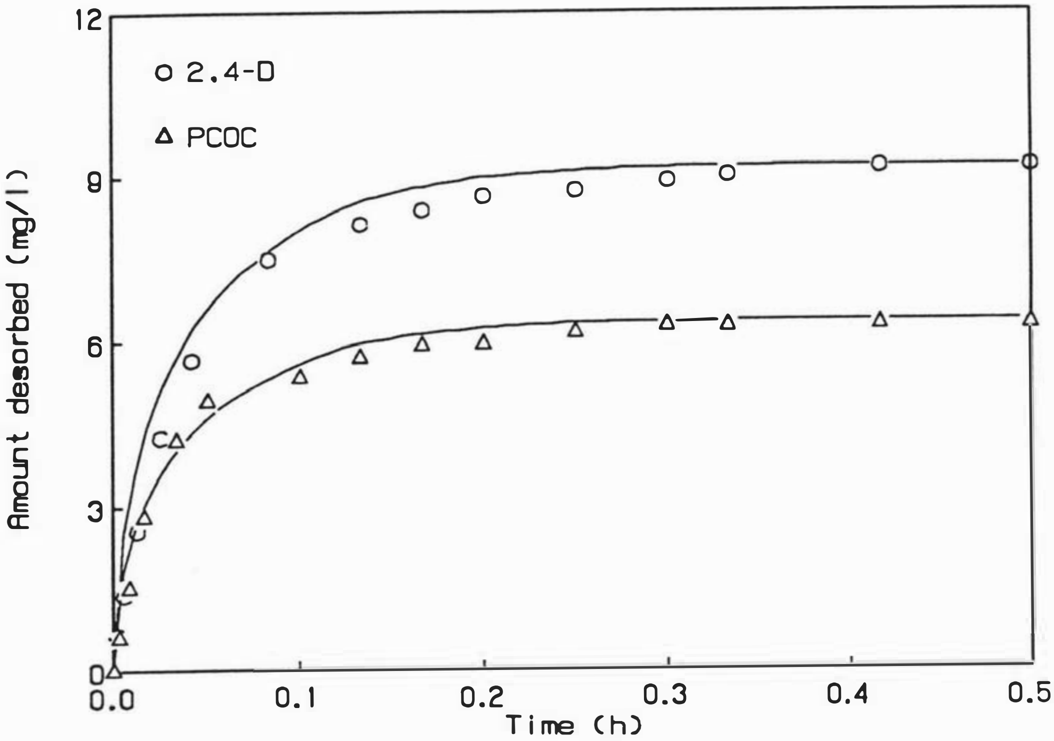


Figure 5.18: Bicomponent desorption kinetic data for 2,4-D-PCOC. Solid lines show model fit to the experimental data.

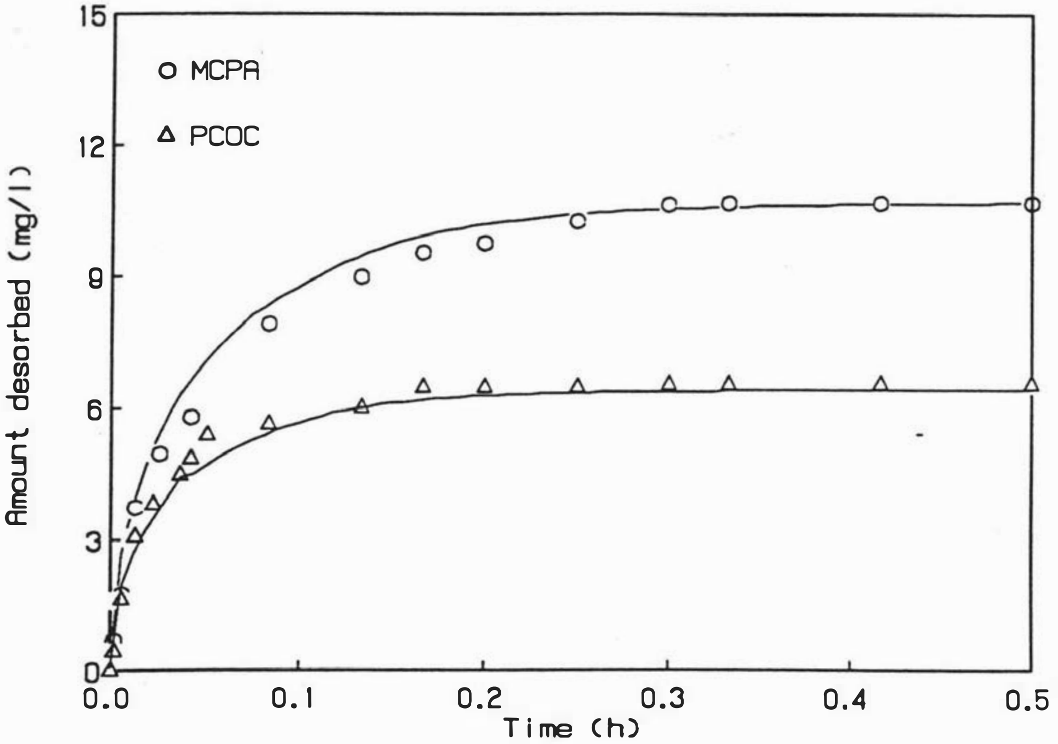


Figure 5.19: Bicomponent desorption kinetic data for MCPA-PCOC. Solid lines show model fit to the experimental data.

The desorption rates of 2,4-D-PCOC and MCPA-PCOC mixtures are shown in Figures 5.17 and 5.19 together with the model fit. The calculated desorption surface diffusion coefficients from the model fit are given in Table 5.5. It can be observed that the $D_{s,des}$ values in bisolute systems were smaller than the single solute system $D_{s,des}$ values. The results reveal that the $D_{s,des}$ values of 2,4-D and PCOC were smaller by about 18% in the presence of MCPA. On the other hand, the value for MCPA was smaller by 5% in the presence of 2,4-D or PCOC. Merk *et al.* (1980) also report a decrease of $D_{s,des}$ values by approximately 10-15% for a $CHCl_3$ and $CHCl_2Br$ combination onto activated carbon.

In all previous studies reported on bicomponent kinetics, displacement effects were observed, whereby the weakly adsorbing solute is adsorbed rapidly, which is displaced by the slower, but more strongly adsorbed solute (Fettig and Sontheimer, 1987 and Kenneth *et al.*, 1992). This is due to the significant difference in the rates of sorption between the two solutes. In the present case, the rates of sorption are not statistically different, hence no displacement effects were observed in the measured data.

The results presented in this section indicate that the effect of competition on the diffusion coefficients is not significant. However, it should be noted that all the work presented here was done at equal concentrations of both solutes. Furthermore, as the soil adsorbed a maximum of only 10% of the initial concentration, a definitive conclusion, on the effects of competition, could not be reached.

CHAPTER 6

ADSORPTION AND DESORPTION IN SOIL COLUMNS

6.1 Introduction

The previous two chapters described the processes of adsorption, desorption, film-mass transfer and surface diffusion mechanisms at particle or microscopic level. The ultimate utility for predicting the fate of contaminants in a soil profile depends on the impact and role of each of the above processes on overall transport at the macroscopic, or field scale. This chapter evaluates the transport of phenoxyacetic acids and chlorophenols in soil columns, incorporating the previously observed mechanisms of sorption.

Sorption processes in field situations are complex, often involving non-linear relationships and rate limited conditions. Thus, to develop predictive models, simplified assumptions are frequently made (Weber *et al.,* 1991). In addition, the experimental design in the laboratory is commonly structured in such a manner to allow close approximation of system behaviour with field conditions. A laboratory soil column is, therefore, an idealized situation, where sorption, mass transfer and hydrodynamic mechanisms are operating simultaneously. The assumptions frequently made to predict the transport of solutes in laboratory columns are:

- homogeneous packing of soil;
- negligible radial gradients;
- no chemical reactions except for sorption;
- constant diffusivity;
- constant velocity across cross-section;
- constant temperature;
- no interaction between solutes; and
- local equilibrium between fluid and solid at all times.

The models for the transport of solutes in soil columns with the above assumptions incorporate advection and dispersion processes, which are generally based on the principles of mass balance (Weber *et al*., 1991). In section 2.5, where the frequently applied models to predict the transport of organic chemicals through soil were presented, for example, a model and numerical solutions for the movement of solutes in a soil with dispersion, mass transfer and linear adsorption were presented by Van Genuchten *et al*. (1977) and Gamerdinger *et al*. (1994). The authors used the model to study the transport of organic chemicals through soil columns and showed that the adsorption and intraparticle diffusion significantly affected transport. However, several of the model parameters were obtained by curve fitting the model solution to the experimental data, thus, failing to test predictive capability.

Rao *et al*. (1982) and Lee *et al*. (1991) report a model incorporating dispersion and diffusion of tracers into porous spheres and glass beads. All the parameters were measured independently, and the model satisfactorily predicted the movement of tracers. However, as the model could not describe the transport of organic chemicals in soil columns, its applications are limited to only tracers.

On the other hand, Crittenden *et al*. (1986) and Smith (1991) developed a surface diffusion model based on film-mass transfer, pore/surface diffusion and adsorption equilibrium. The model successfully predicted the fixed bed data for a variety of adsorbate-adsorbent systems (Crittenden and Weber, 1978; Hand *et al*., 1984); the parameters obtained either from independent experiments or by literature correlations indicating the true predictive nature of the model, which gave excellent results for compounds exhibiting nonlinear isotherms, when pore/surface diffusion is the intraparticle mass transfer mechanism.

The phenoxyacetic acids and chlorophenols (except for 2,4-DCP) in this study exhibited nonlinear isotherms, with film-mass transfer and surface diffusion as transport mechanisms. Hence, it is appropriate to use a column model which incorporates the above mechanisms to describe the solute transport in soil columns. Therefore, a column surface diffusion model was employed to describe the experimental data. The equilibrium and kinetic parameters obtained in previous chapters were used to obtain the model solution. Wherever possible, only independently determined parameters, or from literature correlations were used to predict the transport of solutes in columns.

6.1.1 Water movement in soil

As discussed earlier in section 2.2, a typical soil environment contains solid, liquid and gaseous phases. When water is applied to soil, it enters the soil pores replacing the air contained in them. If sufficient quantity of water is available , the entire pore surface may be filled with water and the excess water move downward by gravitational and pressure potential gradients (hydraulic conductivity) and is known as saturated flow. However, if the application of water is limited, the rate of water movement is reduced, in addition, the water can evaporate from the surface or taken by the plants by which the soil water from the profile is rapidly depleted. Under such conditions, the soil pores will be partially filled with water and the flow of water will occur from a region of high potential to depleted water zones (low potential). Such type of water movement is termed as unsaturated flow (Hillel, 1980). Thus, water movement in soil may be due to saturated or unsaturated flow. The moving force in a saturated soil is the gradient of a positive pressure potential, on the other hand, water in an unsaturated soil is subjected to a suction, which is equivalent to a negative pressure potential. The most important difference between unsaturated and saturated flow is in the hydraulic conductivity. When the soil is saturated, all of the pores are water filled and conducting, when the soil desaturates, some of the pores become air filled and the conductive portion of the soil's cross-sectional decreases correspondingly. The nature of the soil profile, structure and pore size distribution determine the water movement in soil. Hillel (1980) discusses the saturated and unsaturated flow in soils in detail.

The laboratory experiments on transport of solutes in soils are carried out both in saturated (Hutzler *et al.*, 1986; Bhamidimari and Petrie, 1992 and Gamerdinger *et al.*, 1994) and unsaturated systems (Davidson *et al.*, 1980; Harmon *et al.*, 1989 and Hatfield and Stauffer, 1993) using the same transport equations described in section 2.5. As outlined in the introduction, the sludges of phenoxyacetic acids and chlorophenols along with contaminated soil excavated from the previous dump site are kept in a landfill. Currently, water is sprinkled continuously on top of the heap. Generated leachate is collected at the bottom and pumped for further treatment. Rainfall results in additional water entering the heap. It is perceived that the flow within the landfill is likely to be unsteady, saturated and three dimensional. In addition, the experimental investigations in unsaturated systems are complex and difficult to model, therefore, all the experimental data reported here was obtained under saturated conditions.

6.2 Breakthrough and elution curves

The fixed bed adsorption experiments were conducted by continuously contacting the soil with a constant flow of adsorbate solution. Desorption experiments were commenced immediately following the adsorption runs. The detailed procedure is described in section 3.3.4. The conditions for column experiments are tabulated below. The temperature and pH were kept constant throughout the experiment.

Table 6.1 Experimental conditions and physical parameters for fixed beds

Column length, cm	20
Internal diameter, cm	4
Weight of soil, g	258
Column porosity, cm^3/cm^3	0.45
Range of flow rates, l/h	0.5-1
Range of input concentrations, mg/l	100-400
Particle density, g/cm^3	2.6
Particle diameter, cm	0.030
pH	2.0
Temperature, °C	20±1°C

Consider a solution containing 2,4-D at an initial concentration, C_0, pumped through a bed of soil, which is initially free of solute. The solution enters the column and comes in contact with the first few layers of the soil. The soil adsorbs the solute, rapidly, and the remaining solute left in the solution is eventually removed by the subsequent layers in the bed. The effluent from the column is practically free of solute (*A* in Figure 6.1). At this stage, the first few layers of the soil are saturated with solute molecules. As solution is pumped, continuously, the adsorption of 2,4-D takes place in the upper layers in the bed and the effluent concentration is still nearly zero (*B* in Figure 6.1). After a certain time, the concentration of 2,4-D in the effluent reaches an appreciable value (Point *C* in the Figure 6.1). At this stage the bed is saturated with the solute molecules. The solute concentration in the bed rises quickly and is close to the initial value C_0. The portion of the effluent curve between the points *B* and *D* in Figure 6.1 is termed the breakthrough curve. If the 2,4-D solution continues to flow, little adsorption takes place since the bed is saturated, which is in equilibrium with the input solution.

The breakthrough curves generated from the soil columns are generally symmetrical, an *S* shape, but they can sometimes be steep or relatively flat. The rate and mechanism of the sorption process, adsorption equilibrium, fluid velocity and the concentration of the feed all contribute to the shape of the curve (Brusseau and Rao, 1989).

Desorption of the adsorbed solute by a solvent is called elution. In the present study, the column was drained before elution and solute-free water pumped through the column. Initially, as the solute desorbs to a great extent due to the concentration gradient in the bed, the observed concentration in the effluent is high (*E* in Figure 6.1). As more and more solute-free water is pumped through the column, the concentration of solute in the bed decreases; and, after a certain time the effluent concentration reaches a minimum. The area under the curve EFGH represents the quantity of solute desorbed from the soil. In this study, the breakthrough and elution curves are plotted in terms of relative concentration *versus* dimensionless time.

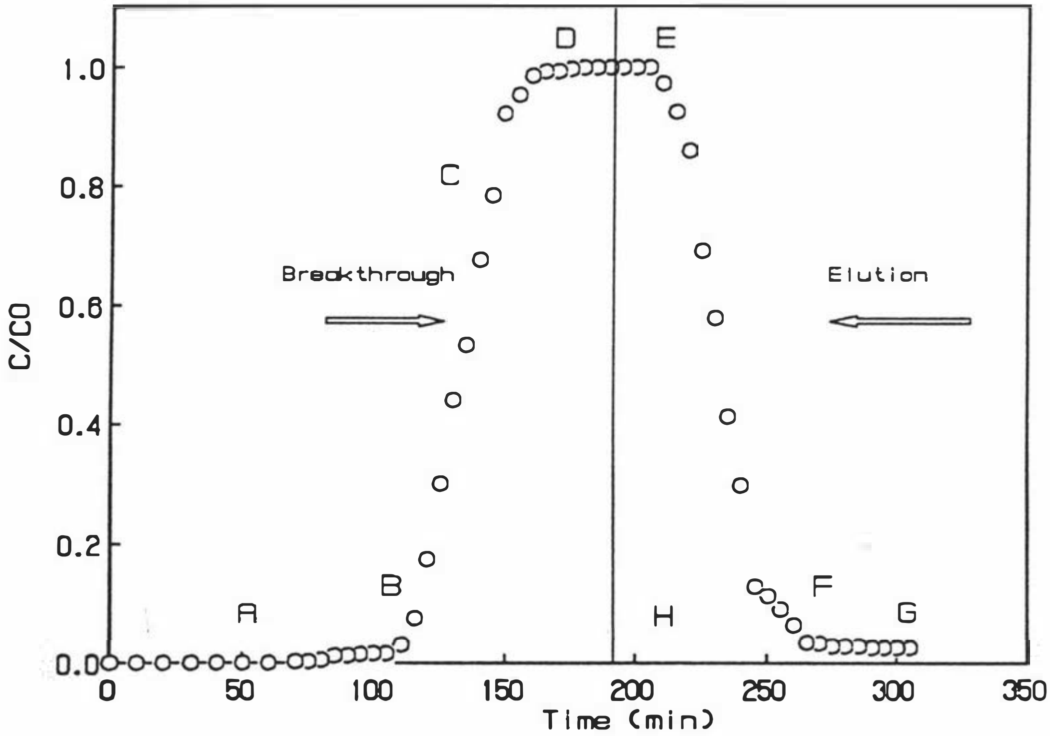


Figure 6.1: Typical breakthrough and elution curves for 2,4-D in a fixed bed at 100 mg/l ($\nu = 0.052$ cm/s, pH = 2 and Temperature = 20°C).

6.3 Homogeneous surface diffusion model (HSDM) - single solute

The model incorporates mathematic description of the following mechanistic processes: fluid diffusion resistance to mass transfer, i.e., the linear driving force approximation commonly referred to as film-mass transfer; local instantaneous adsorption equilibrium adjacent to the soil surface; surface diffusion as the predominant intraparticle mass transfer process; and axial dispersion, due to flow.

Assumptions inherent to the model are: the labyrinth factor can be averaged over the particle radius, which is included in the effective diffusion coefficient; dilute solution conditions prevail, thus no bulk mass flow term is necessary in the surface diffusion equation; the diffusion coefficient is not concentration dependent; the adsorbent is in a fixed position in the reactor (e.g., packed bed); and concentration gradients exist only in a longitudinal direction (e.g., no channelling).

As shown previously, the kinetics of sorption by soil involve several sequential and parallel transport and reaction phenomena. First, liquid diffusion of the solute through the hydrodynamic boundary layer of fluid adjacent to the surface of the particle occurs. Sequentially, the solute diffuses along the pore walls, i.e., an adsorbed molecule can *hop* along the surface when it attains sufficient activation energy and when an adjacent adsorption site is available. Finally, the reaction of the adsorbate with the adsorbent includes local elementary steps involved in determining the energies of adsorption on the surface.

As surface reactions are rarely limiting, it is appropriate to assume local instantaneous adsorption equilibrium (Crittenden *et al.,* 1986). Important factors having an impact on solute flux in the adsorbent are pore structure, which includes pore tortuosity, constriction and branching. Unfortunately, as these pore structure characteristics are not quantifiable, their effects cannot be reasonably estimated *per se.* Flux along a radial dimension is assumed in the transport model, and the pore characteristics are thus reflected in the magnitude of effective intraparticle diffusivities (Hutzler *et al.,* 1986). The mechanisms of HSDM are shown in Figure 6.2.

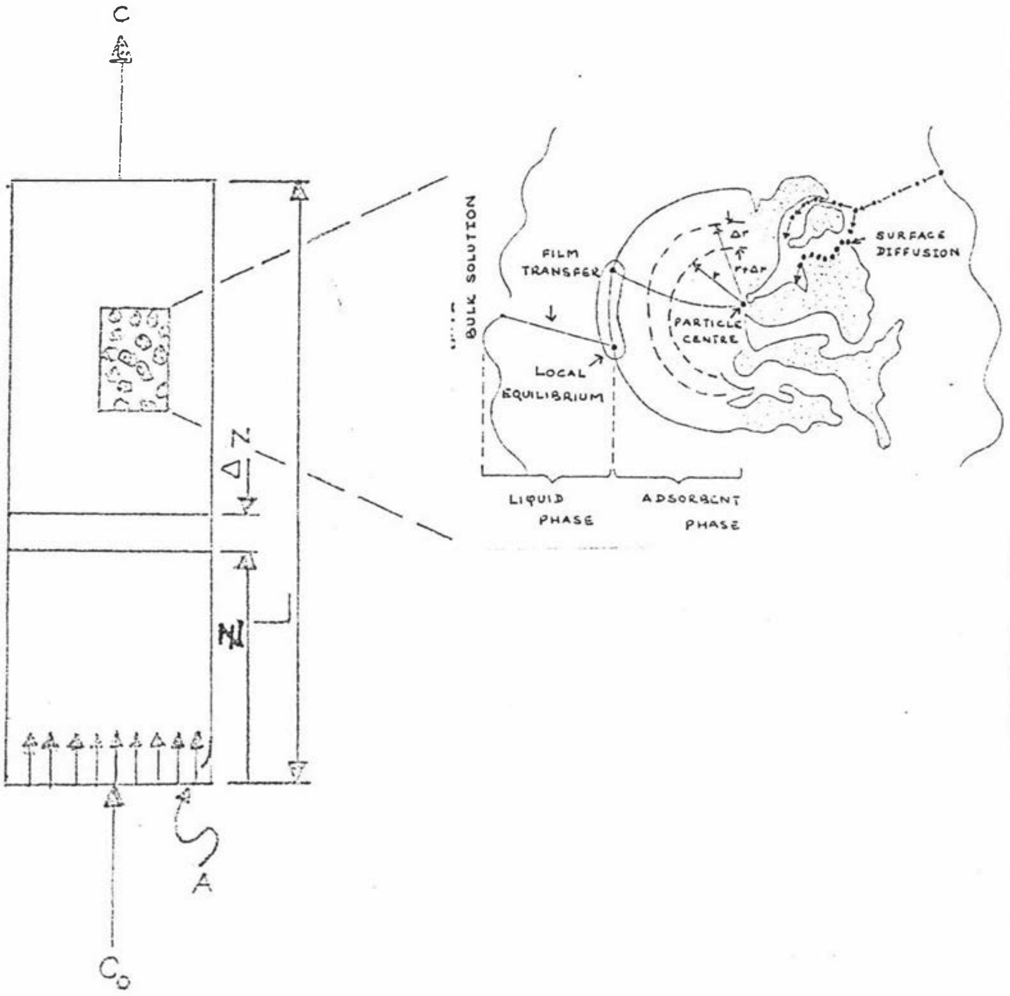


Figure 6.2: Mass transport mechanisms in a fixed bed

Given the mechanisms and the assumptions in the model developed, the mathematical descriptions are derived and shown in Appendix 4. The intraparticle material balance is expressed as:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}[r^2\frac{\partial q}{\partial r}] \tag{6.1}$$

where, r = radial coordinate, cm; q = solid phase concentration, mg/g; D_s = surface diffusion coefficient, cm^2/s; and t = time.

The liquid phase material balance, in a fixed bed with longitudinal dispersion, is expressed as:

$$\frac{\partial C}{\partial t} = D_L\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial Z} - \frac{3(1-\epsilon)}{\epsilon R}k_l(C - C_s) \tag{6.2}$$

where, C = liquid phase concentration, mg/l; C_s = concentration at interface, mg/l; D_L = dispersion coefficient, cm^2/s; z = longitudinal coordinate, cm; k_l = film-mass transfer coefficient, cm/s; R = particle radius, cm; v = interstitial velocity, cm/s; and ε = bed void fraction. The above equation accounts for accumulation in the liquid phase, axial dispersion, advective flow and transport from the liquid to the solid phase by film-mass transfer.

Local instantaneous equilibrium adjacent to the exterior surface of the soil particle was assumed, i.e., the diffusion fluxes are not nearly as fast as the rate of adsorption. A Freundlich isotherm was used to describe the adsorption isotherm behaviour of all solutes in this study, which is expressed as:

$$q_s = KC_s^{\frac{1}{n}} \tag{2.2}$$

where, q_s = solid-phase concentration at liquid-solid interface, mg/g; and K and 1/n are Freundlich isotherm constants.

The pertinent initial and boundary conditions for the particle are expressed as:

$$t = 0, \qquad q = C = 0 \tag{6.3}$$

$$r = 0, \qquad \frac{\partial q}{\partial r} = 0 \tag{6.4}$$

$$r = R, \qquad \rho_p A D_s \frac{\partial q}{\partial r} = k_f A(C - C_s) \tag{6.5}$$

Two different boundary conditions can be imposed at the inlet of the column. The first type is the constant concentration boundary condition:

$$C(0,t) = C_0 \tag{6.6}$$

The second type is the constant flux boundary condition:

$$z = 0, \qquad D_L \frac{\partial C}{\partial z} = -v(C_0 - C) \tag{6.7}$$

In all column experiments, acid washed sand 0.2 cm thick was used at both ends of the column to support the soil. The validity of the boundary condition, Equation 6.7, was examined using an analytical solution proposed by Brenner (1962) at the exit concentration of the acid washed sand-soil interface. The calculations showed that, by using this boundary condition, there was no change in concentration at the exit of the interface. Therefore, the Equation 6.7 is valid for the experimental conditions used.

At the exit boundary of a finite column, the zero concentration gradient condition is applicable (Van Genuchten, 1981),

$$z = L, \qquad \frac{\partial C}{\partial z} = 0 \tag{6.8}$$

This equation is based on the assumption that the concentration is continuous at $z = L$ (Dankwerts, 1953). Brenner (1962) solution was also applied at the exit concentration of the acid washed sand-soil interface at the top end of the column. The results revealed that there was no change in liquid concentration at the exit of the interface.

Using the following dimensionless variables and parameters,

$$Y = \frac{C}{C_0}; \quad u = \frac{q}{q_0}\ ; \ Y_s = \frac{C_s}{C_0}; \quad u_s = \frac{q_s}{q_0} \tag{6.9}$$

$$X = \frac{r}{R}\ ; \quad \xi = \frac{z}{L}\ ; \quad \tau = \frac{D_s t}{R^2} \tag{6.10}$$

$$\psi = \frac{k_f R}{D_s}\ ; \quad \sigma = \frac{\rho_p q_0}{C_0} \tag{6.11}$$

$$Pe = \frac{vL}{D_L}\ ; \quad \omega = \frac{vR^2}{LD_s} \tag{6.12}$$

The definitions of the above mass transport parameters are given in Table 6.2. By introducing the above parameters, Equations 6.1-6.2 become:

$$\frac{\partial u}{\partial \tau} = \frac{1}{X^2}\frac{\partial}{\partial X}[X^2\frac{\partial u}{\partial X}] \tag{6.13}$$

$$\frac{\partial Y}{\partial \tau} = \frac{1}{Pe}\omega\frac{\partial^2 Y}{\partial \xi^2} - \omega\frac{\partial Y}{\partial \xi} - \frac{3(1 - \epsilon)}{\epsilon}\psi[Y - Y_s] \tag{6.14}$$

The dimensionless initial and boundary conditions are expressed as:

$$\tau = 0\ , u = Y = 0 \tag{6.15}$$

$$X = 0\ , \quad \frac{\partial u}{\partial X} = 0 \tag{6.16}$$

$$X = 1\ , \quad \frac{\partial u}{\partial X} = \frac{\psi}{\sigma}(Y - Y_s) \tag{6.17}$$

$$\xi = 0\ , \quad \frac{\partial Y}{\partial \xi} = -Pe(1 - Y) \tag{6.18}$$

$$\xi = 1\,, \qquad \frac{\partial Y}{\partial \xi} = 0 \tag{6.19}$$

$$Y_s = u_s^{1/n} \tag{6.20}$$

A numerical scheme, employing orthogonal collocation, was developed to solve the HSDM equations (Bhaskar and Bhamidimarri, 1992). In this application, the spatial derivative operators are replaced by matrices at specified collocation points representing the roots of a set of trial orthogonal polynomials selected to approximate the solution of the spatial derivatives. This is accomplished by adjusting the coefficients of the trial polynomials until the residual, resulting from substitution of the partial differential equations (PDEs) of interest, is forced to zero at the collocation points, thereby transforming the PDEs into ordinary differential equations (ODEs). The ODEs are then further transformed into sets of algebraic equations and solved by the Runge-Kutta method. The nonlinearity was solved using the Newton-Raphson technique.

Table 6.2 Mass transport dimensionless groups-definitions

Dimensionless parameter	Equation	Definition
Pe	$\nu L/D_L$	Rate of transport by convection / Rate of transport by axial dispersion
ψ	$k_f R/D_s$	Rate of transport by film transfer / Rate of transport by surface diffusion
ω	$\nu R^2/LD_s$	Rate of transport by convection / Rate of transport by surface diffusion
σ	$\rho_p q_0/C_0$	Ratio of adsorbed phase concentration in equilibrium with C_0 to that of initial concentration

6.3.1 Model parameter determination

The parameter values of K, 1/n, k_l, D_s, D_L, ε and R are required for the HSDM solution, and were arranged into four dimensionless groups, as shown in Equations 6.11 and 6.12. The dimensionless group, σ, represents the equilibrium relationship, whereas, Pe, ψ and ω are dynamic mass transfer relationships. The isotherm parameters, K and 1/n obtained previously, for various solutes, were used in column data predictions. Film-mass transfer coefficient and dispersion coefficient are estimated using correlations, as discussed below.

Many correlations (Williamson *et al.*, 1963; Wilson and Geankoplis, 1966; Lightfoot *et al.*, 1982) are proposed in the literature to determine the film-mass transfer coefficient in fixed bed systems for a range of Reynolds and Schmidt numbers. For the range of velocities and particle size used, the Wilson and Geankoplis (1966) relation is best suited to evaluate the film-mass transfer coefficient. This correlation is expressed as:

$$k_l = 1.09v(Re\ Sc)^{-2/3} \tag{6.21}$$

where, Re is the Reynolds number ($\rho_l 2Rv/\mu_l$) and Sc is the Schmidt number ($\mu_l/\rho_l D_m$). This correlation is valid for the range of Re: 0.00016 to 55; Sc: 950 to 70,600; and for ε: 0.35 to 0.75 (Wilson and Geankoplis, 1966). Crittenden *et al.* (1986) and Hutzler *et al.* (1986) also used this relationship to determine k_l for fixed bed predictions.

The Schmidt number in Equation 6.21 contains the parameter D_m, which is the molecular diffusivity of solute in water, estimated using the relationship given by Hayduk and Laudie (1974) for dilute aqueous solutions, expressed as:

$$D_m = \frac{13.26*10^{-5}}{\mu_l^{1.14} V_a^{0.589}} \tag{6.22}$$

where, μ_l is the liquid viscosity and V_a is the molar volume of the solute. These authors report that the above correlation predicts the diffusion coefficient within 7% for a large number of solutes at various temperatures. The film-mass transfer coefficients for phenoxyacetic acids and chlorophenols were estimated using Equation 6.21 and are listed in Table 6.3. The surface diffusion coefficients obtained earlier are used directly to predict the model solution.

Table 6.3 Film-mass transfer coefficients in fixed beds

Solute	Interstitial velocity (cm/s)	$D_m x10^6$ (cm^2/s)	$k_l x10^3$ (cm/s)
2,4-D	0.026	5.72	1.06
	0.052	5.72	1.35
2,4,5-T	0.052	5.35	1.29
MCPA	0.052	5.87	1.37
2,4-DCP	0.052	6.67	1.49
2,4,5-TCP	0.052	6.20	1.42
PCOC	0.026	6.63	1.18
	0.052	6.63	1.48

The dispersion coefficient, D_L, was estimated using a relationship proposed by Fried (1975):

$$\frac{D_L}{D_m} = 0.67 + 0.5(ReSc)^{1.2} \qquad (6.23)$$

The constant 0.67 represents the inverse of the tortuosity of the axial diffusion path length which equals 1.49. This value was determined by assuming the average path to be 45° from the axial direction (Crittenden *et al.*, 1986). The values of D_L, estimated from the above correlation for various solutes, are listed in Table 6.4. The D_L value, determined from this relationship, was used to calculate the Peclet number (Pe) in the HSDM.

The particle diameter, d_p, required for the model solution, was determined from sieve analysis (section 3.1), while column porosity (ε) was measured using the procedure of Hillel (1982), (Table 6.1).

Table 6.4 Input parameters for single component adsorption model solution.

Solute	C_0 (mg/l)	ν (cm/s)	$D_L x 10^3$ (cm^2/s)	ω	ψ	σ	Pe
2,4-D	99.02	0.026	1.05	2.30	84.28	16.81	475
	99.60	0.052	2.40	4.57	107.14	16.79	416
	398.40	0.052	2.40	4.57	107.14	11.87	416
2,4,5-T	99.58	0.052	2.43	6.73	150.00	24.12	410
	399.75	0.052	2.43	6.73	150.00	21.02	410
MCPA	99.30	0.052	2.39	6.68	158.85	19.95	417
	402.47	0.052	2.39	6.68	158.85	13.48	417
2,4-DCP	100	0.052	2.32	3.96	102.26	9.36	430
	394.74	0.052	2.32	3.99	102.26	9.36	430
2,4,5-TCP	100	0.052	2.36	5.16	126.79	13.86	423
	400	0.052	2.36	5.19	126.79	9.94	423
PCOC	99.08	0.026	1.02	2.76	112.74	11.69	489
	100	0.052	2.33	5.53	141.40	11.68	428
	401.33	0.052	2.33	5.53	141.40	10.59	428

Table 6.5 Input parameters for single component desorption model solution.

Solute	v (cm/s)	q_{max} (mg/g)	K_{des}	$1/n_{des}$	ω	ψ	σ	Pe
2,4-D	0.026	0.626	0.174	0.281	2.60	95.20	16.96	475
	0.052	0.582	0.156	0.295	5.17	121.25	17.37	416
	0.052	1.427	0.604	0.151	5.17	121.25	12.64	416
2,4,5-T	0.052	0.879	0.202	0.324	6.38	153.57	24.37	410
	0.052	2.979	1.322	0.138	6.38	153.57	21.45	410
MCPA	0.052	0.724	0.172	0.316	6.93	164.40	20.16	417
	0.052	2.258	0.777	0.174	6.93	164.40	12.98	417
2,4-DCP	0.052	0.343	0.103	0.262	4.50	115.21	9.26	430
	0.052	0.964	0.052	0.552	4.48	115.21	9.34	430
2,4,5-TCP	0.052	0.498	0.251	0.153	5.23	128.31	14.37	423
	0.052	1.198	0.139	0.379	5.26	128.31	10.79	423
PCOC	0.026	0.434	0.098	0.325	2.65	114.93	11.81	489
	0.052	0.382	0.093	0.320	5.30	144.15	11.49	428
	0.052	0.985	0.084	0.390	5.30	144.15	10.51	428

6.3.2 Effect of concentration

A total of twelve experiments, using phenoxyacetic acids and chlorophenols, were carried out at two initial concentrations, approximately 100 and 400 mg/l, with an interstitial velocity of 0.052 cm/s. Column adsorption capacity (q_{max}) measured from the area above the breakthrough curve for all the solutes, and those estimated from the adsorption isotherm are compared in Table 6.6. The results indicate that adsorption capacities observed in equilibrium experiments were higher compared to the column adsorption capacities. The reason for the difference is, in batch studies, where high water to soil ratios allow uniform mixing and adequate soil dispersion, shorter contact time periods are required for equilibration than under flow conditions (Pavlostathis and Jaglal, 1991). The area under the elution curves was calculated to determine the mass of compound desorbed from the soil column. Solute recovery percentages, summarized in Table 6.6, show that adsorption is essentially reversible. The recovery was calculated based on the mass of solute desorbed from the column when the experiment was terminated.

In section 4.3.4 (Chapter 4) the recoveries of phenoxyacetic acids and chlorophenols were in the range of 28-53%. However, in column experiments the elution of all solutes was nearly complete. The reasons for this discrepancy could be explained in terms of solute uptake. Comparing the uptakes in batch and column experiments for 2,4-D reveal that in batch equilibrium experiments 64.9 mg (10 g of soil) was adsorbed compared to 146.2 mg (252 g of soil) in column experiments. The reasons for the low uptake in column experiments is due to hydrodynamic conditions prevailing in the column. In batch equilibrium experiments, each time 20 ml of supernatant was removed and replaced with equal volume of solute free water and reqeuilibrated for 2 hours to achieve desorption, however, in column experiments fresh water was pumped in the column at 1 l/h flow rate with a contact time of 12 min. In column studies, the concentration gradient was higher compared to batch experiments resulting in complete recovery of the solute. However, the observed discrepancy could be explained completely with the above reasons.

Table 6.6 Comparison of equilibrium and column adsorption capacities for phenoxyacetic acids and chlorophenols

Solute	C_0 (mg/l)	q_{max} equilibrium (mg/g)	$q_{max,ads}$ column (mg/g)	$q_{max, des}$ (mg/g)	% recovery
2,4-D	99.60	0.65	0.58	0.56	96.5
	398.40	1.83	1.43	1.38	96.5
2,4,5-T	99.58	0.93	0.88	0.85	96.6
	395.75	3.23	2.98	2.84	95.3
MCPA	99.30	0.77	0.72	0.70	97.2
	402.47	2.08	2.06	2.00	97.1
2,4-DCP	100	0.36	0.34	0.33	97.1
	394.74	1.44	0.96	0.94	97.9
2,4,5-TCP	100	0.53	0.50	0.49	98.0
	400	1.53	1.20	1.18	98.3
PCOC	100	0.45	0.38	0.37	97.4
	401.33	1.63	0.99	0.98	98.9

Elution experiments were conducted immediately after the adsorption runs, as a result, the contact times are short for the solutes to diffuse into the internal adsorption sites and this could be a reason for the observed reversibility of the freshly adsorbed compounds in the soil. In addition, the range of velocities used in the experiments are higher compared to that observed in field conditions. In field conditions, the velocities are low, hence diffusion may control the rate of transfer of compounds from larger pores to micropores, whereas the solute transport is controlled by convection, the greater solid/liquid contact time achieved in the filed would result in a system closer to equilibrium (Brusseau and Rao, 1990). However, the time frame and conditions usually encountered in the field are difficult to simulate in the laboratory (Pavlostathis and Jaglal, 1991). This data indicate that, with regard to overall breakthrough and elution from volcanic soil, the chemicals can be ranked as 2,4-D > MCPA > 2,4,5-T for phenoxyacetic acids, and 2,4-DCP > PCOC > 2,4,5-TCP for chlorophenols, respectively.

The breakthrough and elution for phenoxyacetic acids and chlorophenols are presented in Figures 6.3-6.8, respectively, and compare the experimental results to model simulations for the two concentrations examined. The HSDM solution for breakthrough and elution curves was obtained using the parameters given in Table 6.4 and 6.5, respectively. The model output was obtained as relative concentration *versus* dimensionless time. The experimental data from each column run were also converted to relative concentration *versus* dimensionless time for comparison. To obtain the elution model simulation, the amount of solute adsorbed (q_{max}) in the column was used to determine the Freundlich parameters, K_{des} and $1/n_{des}$, based on the procedure described in section 4.5.4. The nondimensional parameter, σ, was calculated using the relation, $\rho_p q_{max}/C_e$, where, C_e is the effluent concentration in equilibrium with q_{max}. The values of ω and ψ, in Table 6.3, were evaluated based on desorption parameters, while the same Peclet number was used. The elution data of phenoxyacetic acids and chlorophenols could not be predicted accurately with the HSDM as shown in Figures 6.3-6.8. In elution model prediction, K_{des} and $1/n_{des}$ were estimated using relationships (Chapter 4) and k_l was assumed to be the same as in adsorption, in addition, the particle diameter was different for column experiments (300 μm) compared to batch studies (350 μm), therefore, D_s is different. All these factors may have caused the observed deviation.

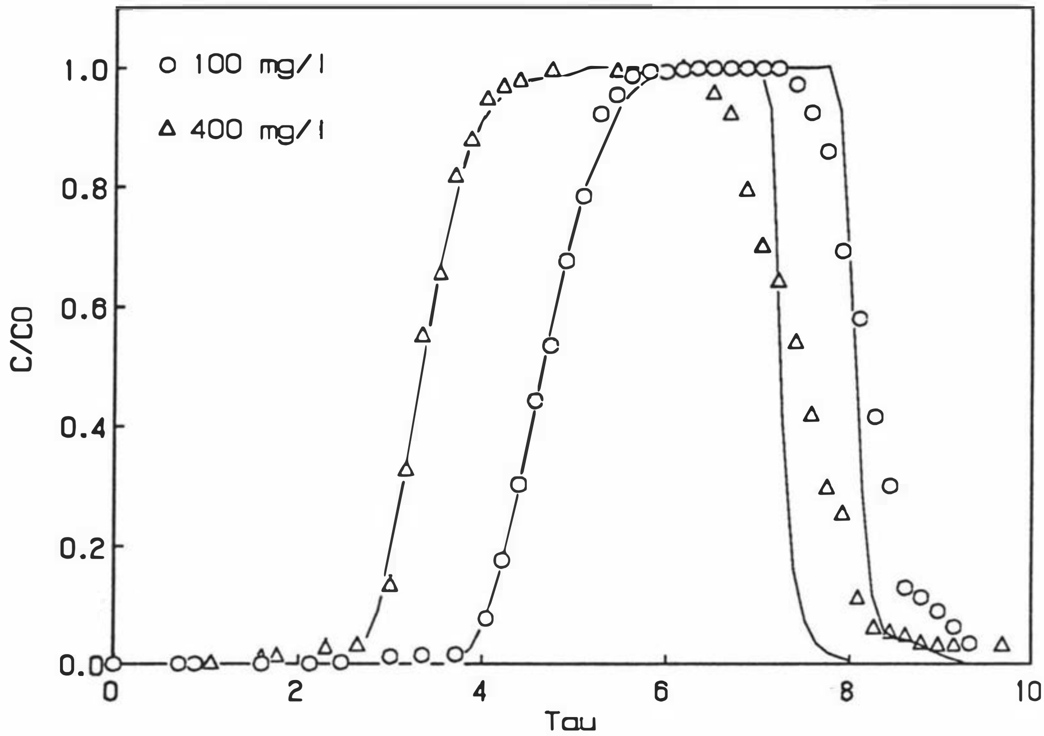


Figure 6.3: Experimental and predicted breakthrough and elution curves for 2,4-D at 100 and 400 mg/l of initial concentration.

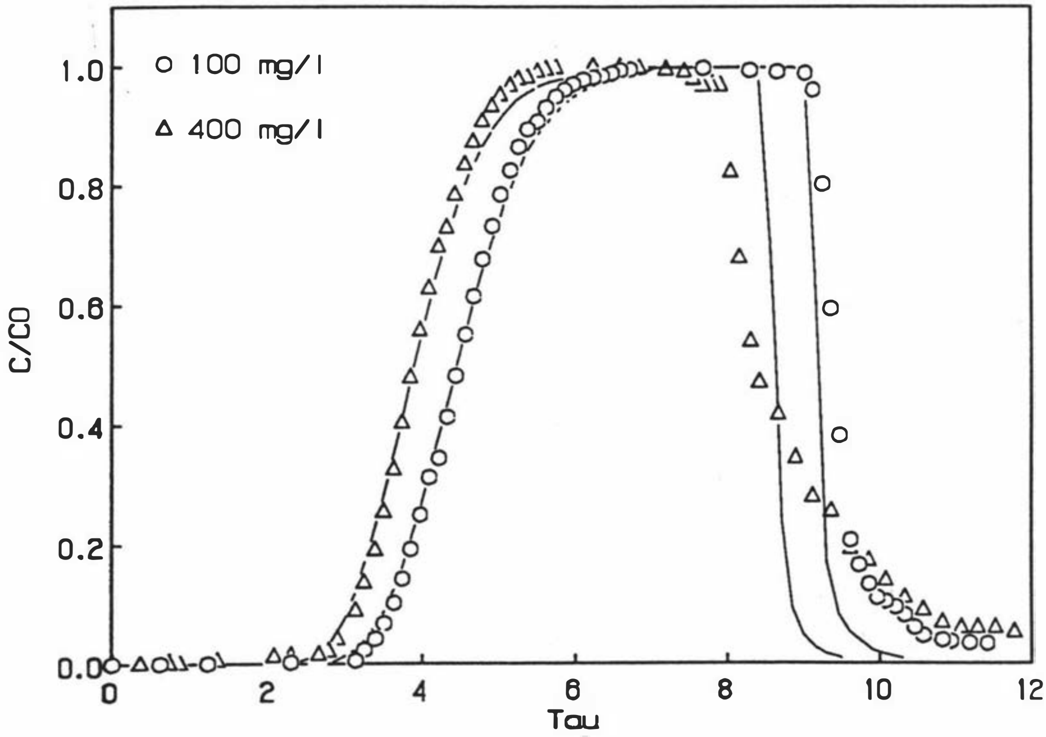


Figure 6.4: Experimental and predicted breakthrough and elution curves for 2,4,5-T at 100 and 400 mg/l of initial concentration.

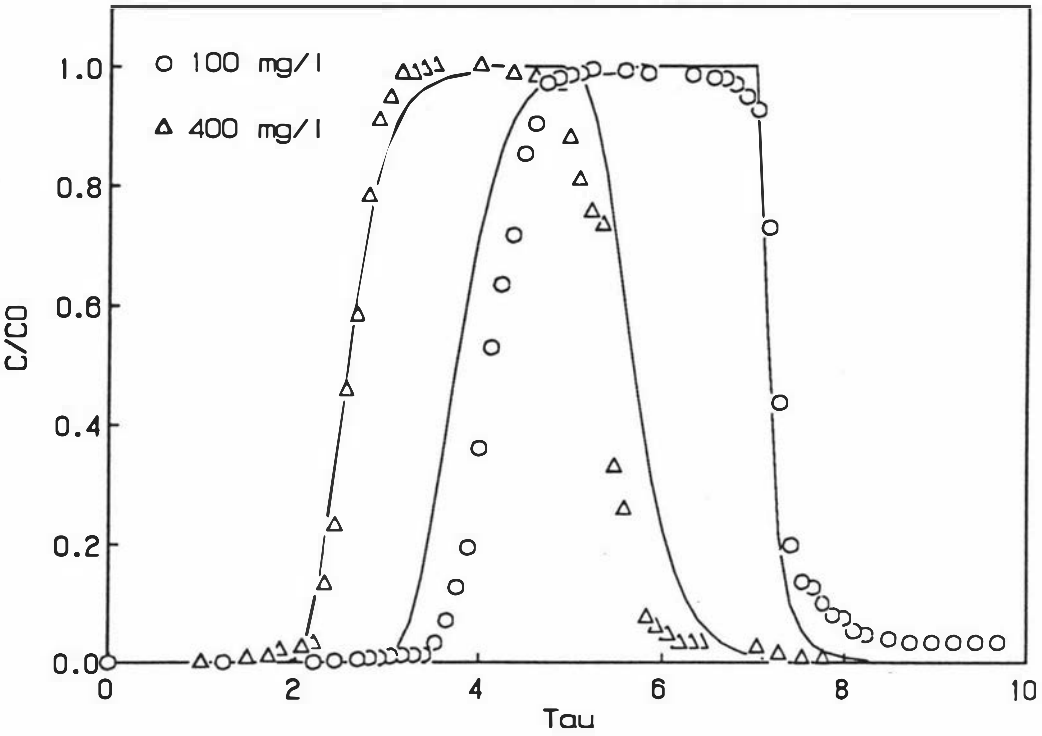


Figure 6.5: Experimental and predicted breakthrough and elution curves for MCPA at 100 and 400 mg/l of initial concentration.

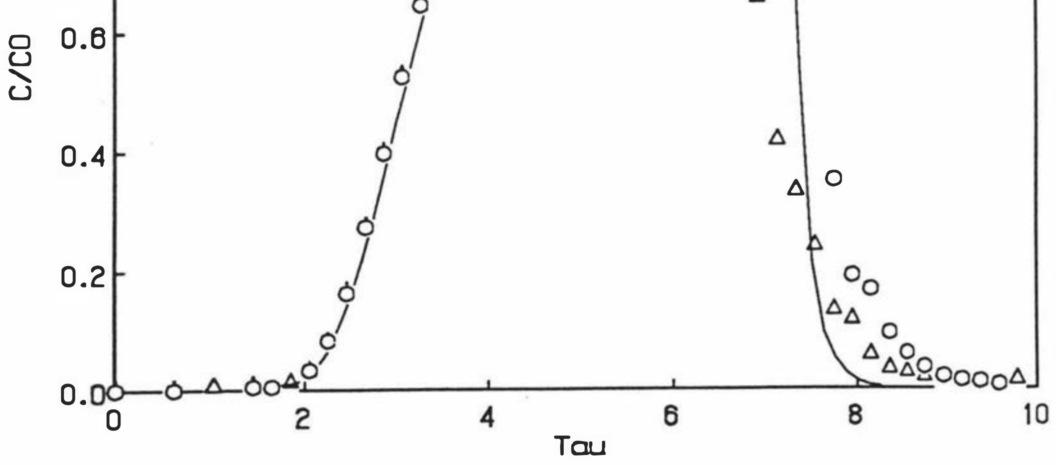


Figure 6.6: Experimental and predicted breakthrough and elution curves for 2,4-DCP at 100 and 400 mg/l of initial concentration.

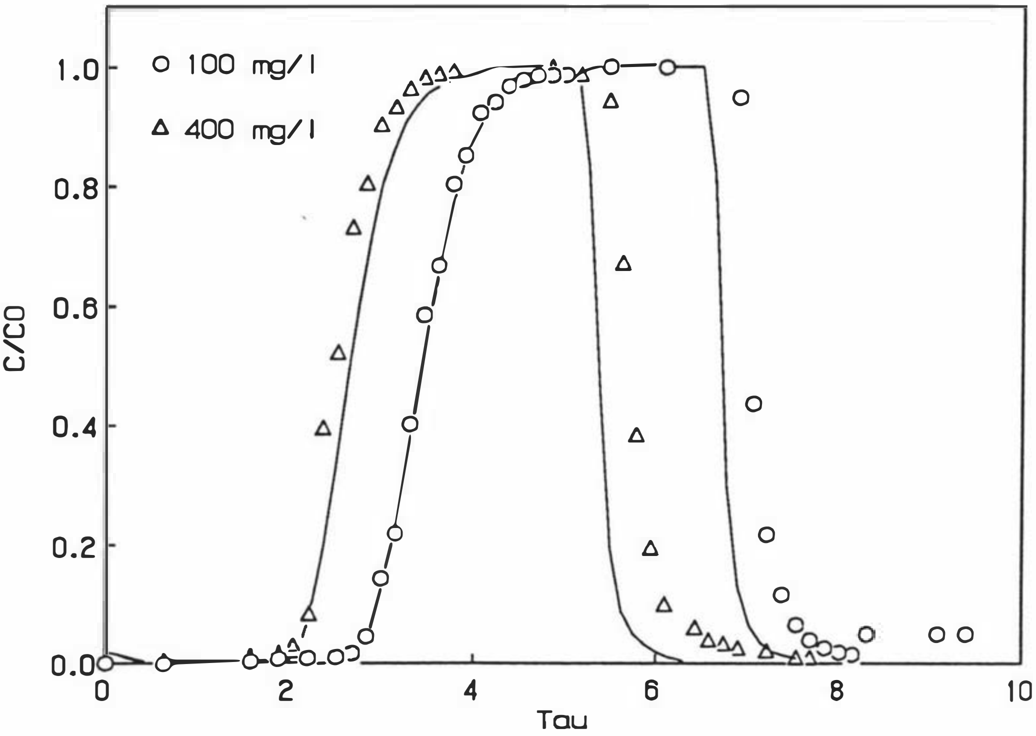


Figure 6.7: Experimental and predicted breakthrough and elution curves for 2,4,5-TCP at 100 and 400 mg/l of initial concentration.

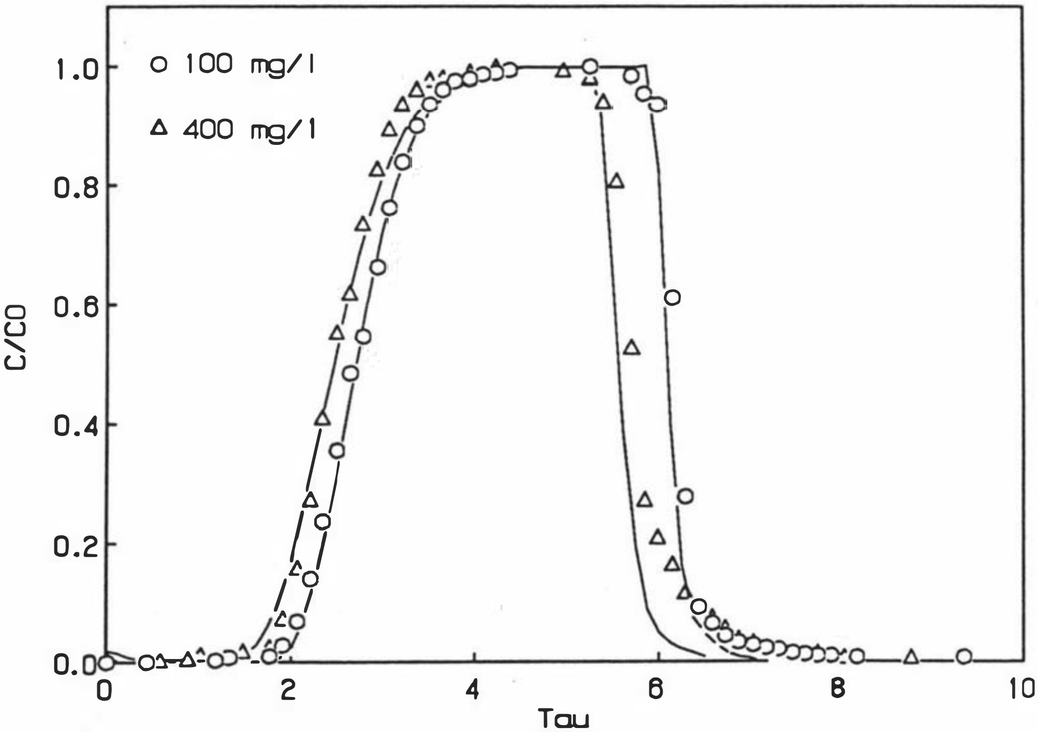


Figure 6.8: Experimental and predicted breakthrough and elution curves for PCOC at 100 and 400 mg/l of initial concentration.

Experimental data for all solutes showed clear evidence of early arrival, asymmetry and tailing of breakthrough and elution at higher concentrations compared to lower ones. This earlier breakthrough time at higher concentration is due to faster movement of the solute in the column. The retardation term (R_f), is a quantitative index of the solute movement in soil; as the input concentration increased from 100 to 400 mg/l, the value of R_f reduced from 1.03 to 1.01 for 2,4,-D, indicating that at higher concentration retardation is lower, therefore, the breakthrough will be faster. Similar results were observed for 2,4,5-T, MCPA, 2,4,5-TCP and PCOC breakthrough and elution curves. However, 2,4-DCP movement was found to be independent of concentration. Rao and Davidson (1979) report similar results for 2,4-D movement in Webster, Cecil and Eustis soil columns for various initial concentrations, implying that the soil sorption capacity, i.e., adsorption sites, saturate at higher concentration, faster, which results in earlier breakthrough from the column.

The value of 1/n can have a significant impact on solute transport (Brusseau and Rao, 1990). For the linear isotherm, 2,4-DCP, K is independent of concentration, R_f, therefore, remains constant. However, the remaining compounds show $1/n < 1$; hence, the adsorption capacity decreases as concentration increases due to the limited number of adsorption sites. Therefore, at higher concentration, retardation will be lower, the solute breakthrough, faster (Brusseau and Rao, 1989). Such an effect was observed for all solutes examined. On the other hand, all solutes exhibited $1/n < 1$ for desorption, which implies that it would be more difficult, and takes longer, to clean up the contaminated soil by desorption.

Isotherm nonlinearity also influences the shape of the solute breakthrough curve (Brusseau and Rao, 1989). For $1/n<1$, nonlinearity sharpens the breakthrough curve and spreads the elution front of the curve. At initial higher solute concentrations, for a breakthrough front, solute uptake decreases as the soil surface gets saturated faster therefore, the solute moves faster in the column resulting in an early appearance (Rao and Davidson, 1979; Brusseau and Rao, 1989). On the other hand, for elution, solute concentration in the liquid phase decreases continuously, consequently, additional sites are available for solute to adsorb causing in slow movement in the column. This results in spreading or tailing of the solute at low concentrations. The adsorption equilibrium has a greater impact on the transport of solutes than any of the mass transport parameters, because the rate parameters for phenoxyacetic acids and chlorophenols do not vary significantly, and the observed differences in transport is solely due to the soil column capacity (Hutzler *et al.*, 1986).

The influence of film-mass transfer and surface diffusion can be evaluated using the Biot number (B), defined as the ratio of the film-mass transfer rate to the intraparticle diffusion transfer rate. As these two resistances act in series, the slower one will dominate the solute-transfer processes. In general, film-mass transfer resistance becomes more important as B decreases below unity (Hatfield *et al.*, 1993). Biot numbers, for fixed bed uniform spherical soil particles, are calculated using the Equation 5.8. Biot numbers for 2,4-D and PCOC were estimated using the equation to ascertain if film-mass transfer was rate controlling. Calculated Biot numbers for 2,4-D ranged from 2.3 to 6.4, and from 3.4 to 12.2 for PCOC at two concentrations. These numbers suggest film-mass transfer 0.15 to 0.4 times faster than surface diffusion for 2,4-D, and 0.08 to 0.30 times faster for PCOC. Hence film-mass transfer is not rate controlling; however, changes in the thickness of the stagnant water film can be important and are expected to be a function of fluid velocity. This finding is consistent with the assertion by Roberts *et al.* (1987) that the contribution of film-mass transfer is usually negligible compared to those of diffusion and/or dispersion. Crittenden *et al.* (1986) report that for 1/n between 0.7 and 1.0, surface diffusion and pore diffusion mechanisms predict identical breakthrough and elution of solutes.

In HSDM, a local instantaneous equilibrium was assumed. In such a situation, the breakthrough and elution curves obtained from the experiment using packed columns should be symmetrical. However, the experimental data exhibited asymmetrical curves, with earlier breakthrough, increased time to reach breakthrough (i.e., breakthrough front-tailing), and increased time for complete desorption (i.e., elution-front tailing). The reasons for a such a behaviour could be due to nonlinearity ($1/n < 1$) resulting in an increasing adsorption capacity as concentration decreases with time (Brusseau and Rao, 1989); due to the existence of a fraction of solute that is resistant to desorption (Connaughton *et al.*, 1993); due to diffusive mass-transfer resistances causing a rate controlled approach to equilibrium at low concentrations (Kan *et al.,* 1994); and intraparticle diffusion, where diffusion of solute into the sorbent matrix causes rate-limited sorption (Miller and Pedit, 1992).

In addition to the above factors, the observed tailing at low concentrations, could be attributed to sorption; the sorption of neutral phenoxyacetic acids and chlorophenols viewed to involve van der Waal and hydrogen-bonding type interactions between the soil and solute. However, the sorption of these compounds may also involve specific sorbate-sorbent interactions, such as charge transfer between the solute and functional groups of the organic matter components of the soil as well as van der Waals interactions (Brusseau and Rao, 1991). In the sorption reaction, where site specific sorption occurs onto soil surface, the sites include specific, molecular scale, reaction sites; sites of differing degrees of accessability, sites of different sorbent type, and sites of different sorption mechanisms. Hence, the slow desorption or tailing can be associated with specific solute-soil interactions and diffusive mass transfer.

In section 4.3.3 (Chapter 4), the energies of adsorption for phenoxyacetic acids and chlorophenols were evaluated; the results show that the energy of adsorption is in the range of 4.08-4.72 kcal/mole for phenoxies and 4.30-7.30 kcal/mole for chlorophenols. According to Morrill *et al.* (1982), the higher the adsorption energy the stronger the bonding, therefore, difficult to desorb the solute from the soil. Comparing the relative breakthrough for 2,4,5-T and MCPA in terms of energies of adsorption, it is apparent that MCPA breakthroughs earlier in the column than 2,4,5-T which is consistent with the values obtained in Table 4.3. Similarly, for 2,4-DCP and PCOC based on energy of adsorption it can be concluded that 2,4-DCP (6.63 kcal/mole) breakthroughs earlier compared to PCOC (7.30 kcal/mole). Based on the above results, it is obvious that the breakthrough times are dependent on the adsorption energies of the respective solutes.

6.3.3 Effect of velocity

The interstitial velocity is reported to be an important factor in the movement of solutes (Gaber *et al.,* 1992). The movement of 2,4-D and PCOC were studied at two interstitial velocities, 0.026 cm/s and 0.052 cm/s. The experimental data and HSDM predictions are shown in Figure 6.9 and 6.10 for 2,4-D and PCOC, respectively. The results indicate that the breakthrough and elution curves appear earlier at higher velocity, 0.052 cm/s compared to a lower velocity, 0.026 cm/s. In addition, the data showed increased asymmetry and significant tailing; also, the breakthrough and elution times were shorter at higher velocity, as demonstrated in Figure 6.9. A shift in the breakthrough curve with an increase in velocity was also observed by several other researchers (Rao *et al.*, 1980; Nkedi-Kizza *et al.,* 1982; Gaber *et al.,* 1992). Average 2,4-D and PCOC recoveries were 97 and 99% for two flow rates, respectively, indicating the adsorption and desorption processes are reversible. The dispersion coefficients for 2,4-D and PCOC ranged between 1×10^{-3} and 2.4×10^{-3} cm^2/s. Increases in dispersivity, with increasing velocity, have been observed in other transport studies (Gaber *et al.,* 1992).

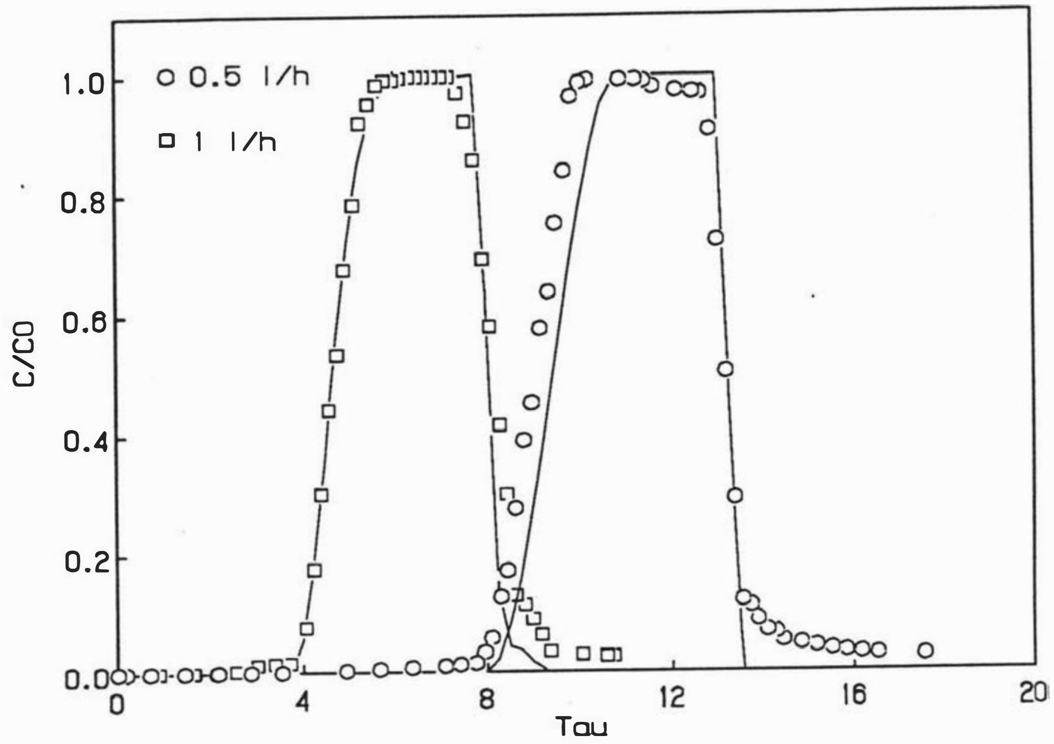


Figure 6.9: Experimental and predicted breakthrough and elution curves for 2,4-D at interstitial velocities of 0.026 and 0.052 cm/s.

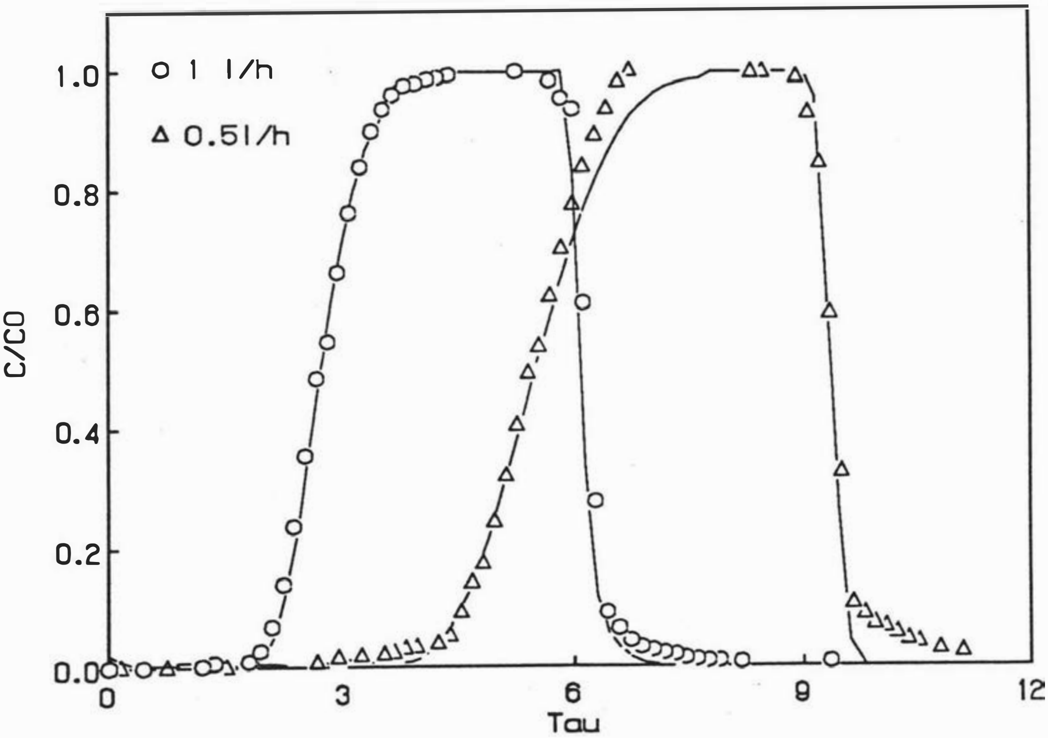


Figure 6.10: Experimental and predicted breakthrough and elution curves for PCOC at interstitial velocities of 0.026 and 0.052 cm/s.

The breakthrough and elution times for 2,4-D were 290 min and 210 min at lower velocity, compared with values of 165 min and 140 min at higher velocity. The shorter times at higher velocities are due to insufficient contact time (6 min) in the column to allow solute diffusion to all adsorbing sites. On the other hand, at low velocities, the contact time available for the solute was higher (12 min), and as a result, a greater portion of the adsorbing sites were reached by the solute resulting in longer breakthrough and elution times.

The transport experiments demonstrate that increasing velocities resulted in a left-hand displacement of 2,4-D and PCOC breakthrough curves on the time axis. Van Genuchten *et al.* (1974) report that changes in velocities affect the slope of the front portions of the breakthrough curves but should not displace the BTCs, provided equilibrium conditions exists. However, the results indicate that nonequilibrium existed during the transport of 2,4-D and PCOC at higher velocities, since the symmetry and position of the curves were altered.

The criteria established by Bahr and Rubin (1987) identifies the transport conditions that result in deviations from the equilibrium behaviour. Although, the kinetic sorption experiments indicate that equilibrium was achieved relatively rapidly (30 min), equilibrium conditions were not achieved in column experiments at higher velocities. Bahr (1990) established scaling relationships between batch equilibration times and transport times required to approach equilibrium, and reports that the equilibrium applicability requires a travel time (travel distance/velocity) that is twice great as the batch equilibration time. Based on experimental conditions, the travel times for the two velocities were 6 min and 12 min; only the slowest velocity produced a travel time (i.e., 12 min) that was approximately twice as great as the equilibrium time. Hence, equilibrium conditions were established only at lower velocities.

Van Genuchten *et al.* (1974) evaluated three kinetic transport models and found them to be inadequate in predicting picloram transport at a velocity of 145 cm/day. They concluded that, at higher velocities, less picloram was reaching the adsorption sites inside the aggregates, and that the residence time was too short to allow diffusion to all adsorbing sites. Therefore, only a fraction of the soil's adsorption sites were in direct contact with the displacing solution.

Since the symmetry and position of the breakthrough curves is largely influenced by the velocity, the mechanism responsible for this behaviour is probably related to the sorption processes. Nkedi-Kizza *et al.* (1989) conducted transport experiments with atrazine and diuron and found evidence of nonequilibrium transport. By conducting transport experiments with soils varying in organic matter, they provided strong evidence for concentration dependent on intraparticle diffusion suggesting that this mechanism was primarily responsible for the observed nonequilibrium transport. The same can also be true for 2,4-D and PCOC transport. Brusseau *et al.* (1989) separated the processes responsible for nonequilibrium transport into two general classes: physical nonequilibrium and sorption-related nonequilibrium. Physical nonequilibrium results from the existence of mobile and immobile domains within the porous medium. Sorption-related nonequilibrium arises from intraparticle diffusion and sorption to specific sites of the adsorbent. The BTCs observed were not symmetrical and can be attributed to a sorption-related nonequilibrium; tailing is typical for BTCs obtained under nonequilibrium conditions (Brusseau and Rao, 1989). Thus, the observed behaviour at high velocity could be attributed to the nonequilibrium conditions prevailing in the soil column.

6.4 Bicomponent systems

This section presents the adsorption and desorption for three bicomponent mixtures in soil columns. The experiments were conducted at an initial concentration of 100 mg/l of each solute at a solution of pH 2, while the conditions under which the experiments were carried out are given in Table 6.7.

There are only a few studies (Crittenden, 1976; Crittenden and Weber, 1978; Merk *et al.*, 1980; Kenneth *et al.*, 1992) on the breakthrough behaviour of solutes in bicomponent systems. Virtually all of them used activated carbon as the adsorbent. Merk *et al.* (1980) used single component experimental parameters in combination with a bicomponent adsorption isotherm to predict the fixed bed breakthrough data of *p*-nitrophenol-phenol and *p*-nitrophenol-*p*-chlorophenol mixtures. They report that the surface diffusion model predicted a later breakthrough for the strongly adsorbed *p*-nitrophenol, an earlier one for the weakly adsorbed phenol. Crittenden (1976) reports similar deviations between the experimental breakthrough data and model predictions for the sorption of chlorophenols.

Recently, Kenneth *et al.* (1992) compared the breakthrough curves for phenol-*p*-chlorophenol onto XAD-4 resin, using a surface diffusion model, and a combined pore and surface diffusion model. Both models satisfactorily described the breakthrough curves, the authors reporting that the strongly adsorbed *p*-chlorophenol displaced the weakly adsorbed phenol in the column, and the solutes moving faster in the column compared to the single solute systems.

In all the above studies (Merk *et al*., 1980; Kenneth *et al*., 1992 and others), the single component model equations were extended to bicomponent systems to predict the breakthrough curves of each solute, with varying degrees of success. The results from the single component fixed bed runs from this study, indicate that the movement of phenoxyacetic acids and chlorophenols could be described using a homogeneous surface diffusion model. To predict transport in bicomponent mixtures, the same mechanisms observed earlier are incorporated by extending the HSDM equations to bicomponent mixtures.

6.4.1 Homogeneous surface diffusion model (HSDM)-Bicomponent system

The HSDM equations used for a single component system were extended to bicomponent systems. Mass balance equations are written for each component in the bicomponent mixture with the following assumptions:

- intraparticle transport of each component is due to surface diffusion mechanism and each component diffuses independently of the other;

- film-mass transfer resistance is between the liquid-solid interphase and is independent of the other component. The film-mass transfer coefficient is assumed to be the same as in single component fixed beds; and
- instantaneous equilibrium at the interface between the adsorbate and adsorbent. The competitive effects during the adsorption are accounted for using a bicomponent adsorption isotherm.

With the above assumptions, the governing mass balance equations for each component in a bicomponent system are expressed as:

Particle

$$\frac{\partial q_1}{\partial t} = \frac{D_{s,1}}{r^2}\frac{\partial}{\partial r}[r^2\frac{\partial q_1}{\partial r}] \tag{6.24}$$

$$\frac{\partial q_2}{\partial t} = \frac{D_{s,2}}{r^2}\frac{\partial}{\partial r}[r^2\frac{\partial q_2}{\partial r}] \tag{6.25}$$

The above equations account for the surface diffusion and accumulation in the soil particle for each component.

Fixed bed

$$\frac{\partial C_1}{\partial t} = D_{L,1}\frac{\partial^2 C_1}{\partial z^2} - v\frac{\partial C_1}{\partial Z} - \frac{3(1-\epsilon)}{\epsilon R}k_{l,1}(C_1 - C_{1,s}) \tag{6.26}$$

$$\frac{\partial C_2}{\partial t} = D_{L,2}\frac{\partial^2 C_2}{\partial z^2} - v\frac{\partial C_2}{\partial Z} - \frac{3(1-\epsilon)}{\epsilon R}k_{l,2}(C_2 - C_{2,s}) \tag{6.27}$$

where, $D_{L,1}$ and $D_{L,2}$ are the dispersion coefficients, for components 1 and 2, respectively.

The liquid-solid interface concentrations are related by the competitive Freundlich isotherms, Equations 4.11 and 4.12. The pertinent initial and boundary conditions for the particle and fixed bed are expressed as:

$$t = 0, \quad q_1 = q_2 = C_1 = C_2 = 0 \tag{6.28}$$

$$r = 0, \quad \frac{\partial q_1}{\partial r} = \frac{\partial q_2}{\partial r} = 0 \tag{6.29}$$

$$r = R, \quad \rho_p A D_{s,1}\frac{\partial q_1}{\partial r} = k_{l,1}(C_1 - C_{1,s}) \tag{6.30}$$

$$r = R, \quad \rho_p A D_{s,2}\frac{\partial q_2}{\partial r} = k_{l,2}(C_2 - C_{2,s}) \tag{6.31}$$

$$z = 0, \quad D_{L,1}\frac{\partial C_1}{\partial z} = -v(C_{1,0} - C_1) \tag{6.32}$$

$$z = 0, \quad D_{L,2}\frac{\partial C_2}{\partial z} = -v(C_{2,0} - C_2) \tag{6.33}$$

$$z = L, \quad \frac{\partial C_1}{\partial z} = \frac{\partial C_2}{\partial z} = 0 \tag{6.34}$$

Non-dimensional variables and parameters are expressed as:

$$X = \frac{r}{R}\ ; \quad \xi = \frac{z}{L}\ ; \quad \tau = \frac{D_{s,1}t}{R^2} \tag{6.36}$$

$$\psi = \frac{k_{l,1}R}{D_{s,1}}\ ; \ \sigma = \frac{\rho_p q_{1,0}}{C_{1,0}}; \tag{6.37}$$

$$Pe = \frac{vL}{D_{L,1}}\ ; \ \omega = \frac{vR^2}{LD_{s,1}} \tag{6.38}$$

Equations 6.24-6.34 become:

$$\frac{\partial u_1}{\partial \tau} = \frac{1}{X^2}\frac{\partial}{\partial X}[X^2\frac{\partial u_1}{\partial X}] \tag{6.39}$$

$$\frac{\partial u_2}{\partial \tau} = \frac{D_{s,2}}{D_{s,1}}\,\frac{1}{X^2}\frac{\partial}{\partial X}[X^2\frac{\partial u_2}{\partial X}] \tag{6.40}$$

$$\frac{\partial Y_1}{\partial \tau} = \frac{1}{Pe}\omega\frac{\partial^2 Y_1}{\partial \xi^2} - \omega\frac{\partial Y_1}{\partial \xi} - \frac{3(1-\epsilon)}{\epsilon}\psi[Y_1 - Y_{1,s}] \tag{6.41}$$

$$\begin{aligned}\frac{\partial Y_2}{\partial \tau} = \frac{D_{L,2}}{D_{L,1}}\,\frac{1}{Pe}\omega\frac{\partial^2 Y_2}{\partial \xi^2} - \omega\frac{\partial Y_2}{\partial \xi} - \\ \frac{k_{l,2}}{k_{l,1}}\,\frac{3(1-\epsilon)}{\epsilon}\psi[Y_2 - Y_{2,s}]\end{aligned} \tag{6.42}$$

$$\tau = 0\,,\ u_1 = u_2 = Y_1 = Y_2 = 0 \tag{6.43}$$

$$X = 0\,,\quad \frac{\partial u_1}{\partial X} = \frac{\partial u_2}{\partial X} = 0 \tag{6.44}$$

$$X = 1\,,\quad \frac{\partial u_1}{\partial X} = \frac{\psi}{\sigma}(Y_1 - Y_{1,s}) \tag{6.45}$$

$$X = 1\,,\quad \frac{\partial u_2}{\partial X} = \frac{k_{l,2}}{k_{l,1}}\frac{1}{(\frac{D_{s,2}}{D_{s,1}})}Fr\frac{\psi}{\sigma}(Y_2 - Y_{2,s}) \tag{6.46}$$

$$\xi = 0\,,\quad \frac{\partial Y_1}{\partial \xi} = -Pe(1 - Y_1) \tag{6.47}$$

$$\xi = 0\,,\quad \frac{\partial Y_2}{\partial \xi} = -\frac{D_{L,1}}{D_{L,2}}Pe(1 - Y_2) \tag{6.48}$$

$$\xi = 1\ , \quad \frac{\partial Y_1}{\partial \xi} = \frac{\partial Y_2}{\partial \xi} = 0 \qquad (6.49)$$

where, Fr is defined as $(q_{1,0}/C_{1,0})/(q_{2,0}/C_{2,0})$.

The model equations, together with the bicomponent Freundlich isotherm Equations 5.40 and 5.41, were solved using orthogonal collocation, Newton-Raphson and numerical integration techniques. The above Equations 5.40-5.41 and 6.35-6.49, were used to predict the elution of each component in a bicomponent mixture, using the same procedure followed for single solute systems.

6.4.2 Model parameters

The model parameters, $1/n_1$, $1/n_2$, ψ, ω, σ, $a_{i,j}$ and Pe are required for the bicomponent HSDM solution. The isotherm parameters obtained earlier were used directly, the other parameters were calculated based on equilibrium capacity of each component in a mixture, and surface diffusion coefficients obtained for each bicomponent mixture were used in model parameters. The film-mass transfer coefficient, k_l, was determined from Wilson and Geankoplis (1966) relationship. The competition coefficients, $a_{i,j}$, for each component at an initial concentration of 100 mg/l, were determined using the Equation 4.16, while the Peclet number was obtained using Equation 6.12. The competitive effects of the second component was evaluated in terms of the ratios of axial dispersion, $(D_{L,2}/D_{L,1})$; surface diffusion coefficient, $(D_{s,2}/D_{s,1})$; film-mass transfer coefficient, $(k_{l,2}/k_{l,1})$; and sorption equilibrium (Fr). The model parameters used for HSDM solution for breakthrough are given in Table 6.7. For elution, the relationships developed previously for bicomponent systems were assumed to hold, accordingly, and the parameters were evaluated based on the amount of each component adsorbed (q_{max}). The desorption competition coefficients, $(d_{i,j})$, were determined using Equation 4.18. The same k_l values determined for breakthrough were also used for elution model prediction. The values of the input data for the elution model solution are given in Table 6.7.

6.4.3 Results and discussion

Three experiments were conducted using, 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC bicomponent mixtures with an initial concentration of approximately 100 mg/l of each component at an interstitial velocity of 0.052 cm/s. The mass of compounds adsorbed and eluted from the soil column, and percent recovery are given in Table 6.8, showing that adsorption was essentially reversible. The breakthrough and elution for bicomponent mixtures indicate that each solute breakthroughs earlier compared to a single solute. The percentage of solute recovered from the column for all three mixtures was similar to that of a single solute. In section 6.3.2 (Chapter 6) the reasons for the complete solute recovery in column experiments were explained; the same were also true for the observed discrepancy in bicomponent column experiments.

The results reveal that PCOC breakthroughs earlier in the presence of 2,4-D compared to MCPA. This could be attributed to competition between the solutes and agree with the results presented in Chapter 4, which suggested that PCOC adsorbs less in presence of 2,4-D compared to MCPA. Similar conclusions can be made for 2,4-D and MCPA in presence of other competing solute. The data indicate that, with regard to overall breakthrough and elution from volcanic soil, the chemicals can be ranked as PCOC > 2,4-D > MCPA for the three mixtures examined.

The bicomponent experimental data and HSDM predictions for the three mixtures, 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC, are shown in Figures 6.11-6.13, respectively. All the parameters used to predict breakthrough and elution profiles were obtained independently or from literature correlations. Figure 6.11 shows the breakthrough and elution of 2,4-D and MCPA in the presence of each other. The experimental data indicate that 2,4-D and MCPA breakthrough simultaneously from the column; also, there was not significant tailing, at low concentrations, as observed for single component data. The reasons for this is not clear and more experimental work is needed to understand the mechanisms of bicomponent sorption in soil columns. Similar results were observed for other bicomponent mixtures.

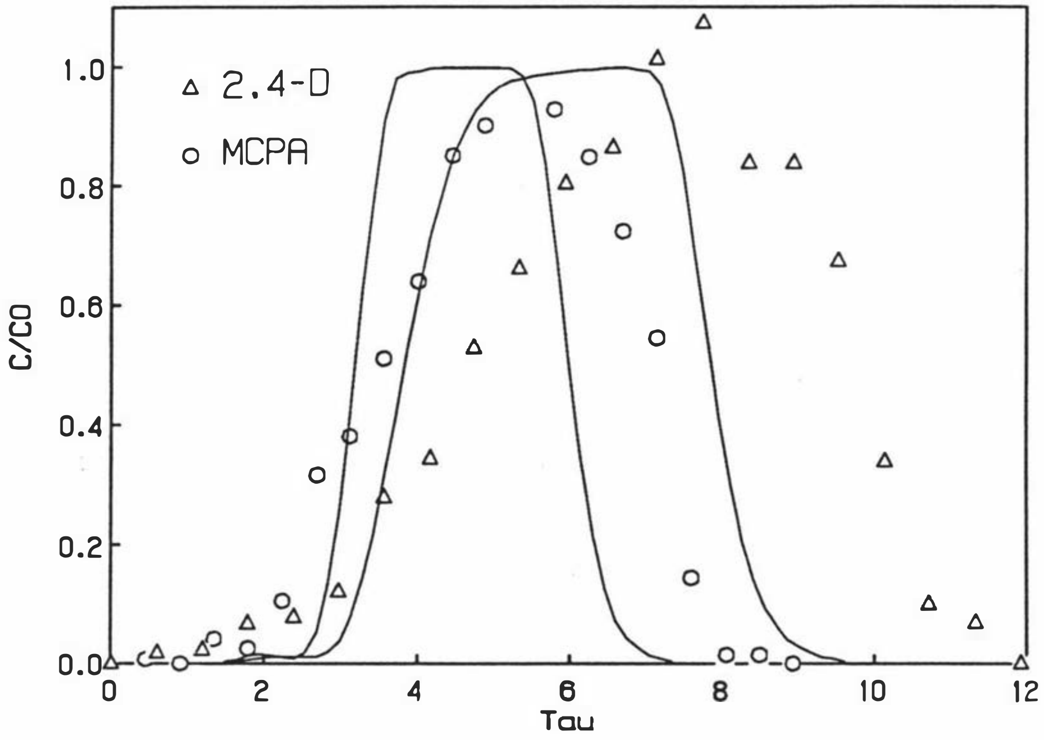


Figure 6.11: Experimental and predicted breakthrough and elution curves for bicomponent mixture of 2,4-D-MCPA.

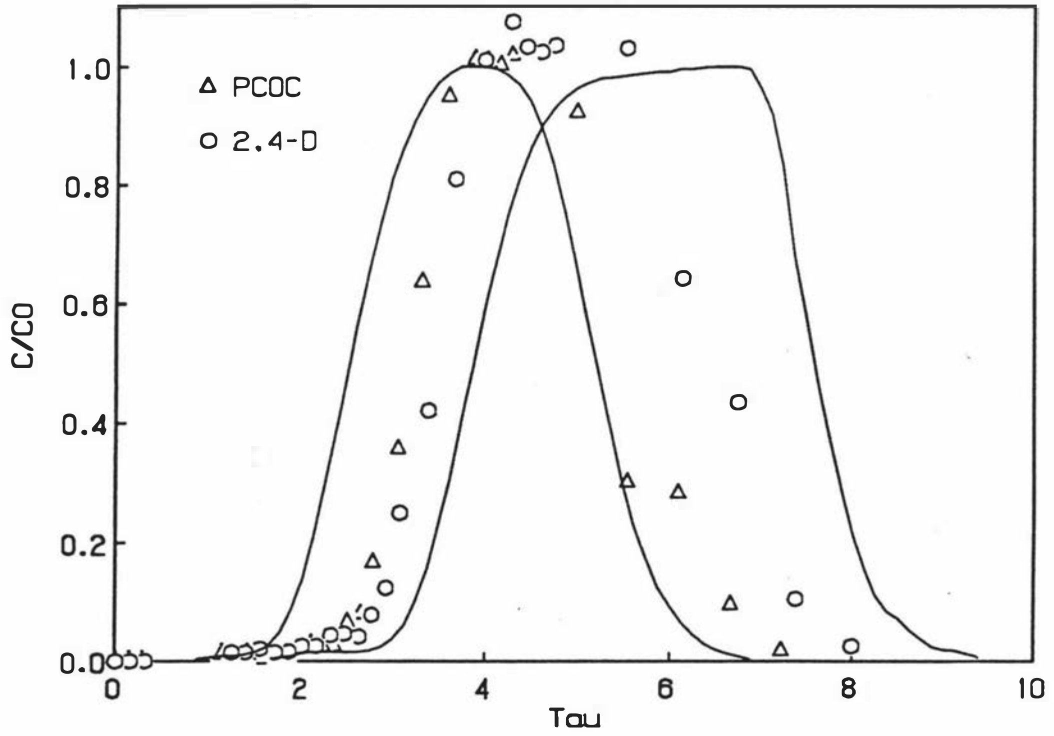


Figure 6.12: Experimental and predicted breakthrough and elution curves for bicomponent mixture of 2,4-D-PCOC.

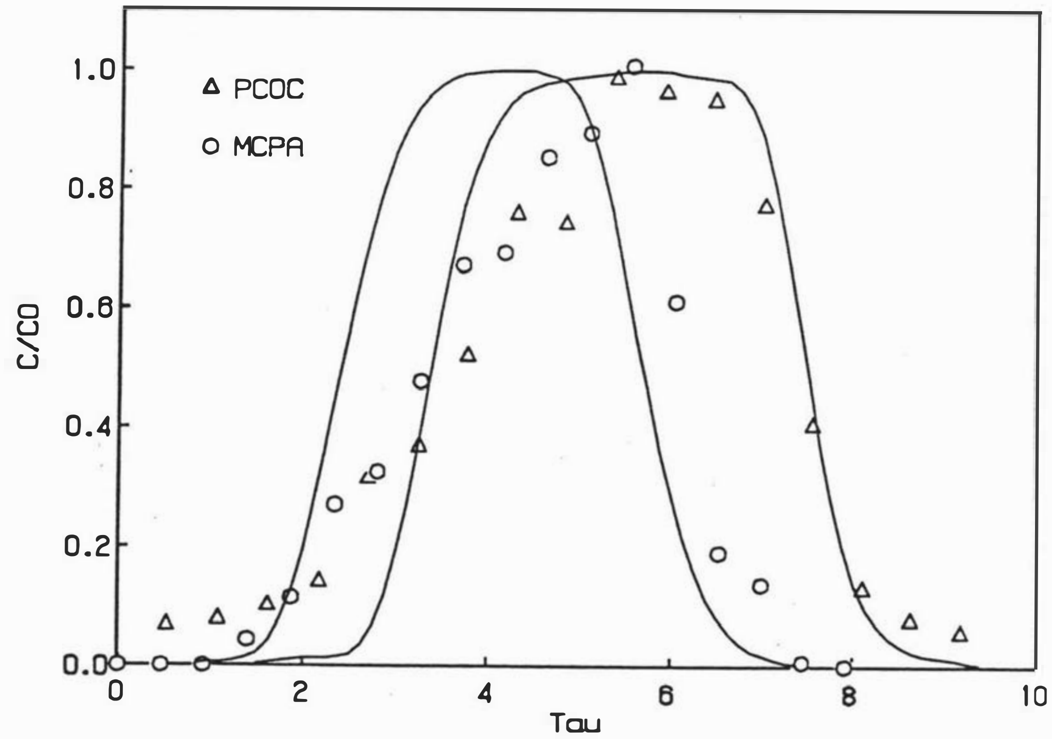


Figure 6.13: Experimental and predicted breakthrough and elution curves for bicomponent mixture of MCPA-PCOC.

Table 6.7 Input data for bicomponent adsorption and desorption ($\varepsilon = 0.45$, pH = 2, Temperature = 20°C).

				Adsorption parameters						Desorption parameters			
Bisolute mixture	C_0 (mg/l)	ν	$a_{i,j}$	ω	ψ	σ	Pe	K_{des}	$1/n_{des}$	d_{ij}	ω	ψ	σ
2,4-D-MCPA													
2,4-D	100.63	0.052	0.15	5.20	121	16.2	416	0.064	0.432	0.147	6.41	149	13.75
MCPA	104.27	0.052	0.70					0.071	0.420	0.209			
2,4-D-PCOC													
2,4-D	101.12	0.052	0.10	5.26	122	16.4	416	0.042	0.519	0.065	5.22	121	15.08
PCOC	101.55	0.052	0.72					0.060	0.302	0.115			
MCPA-PCOC													
MCPA	102.58	0.052	0.14	6.98	164	19.2	417	0.074	0.414	0.149	7.39	174	17.91
PCOC	109.24	0.052	0.55					0.069	0.306	0.189			

Table 6.8 Amounts of solute adsorbed and eluted in bicomponent column experiments.

Bisolute mixture	C_0 (mg/l)	$q_{max,\ ads}$	$q_{max,\ des}$	% recovery
2,4-D-MCPA				
2,4-D	100.63	0.54	0.53	99.0
MCPA	104.27	0.70	0.69	99.8
2,4-D-PCOC				
2,4-D	101.12	0.56	0.54	97.3
PCOC	101.55	0.33	0.32	98.1
MCPA-PCOC				
MCPA	102.58	0.71	0.70	99.5
PCOC	109.24	0.32	0.31	99.5

The HSDM could not predict the breakthrough and elution fronts of each component in a bicomponent mixture, for example, the model predicted an early appearance and elution of 2,4-D compared to MCPA as shown in Figure 6.11. In bicomponent HSDM (section 6.4.1), the competition between the components was accounted for in terms of equilibrium sorption capacities using competition coefficients, while assuming the competition from surface diffusion, film-mass transfer and dispersion to be negligible on the movement of solutes. However, the experimental data could be described more accurately by accounting for the competition between the film and surface diffusion coefficients. The observed deviation in model prediction could also be due to different soils used for batch and column experiments. In batch kinetic experiments, an average particle size of 359 μm was used compared to 300 μm for column experiments, therefore the surface diffusion coefficients obtained in batch were higher due to larger surface area for diffusion (Weber *et al.,* 1991).

The soil used for column experiments was different to that used for equilibrium and rate experiments; the parameters determined from earlier experiments and from correlations were used directly for HSDM predictions; the difference in aggregate radius between the two soils could lead to the observed discrepancies in the model predictions. It appear that at least one additional mechanism is needed to completely predict the breakthrough and elution of bicomponent mixtures from soil columns.

From the fixed bed adsorption and desorption studies, the following conclusions can be made on the transport of phenoxyactic acids and chlorophenols:

1. The breakthrough and elution of phenoxyacetic acids was much slower compared to chlorophenols as a single component.
2. 2,4-D breakthrough and elution times were faster compared to the other two phenoxyacetic acids, 2,4,5-T and MCPA. The order of appearance from the column was 2,4-D > MCPA > 2,4,5-T. For chlorophenols, the order was, 2,4-DCP > PCOC > 2,4,5-TCP. The soil column adsorption capacity appears to be the major factor for the transport of solutes in columns.
3. Higher concentrations and flow rates result in the early breakthrough and elution of solutes from the column.
4. An extensive tailing at low concentrations was observed for all the solutes and attributed to the nonequilibrium conditions prevailing in the soil column. This indicates that in field situations, it requires a longer time to flush the soil free of a chemical.
5. The recovery of chlorophenols was higher compared to phenoxyacetic acids.
6. The homogeneous surface diffusion model satisfactorily predicted the breakthrough portion of the curve; however, elution of the solutes from the soil column could not be accurately due to estimation of parameters and simplifying assumptions.
7. The solutes appeared early in the column in the presence of another solute, compared to a single component, indicating that solute movement is faster in the presence of another competing solute.
8. A homogeneous surface diffusion model, with the assumptions listed, is not satisfactory in predicting the movement in bicomponent systems. Inclusion of an additional sorption mechanism may lead to better model predictions.

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSIONS

The main feature of this research is the study of the adsorption and desorption characteristics of phenoxyacetic acids and chlorophenols in a volcanic soil. 2,4-D, MCPA, 2,4,5-T, 2,4-DCP, 2,4,5-TCP and PCOC, the major components representing phenoxy and chlrophenol groups present in the landfill, were used as the solutes. Volcanic soil, procured from the landfill, was employed to study the sorption behaviour.

For leaching of chemicals from the landfill to be successful, it is necessary to determine the sorption characteristics of the compounds present in the leachate. The widely used batch method for sorption measurement was found to be appropriate for the experiments, where sorption characteristics were determined at different concentrations, pH and temperature. Preliminary experiments, described earlier, indicated that the adsorption of the chemicals was sensitive to pH and temperature, with the sorption occurring at below a pH of 3.5. The concentration measurements, undertaken using UV and HPLC, indicate that the negligible sorption observed was not due to an artifact of the procedure used. An increase in temperature reduced the sorption capacity of all solutes, while the range of heat of adsorption values, calculated from vant Hoff's equation, demonstrated that both physical and hydrogen bonding may be the principal mechanisms of adsorption onto volcanic soil.

Equilibrium adsorption of solutes in a pure component system, was determined at pH 2 and at a temperature of 20°C. The adsorption data of all compounds were described by a nonlinear Freundlich-type isotherm over the concentration range studied, with 1/n values ranging from 0.72-1.0. However, many researchers have used linear isotherms to describe the sorption data, even though the data suggests a nonlinear type. Linear models have an advantage over the nonlinear models, namely, that the simulations of solute transport is easy in laboratory and field situations. In this study, no attempts were made to linearize the isotherms. The adsorption capacity of solutes was in the order: 2,4,5-T > MCPA > 2,4-D > 2,4,5-TCP > PCOC > 2,4-DCP, indicating phenoxyacetic acids adsorbed more compared to chlorophenols. The results demonstrate that the adsorption capacity was inversely related to the solubility of the respective compounds. In the case of the present study, the maximum amount of each solute adsorbed corresponded to only 2-4.5% of the total surface area. This shows that the phenoxyacetic acids and chlorophenols may be adsorbed to only specific sites or functional groups present in the organic matter.

In the present study, desorption data were obtained from the same soil-chemical mixture used for adsorption studies, and was described using a Freundlich-type isotherm. However, the desorption parameters were found to be different from adsorption parameters. In addition, the desorption was dependent on the amount adsorbed (q_{max}) in the soil. In modelling solute transport, the adsorption/desorption process is often simplified by assuming ideal conditions of isotherm linearity and desorption reversibility. However, the results obtained here show that the desorption isotherms were also nonlinear, and that a fraction of the chemical adsorbed was not desorbed in ten stages. This could be due to the diffusion of solute into internal adsorption sites. It was noted that the fraction resistant to desorption was higher for phenoxyacetic acids than chlorophenols. However, the results indicate that all the solute could be desorbed eventually. In this study, the ratio of adsorption $1/n$ to desorption $1/n$ was linearly related to the amount adsorbed, q_{max}. Using this relationship, the Freundlich constants for desorption were determined from the adsorption parameters, a relationship unique to this study, and used throughout the work to estimate the desorption parameters.

A study of competitive sorption, carried out for three solute combinations, 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC, shows that interactions between the solutes had a major effect on their uptake onto soil: the adsorption capacities of 2,4-D and MCPA in the presence of each other was decreased by 11 and 31%, respectively, while the reduction in adsorption capacity was in the range of 8-10% for PCOC. It was found that a bicomponent Freundlich-type isotherm was able to model the competitive sorption. The use of competition coefficients in the model to describe the interaction between the solutes was not previously reported in soil systems. In this study, the competition coefficient values were linearly dependent on the initial concentrations of the two solutes. The inclusion of concentration dependent competition coefficients in the model is an improvement on the model of Sheindorf *et al.* (1981). The model is very simple, with a competition coefficient accounting for the presence of other solute. It is shown that the model fit, between measured and predicted data is satisfactory, indicating the model was suitable for further use. This model was also used to describe the competitive desorption of solutes. In case of desorption, the competition coefficients were linearly related to the amount of each solute adsorbed (q_{1max}) in the soil. The results indicate that the adsorbed solutes were difficult to desorb in a bicomponent mixture compared to the single component.

The sorption results indicate that a fraction of the chemical is released slowly during desorption. For nearly two decades many researchers have observed that desorption of organic chemicals from soils frequently display hysteretic or history-dependent path (Miller and Pedit, 1992). The observed desorption hysteresis is explained on the basis that the rate of desorption is sufficiently slow such that equilibrium does not exist between the solution and soil after a desorption step. Therefore, an apparent hysteresis would be observed, assuming equilibrium is achieved during adsorption phase, but equilibrium is not achieved during desorption steps. Several studies have suggested this explanation, however, numerous additional experiments and theoretical studies are needed to elucidate the slow release of chemicals from the soil.

The batch method used for the determination of the kinetic parameters of phenoxyacetic acids and chlorophenols is simple and easy, when compared to the mini-column and other methods. The sorption data for the pure component system clearly demonstrates the two regimes present in the uptake rate, a fast initial adsorption in the first 45 seconds and a slower one reaching equilibrium in 30 minutes. Many authors have reported, that for low molecular weight compounds having nonlinear isotherms, a surface diffusion model describes the kinetic data accurately compared to a pore diffusion model. Therefore, diffusion coefficients of all solutes were determined by fitting the concentration-time data to a homogeneous surface diffusion model, incorporating equilibrium parameters and a film-mass transfer coefficient. The desorption surface diffusion coefficients obtained from the model solution were found to be of a similar order of magnitude to those of adsorption surface diffusion coefficients.

Crittenden *et al.* (1986) report that when 1/n is between 0.7-1.0, the use of pore and surface diffusion models give identical results. Hence, the observed data could be fitted to either a surface diffusion model or to a pore diffusion model. The competitive adsorption and desorption kinetics data were used to determine the surface diffusion coefficients in bicomponent mixtures. The single component HSDM equations were extended to a bicomponent system, incorporating the competitive isotherms, whereby the competitive effects are accounted for by the use of competition coefficients. The measured surface diffusion coefficients in bicomponent systems were found to be slightly smaller (less than 10%) than those of the single component values, indicating some competition between the solutes. In kinetic experiments, the present study assumes that the diffusion coefficient was independent of solute concentration, however, this assumption may not be valid at lower concentration ranges, and further experimental work is needed to examine the influence of concentration on diffusion coefficients in single, as well as bicomponent systems. The use of same k_f for adsorption and desorption is valid as previous experimental work with similar soils (Miller and Pedit, 1992) found that film-mass transfer resistance was an unimportant factor in determining the rate of sorption. The accuracy of these simulations suggest that the surface diffusion model was a reasonable for determining the kinetics of adsorption and desorption for the system investigated. The observed reversibility of the kinetic data in the present studies is due to the high soil to solution ratio used for these experiments, whereby the adsorbent particles exist as individual grains, however, experiments with different soil to solution ratios can give a better estimate of diffusion coefficients comparable to field situations.

The solute transport model developed for the pure component system was based on the mechanisms of adsorption/desorption, film-mass transfer, surface diffusion coefficient and dispersion. A convective-dispersive model incorporating these mechanisms was solved numerically to predict the transport of chemicals in laboratory soil columns. As stated earlier, currently, most of the solute transport models use curve-fitting techniques to obtain the model parameters and to predict the movement of solutes in laboratory soil columns. However, in the present work all the model parameters were obtained from independent experiments or from literature correlations. The column experimental results indicate that increasing the concentration from 100 to 400 mg/l resulted in an early breakthrough and elution of solute. An extensive tailing of the elution data was observed due to the slow release of the chemical at low solute concentrations, attributed to the prevailing nonequilibrium conditions and site specific sorption, where a fraction may be resistant to desorption. Similar results were also observed when concentration was kept constant and flow rate was varied. The order of breakthrough for phenoxyacetic acids from the column was: 2,4-D > MCPA > 2,4,5-T, for chlorophenols the order was: 2,4-DCP > PCOC > 2,4,5-TCP. The results of column experiments demonstrate that sorption capacity plays a dominant role in the transport of solutes in soil.

The predictions of HDSM for the desorption of compounds from soil columns were not satisfactory. This could be due to the different particle size distribution used for column experiments and other simplifying assumptions made in the prediction. The recovery of solutes showed that all the solutes adsorbed could be desorbed using water as the flushing medium.

In the case of the adsorption and desorption for bicomponent mixtures, the single component model equations were extended to bisolute mixtures to predict the transport in soil columns. The results from this study indicate that the breakthrough and elution curves appear earlier compared to single component systems. The results also reveal that sorption capacity plays a major role in transport of solutes in mixtures. The order of breakthrough in a bicomponent system is, PCOC > 2,4-D > MCPA. Agreement between model predictions and experimental data for bicomponent systems is not good. However, the results suggest the validity of the theory and the applicability of the surface diffusion model to solute transport in general.

In conclusion, this study has illustrated that the importance of sorption on leaching characteristics of the chemicals in single and bicomponent systems of phenoxyacetic acids and chlorophenols, identifying the mechanisms and processes responsible for the leaching of the chemicals and is of use in remediation of contaminated soils.

APPENDIX 1

Summary of soil surface area determination[*]

BET surface area	49.7178 sq. m/g
Cumulative adsorption surface area (pores between 17 and 3000 A)	30.3225 sq. m/g
Cumulative desorption surface area (pores between 17 and 3000 A)	37.7875 sq .m/g
Micropore area	7.8613 sq. m/g
Average pore diameter	40.7617 A

[*] The surface area analysis was carried out by Chemical Engineering Department, University of Queensland, Australia using Mercury porosimetry.

APPENDIX 2

Comparison of different competitive isotherm models

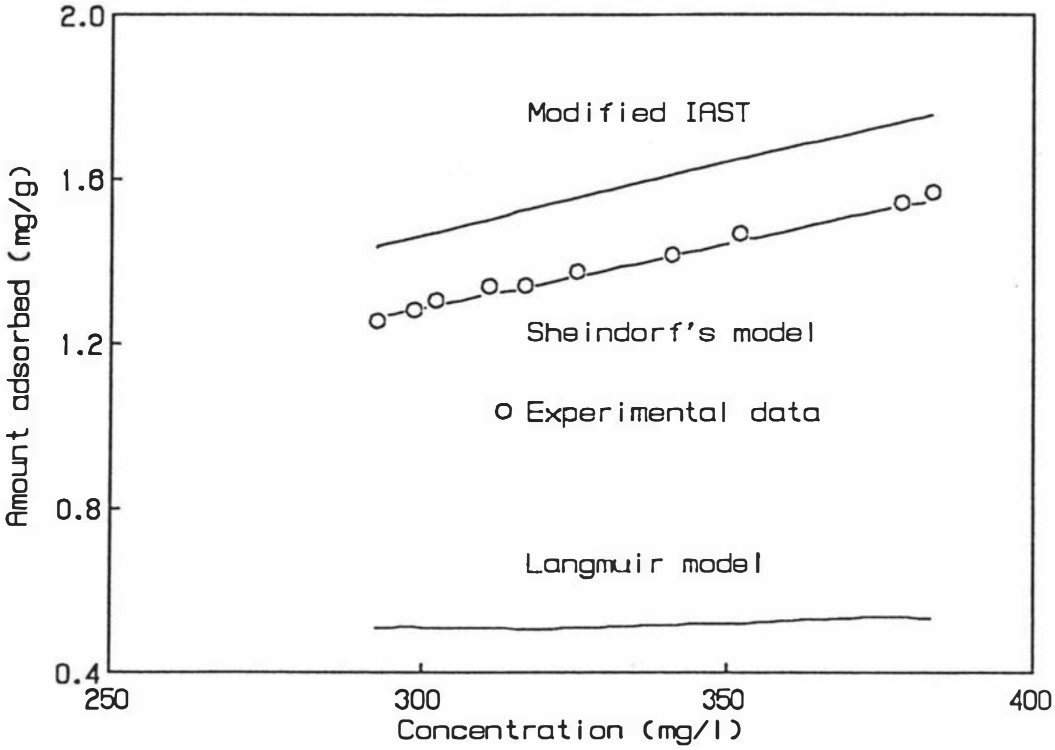


Figure A2.1 Bicomponent adsorption isotherm of 2,4-D in presence of MCPA. C_0 = 400 mg/l of each solute.

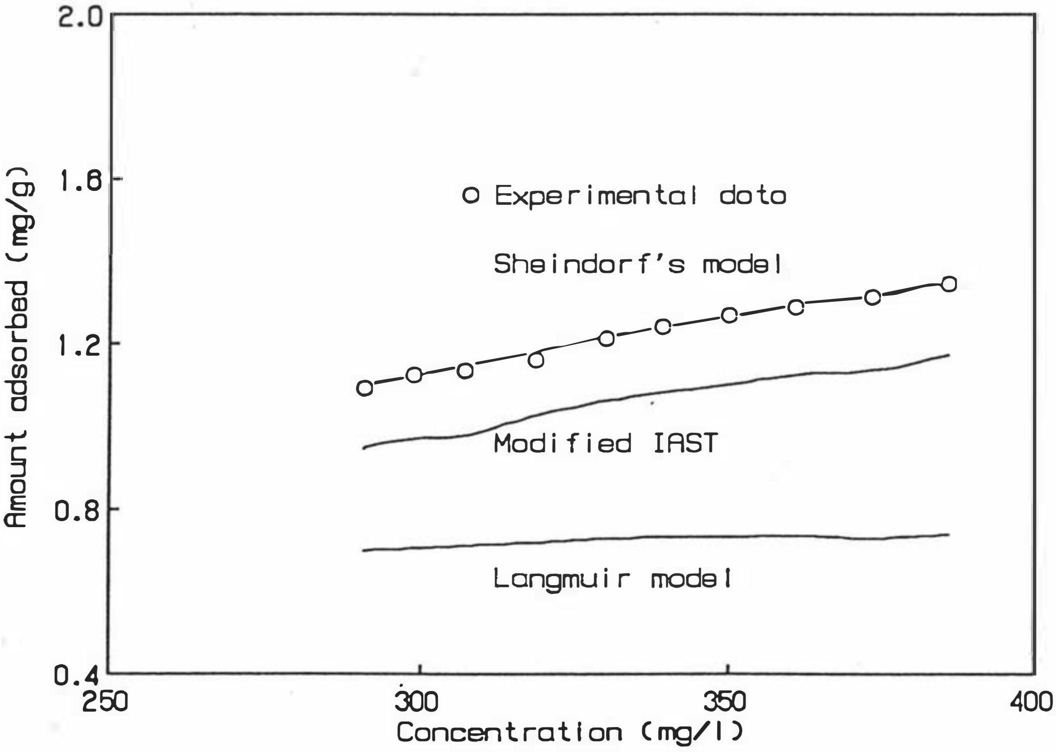


Figure A2.2 Bicomponent adsorption isotherm of MCPA in presence of 2,4-D. C_0 = 400 mg/l of each solute.

APPENDIX 3

The sorption kinetics in literature are usually described by pore or surface diffusion mechanisms. Brusseau and Rao (1989) investigated the sorption of low molecular weight compounds having nonlinear isotherms and concluded that surface diffusion mechanism predominates the sorption phenomenon. Moreover, for strongly adsorbed chemicals ($1/n < 1$), Furusawa and Smith (1973) and Crittenden (1976) report that the surface diffusion gives a more rational description of transport than the pore diffusion mechanism. The dominance of surface diffusion is due to large tortuosity, associated with the pore structure of the soil, which results in very slow pore diffusion (Brusseau and Rao, 1989).

Fritz *et al.* (1981) describes the methods to delineate which mechanism is rate limiting. For example, the effect of solute concentration on the Biot number can be used to differentiate between the models. For pore diffusion, the Biot number, which is the ratio of internal to external resistance is expressed as:

$$B_p = \frac{k_1 R}{D_p} \tag{A3.1}$$

and is independent of initial concentration. In contrast, the Biot number for the surface diffusion mechanism is expressed as:

$$B_s = \frac{(k_1 A/V)}{(D_s/R^2)} \frac{(VC_0)}{(Wq_0)} \tag{A3.2}$$

and is dependent on the initial solute concentration. The experimental results suggest that the Biot number is dependent on the initial concentration of the solute and, therefore, the assumption of surface diffusion mechanism is justified for the present work.

Another way to delineate the existence of a surface diffusion component is by comparing the pore diffusion coefficient values obtained from different methods. In the first method, the pore diffusivity (D_p) is estimated from the molecular diffusivity (D_m) using the relationship,

$$D_p = \frac{D_m \epsilon}{\lambda} \tag{A3.3}$$

where, D_m is the molecular diffusivity, ε is porosity and λ is tortuosity.

It is often assumed that porosity and tortuosity are related as, (Brussaeu and Rao, 1989),

$$\lambda = \frac{1}{\epsilon} \tag{A3.4}$$

Substituting Equation (A3.4) into Equation (A3.3), results in

$$D_p = D_m \epsilon^2 \tag{A3.5}$$

In the second method, a relationship is obtained between surface diffusion coefficient and pore diffusion coefficients. The particle equation for a surface diffusion mechanism is written as (Equation 5.2),

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}[r^2\frac{\partial q}{\partial r}] \tag{A3.6}$$

The particle equation for the pore diffusion mechanism is expressed as:

$$\epsilon\frac{\partial C}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \frac{\epsilon}{r^2}D_p\frac{\partial}{\partial r}[r^2\frac{\partial C}{\partial r}] \tag{A3.7}$$

where, C is the liquid concentration.

For a linear isotherm (e.g. 2,4-DCP)

$$q = KC \tag{A3.8}$$

Substituting Equation (A3.8) for Equation (A3.7) and rearranging, becomes

$$\frac{\partial q}{\partial t} = [\frac{\epsilon}{\epsilon + \rho_p K}] \frac{D_p}{r^2} \frac{\partial}{\partial r} [r^2 \frac{\partial q}{\partial r}] \tag{A3.9}$$

The result of comparing Equation (A3.9) with Equation (A3.6), is

$$D_p = \frac{D_s (\epsilon + \rho_p K)}{\epsilon} \tag{A3.10}$$

For 2,4-DCP, $D_m = 6.67 \text{x} 10^{-6}$ cm^2/s, $\varepsilon = 0.45$, the estimated pore diffusion coefficient value from Equation (A3.5) is $1.35 \text{x} 10^{-6}$ cm^2/s. Similarly, using Equation (A1.10) with K = 0.0036 and $D_s = 2.19 \text{x}^{-7}$ cm^2/s, the estimated pore diffusivity is $2.23 \text{x} 10^{-7}$ cm^2/s. Comparing D_p values obtained from the two methods reveals that they both differ by an order of magnitude, indicating the inconsistencies of the pore diffusion coefficient.

On the other hand, 2,4-D showed a nonlinear isotherm, i.e.,$q = KC^{1/n}$. Due to strong adsorption ($1/n < 1$) the surface diffusion flux is much higher than that of a linear isotherm. For a nonlinear isotherm the relationship between pore and surface diffusivities is obtained by using a similar analysis as given above,

$$D_p = \frac{D_s \ (\epsilon \frac{1}{n} + \rho_p K C^{1/n - 1})}{(\frac{1}{n} \epsilon)} \tag{A3.11}$$

The D_p values obtained using Equations (A3.5) and (A3.11), with the parameters K = 0.020, 1/n = 0.75, $D_m = 5.72 \text{x} 10^{-6}$ cm^2/s, are $1.16 \text{x} 10^{-6}$ cm^2/s and $1.98 \text{x} 10^{-7}$ cm^2/s, respectively. Again, the values of D_p obtained are different from the two methods showing that a surface diffusion mechanism is the most likely mechanism for the intraparticle transport.

APPENDIX 4

Derivation of intraparticle mass transfer

To derive the intraparticle phase mass balance equation for a solute, a mass balance is written on a thin shell of Δr, as shown in Figure 5.1. The mass flux at any radial position is assumed, due to surface diffusion:

$$J = -D_s \rho_p \frac{\partial q(r,t)}{\partial r} \tag{A4.1}$$

where, J is the total mass flux for the solute and D_s is the effective surface diffusion coefficient. Some researchers (Fritz *et al.*, 1981; Neretneiks, 1976) have reported that the surface diffusion coefficient is dependent on initial solute concentration. Consequently, the effective surface diffusivity includes this dependence on initial concentration.

Writing a mass balance on the spherical shell for a solute yields:

Mass of solute entering at r - Mass of solute leaving at r+Δr = Mass of solute accumulation in the spherical shell

With the use of Equation (A4.1), the intraparticle phase mass balance for a solute in mathematical terms is expressed as:

$$[-D_s \rho_p \frac{\partial q(r,t)}{\partial r}] 4\pi r^2 \Delta t - [D_s \rho_p \frac{\partial q(r+\Delta r,t)}{\partial r}] 4\pi (r+\Delta r)^2 \Delta t$$

$$= [\rho_p q(r,t+\Delta t)] 4\pi r^2 \Delta r \;-\; [\rho_p q(r,t)] 4\pi r^2 \Delta r \tag{A4.2}$$

Equation (A4.2) accounts for the mass of solute entering the spherical shell by surface diffusion. The final form of the intraparticle phase mass balance for a solute is obtained by dividing Equation (A4.2) by $4\pi r^2 \Delta r \Delta t$ and taking the limits as Δr and Δt approach zero:

$$\frac{1}{r^2}\frac{\partial}{\partial r}[r^2 D_s \frac{\partial q(r,t)}{\partial r}] = \frac{\partial}{\partial t}[q(r,t)] \tag{A4.3}$$

In order to solve Equation (A4.3), one initial condition and two boundary conditions are required. The initial condition assumes that there is no solute in the adsorbent initially:

$$q(r,t)\ (0 \le r \le R,\ t=0) = 0 \tag{A4.4}$$

Due to symmetry at the centre of the particle, the first boundary condition is expressed as:

$$\frac{\partial}{\partial r}[q(r,t)](r=0,\ t) = 0 \tag{A4.5}$$

The second boundary condition describes the situation at the exterior of the particle surface. Writing a mass balance at the adsorbent boundary, the amount of mass leaving the liquid phase must equal the amount of mass transferred to the adsorbent phase:

Mass of solute transferred through the liquid phase boundary layer = Mass of solute transferred away from exterior surface by surface diffusion

In mathematical terms this becomes

$$k_l[C - C_s(r = R,\ t)]4\pi R^2 = D_s \rho_p [\frac{\partial q(r=R,\ t)}{\partial r}]4\pi R^2 \tag{A4.6}$$

The final form of this boundary condition is obtained after dividing Equation (A4.6) by $4\pi R^2$, and rearranging this as:

$$D_s \rho_p A \frac{\partial(r = R,\ t)}{\partial r} = k_f A[C - C_s(r = R,\ t)] \tag{A4.7}$$

To solve the liquid phase and intraparticle phase mass balances, the solute concentration on the adsorbent, $C_s(r,t)$, is expressed in terms of the adsorbent phase concentration, $q(r,t)$, assuming that a local equilibrium exists throughout the adsorbent between C_s (r,t) and q_s(r,t), which is expressed as the Freundlich isotherm equation. For a single solute, the Freundlich equation is:

$$q_s(r,t) = KC_s(r,t)^{\frac{1}{n}} \tag{A4.8}$$

where, K and 1/n are Freundlich isotherm constants.

Derivation of the mass balances in a fixed bed adsorber

To derive the overall mass balances for a solute in a fixed bed, a mass balance is written on a differential slice in the bed as shown in Figure 6.1. Mass can be transferred into or out of the slice by convection, dispersion and diffusion. As a result, the overall mass balance for a component can be expressed in words, as:

> *Mass of solute entering by convection at z - Mass of adsorbate leaving by convection at z + Δz + Mass of solute entering by dispersion and diffusion at z - Mass of solute leaving by dispersion and diffusion at z+Δz = Mass of solute accumulated in the liquid phase + Mass of adsorbate accumulated in the adsorbent phase*

In mathematical terms this becomes:

$$\begin{aligned} &\epsilon v A_c[C(z,t) - C(z+\Delta z,t)]\Delta t - \epsilon A D_L\left[\frac{\partial C(z,t)}{\partial z} - \frac{\partial C(z+\Delta z,t)}{\partial z}\right]\Delta t \\ &= \epsilon A_c[C(z,t+\Delta t) - C(z,t)]\Delta z + A_p k_l[C(z,t) - C_s(r = R, z, t)] \end{aligned} \tag{A4.9}$$

where, ε is the fixed bed porosity, v is the interstitial velocity, A_c is the cross-sectional area of the slice, C(z,t) is the liquid phase concentration of the solute, D_l is the axial dispersion, ρ_p is the particle density, q(z,t) is the adsorbent phase concentration of solute, C_s is the solute concentration on the adsorbent surface, z is the axial coordinate, t is the time, A_p is the total external surface area of the adsorbent particle available for mass transfer, k_l is the film-mass transfer coefficient of component, and C_s (r = R,z,t) is the adsorbate concentration at the adsorbent surface.

Dividing Equation (A4.9) by AΔzΔt, and taking the limits as Δz and Δt, approach zero yields:

$$-v\frac{\partial C(z,t)}{\partial z} + D_L\frac{\partial^2 C(z,t)}{\partial z^2} = \frac{\partial C(z,t)}{\partial t} + \frac{A_{pk_l}}{A_c \epsilon \Delta z}[C(z,t) - C_s(r = R, z, t)] \tag{A4.10}$$

The total external surface area, A_p is expressed as:

$$A_p = \frac{3m}{\rho_p R} \tag{A4.11}$$

where, m is the mass of adsorbent in the differential slice.

The dosage of adsorbent in the differential slice may be expressed in words as:

$$W = \frac{Massofadsorbent}{Volumeofadsorbent} x \frac{Volumeofadsorbent}{volumeofdiffrentialslice} \tag{A4.12}$$

In mathematical terms, this becomes:

$$W = \frac{m}{A_c \Delta z} = \rho_p(1 - \epsilon) \tag{A4.13}$$

while substituting Equations (A4.11), and (A4.13) yields the final form of the liquid phase mass balance for the solute in a fixed bed:

$$-v\frac{\partial C(z,t)}{\partial z} + D_L\frac{\partial^2 C(z,t)}{\partial z^2} = \frac{\partial C(z,t)}{\partial t} + \frac{3k_f(1 - \epsilon)}{\epsilon R}[C(z,t) - C_s(r = R, z, t)] \tag{A4.14}$$

In order to solve the Equation (A4.14) one initial condition and two boundary conditions are required. The initial condition is expressed as:

$$C(0< = z< = L, t = 0) = 0 \tag{A4.15}$$

where, L is the length of the bed.

The first boundary condition is the Danckwerts (1953) condition at the inlet boundary, $z = 0^+$. This is expressed in words as:

Mass of solute entering at $z = 0^-$ *by convection - Mass of adsorbate leaving at* $z = 0^+$ *by convection + dispersion = Mass of adsorbate accumulated at boundary by dispersion*

In mathematical terms, this becomes:

$$\epsilon A_c v[C_0 - C(z = 0^+,t)]\Delta t = -\epsilon A D_l \frac{\partial C(z = 0^+,t)}{\partial z}\Delta t \tag{A4.16}$$

where, C_0 is the influent concentration of the solute entering the fixed bed. Dividing Equation (A4.16) by $A_cV\Delta t$, and rearranging, yields the final form of the Danckwerts entrance condition:

$$C(z = 0^+,t) = C_o + \frac{D_l}{v}\frac{\partial C(z = 0^+,\ t)}{\partial z} \tag{A4.17}$$

The second boundary condition for the overall mass balance is the Danckwerts condition at the exit boundary, $z = L^-$. Expressing this condition in words:

> *Mass of solute entering at z = L⁻ by dispersion + convection - Mass of solute leaving at z = L⁺ by convection = Mass of solute accumulated at boundary by dispersion*

In mathematical terms, this becomes:

$$\epsilon A_c v[C(z = L^-,t) - C(z = L^+,t)]\Delta t = \epsilon A D_L \frac{\partial C(z = L^-,t)}{\partial z}\Delta t \tag{A4.18}$$

Dividing Equation (A4.18) by $A_cV\Delta t$, and rearranging, yields:

$$C(z = L^-,t) = C(z = L^-,t) + \frac{D_L}{v}\frac{\partial C(z = L^+,t)}{\partial z} \tag{A4.19}$$

Inspecting the Equation (A4.19), consider the possibility that $\partial C(z = L^-,t)/\partial z > 0$. From Equation (A4.19) this results in $C(z = L^+,t) < C(z = L^-,t)$. This result conveys that C should be increasing at the boundary which contradicts the initial assumption. When considering the other possibility, $\partial C(z=L^-,t)/\partial z > 0$, the Equation (A4.19) reduces to $C(z = L^+,t) > C(z = L^-,t)$. This result also states that C should be increasing across the boundary. A positive concentration gradient implies that the concentration passes through a minium somewhere before the exit. This violates the assumed initial condition. Therefore, Equation (A4.19) can be valid only if $\partial C(z=L^-,t)/\partial z = 0$. This deduction becomes the final form of the boundary condition expressing the Danckwerts exit condition:

$$\frac{\partial C(z = L^{-},t)}{\partial z} = 0 \tag{A4.20}$$

The fixed bed equation is solved using the above initial condition and the boundary conditions.

APPENDIX 5

A	Total interfacial surface area, cm^2 (Equation 5.1)
A_c	Cross-sectional area for a slice, cm^2 (Equation A4.9)
A_m	Area occupied by each molecule, cm^2 (Equation 4.4)
A_p	Total external surface area of the adsorbent particle, cm^2 (Equation A4.9).
a_{12}	Adsorption competition coefficient, (Equation 2.6)
a_{21}	Adsorption competition coefficient, (Equation 2.7)
b_1,b_2	Empirical constants, (Equation 4.10)
B	Biot number, (Equation 5.8)
B_p	Biot number for pore diffusion (Equation A3.1)
B_s	Biot number for surface diffusion (Equation A3.2)
B_1	Biot number for component 1 (Equation 5.27)
B_2	Biot number for component 2 (Equation 5.27)
C	Liquid concentration, mg/l
C_e	Equilibrium concentration, mg/l
C_1	Equilibrium concentration for component 1, mg/l
C_2	Equilibrium concentration for component 2, mg/l
C_0	Initial solute concentration, mg/l
$C_{1,0}$	Initial solute concentration for component 1, mg/l (Equation 5.22)
$C_{2,0}$	Initial solute concentration for component 2, mg/l (Equation 5.22)
C_s	Bulk solute concentration at the interface, mg/l
$C_{1,s}$	Bulk concentration at the interface for component 1, mg/l (Equation 5.20)
$C_{2,s}$	Bulk concentration at the interface for component 2, mg/l (Equation 5.21)

$d_{i,j}$	Desorption competition coefficient, (Equation 4.17)
D_L	Dispersion coefficient, cm^2/s (Equation 6.2)
$D_{L,1}$	Dispersion coefficient for component 1, cm^2/s (Equation 6.26)
$D_{L,1}$	Dispersion coefficient for component 2, cm^2/s (Equation 6.27)
D_m	Liquid diffusivity, cm^2/s
d_p	Average particle diameter, cm
D_p	Pore diffusion coefficient, cm^2/s (Equation A3.1)
D_s	Surface diffusion coefficient, cm^2/s (Equation 5.2)
$D_{s,1}$	Surface diffusion coefficient for component 1, cm^2/s (Equation 5.18)
$D_{s,2}$	Surface diffusion coefficient for component 2, cm^2/s (Equation 5.18)
e	Fraction of supernate replaced (Equation 4.6)
f	Sorption coefficient, (Equation 2.3)
f_1	Sorption coefficient for component 1 (Equation 2.4)
f_2	Sorption coefficient for component 2 (Equation 2.5)
F	Separation factor, (Equation 5.8)
F_1	Separation factor for component 1, (Equation 5.28)
F_2	Separation factor for component 2, (Equation 5.28)
Fr	$(q_{1,0}/C_{1,0})/(q_{2,0}/C_{2,0})$, (Equation 6.46)
ΔH	Heat of adsorption, (Equation 4.1)
J	Total mass flux mg/cm s (Equation A4.1)
K_a	Acid equilibrium constant (Equation 4.1)
K_d	Distribution coefficient, (Equation 2.1)
k_a	Adsorption rate constant, 1/s
k_d	Desorption rate constant, 1/s

k_l	Film-mass transfer coefficient, cm/s (Equation 5.1)
$k_{l,1}$	Film-mass transfer coefficient for component 1, cm/s (Equation 5.16)
$k_{l,2}$	Film-mass transfer coefficient for component 2, cm/s (Equation 5.17)
K	Freundlich isotherm constant, (Equation 2.2)
K_1	Freundlich isotherm constant for component 1 (Equation 2.6)
K_2	Freundlich isotherm constant for component 2 (Equation 2.7)
K_{ads}	Freundlich adsorption isotherm constant (Equation 4.8)
K_{des}	Freundlich desorption isotherm constant (equation 4.8)
l_1	Defined as $a_{12}C1_{1,0}/C_{2,0}$
l_2	Defined as $a_{21}C_{2,0}/C_{1,0}$
L	Length of fixed bed, cm
m	Mass of adsorbent, g
N_{av}	Avagadro's number (equation 4.4)
1/n	Freundlich isotherm constant, (Equation 2.2)
$1/n_1$	Freundlich isotherm constant for component 1 (Equation 2.6)
$1/n_2$	Freundlich isotherm constant for component 2 (Equation 2.7)
$1/n_{ads}$	Freundlich adsorption isotherm constant (Equation 4.8)
$1/n_{des}$	Freundlich desorption isotherm constant (equation 4.8)
Pe	Peclet number (Equation 6.12)
p_i, p_j	Empirical constants, (Equation 4.16)
Q^o	Amount of solute adsorbed corresponding to a monolayer, mg/g (Equation 2.3)
$Q^o{}_1$	Amount adsorbed corresponding to a monolayer for component 1, mg/g (Equation 2.4)

Q^o_2	Amount adsorbed corresponding to a monolayer for component 2, mg/g (Equation 2.4)
Q	Flow rate, l/h
q	Amount of solute adsorbed, mg/g
q_0	Solid phase concentration in equilibrium with C_0, mg/g
$q_{1,0}$	Solid phase concentration in equilibrium with C_0 for component 1, mg/g (Equation 5.25)
$q_{2,0}$	Solid phase concentration in equilibrium with C_0 for component 2, mg/g (Equation 5.25)
q_1	Amount of solute adsorbed for component 1, mg/g (Equation 2.4)
q_2	Amount of solute adsorbed for component 2, mg/g (Equation 2.5)
q_{max}	Amount adsorbed, mg/g
q_{re}	Amount of solute remaining in soil, mg/g
q_s	Solid phase concentration at the liquid-solid interface, mg/g
$q_{1,s}$	Solid phase concentration at the liquid-solid interface for component 1, mg/g (Equation 5.24)
$q_{2,s}$	Solid phase concentration at the liquid-solid interface for component 2, mg/g (Equation 5.24)
r	Particle spatial variable, cm
R	Particle radius, cm
Re	Reynolds number (Equation 6.21)
R_f	Retardation factor, (Equation 2.11)
R_g	Universal gas constant, (Equation 4.5)
S	Total surface coverage, cm^2 (Equation 4.4)

s_i,s_j	Empirical constants, (Equation 4.18)
Sc	Schmidt number (Equation 6.21)
t	Time, s
T_1,T_2	Temperatures, °K (Equation 4.5)
u	Dimensionless solid phase concentration (Equation 5.7)
u_1	Dimensionless solid phase concentration (Equation 5.31)
u_2	Dimensionless solid phase concentration (Equation 5.32)
u_s	Dimensionless solid phase concentration at the interface (Equation 5.13)
$u_{1,s}$	Dimensionless solid phase concentration at the interface for component 1 (Equation 5.37)
$u_{2,s}$	Dimensionless solid phase concentration at the interface for component 2 (Equation 5.37)
ν	Average interstitial velocity, cm/s (Equation 6.2)
V_a	Molal volume of solute at boiling point, l^3/g (Equation 6.22)
V	Liquid phase volume, cm^3
W	Weight of adsorbent, g (Equation 5.8)
X	Dimensionless spatial variable (Equation 5.7)
Y	Dimensionless bulk concentration (Equation 5.7)
Y_1	Dimensionless bulk concentration for component 1, mg/l (Equation 5.29)
Y_2	Dimensionless bulk concentration for component 2, mg/l (Equation 5.29)
Y_s	Dimensionless bulk concentration at the particle surface (Equation 5.9)
$Y_{1,s}$	Dimensionless bulk concentration for component 1 at the interface (Equation 5.29)

$Y_{2,s}$	Dimensionless bulk concentration for component 2 at the interface (Equation 5.30)
z	Spatial variable, cm

Greek Letters

α	Ratio of $(1/n_{ads})/(1/n_{des})$, (Equation 4.9)
β_1,	As in Equation 4.15a
β_2	As in Equation 4.15b
τ	Dimensionless time (Equation 5.7)
ψ	Dimensionless external film resistance parameter (Equation 6.11)
ρ_l	Liquid density, gm/cc
ρ_b	Bulk density, gm/cc
ρ_p	Particle density, gm/cc (Equation 5.3)
θ	Volumetric Water content, cm^3/cm^3
ε	Porosity of the fixed bed (Equation 6.2)
ξ	Dimensionless axial distance in the fixed bed (Equation 6.10)
σ	Dimensionless equilibrium parameter (Equation 6.11)
ϖ	Dimensionless hydrodynamic parameter (Equation 6.12)
μ_l	Liquid viscosity, (g/cm s)

Subscripts

1	Solute 1
2	Solute 2

ads	Adsorption
des	Desorption
i	Component 1
j	Component 2
max	Amount adsorbed before desorption

APPENDIX 6

2,4-D	2,4-dichlorophenoxyacetic acid
2,4-DCP	2,4-dichlorophenol
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,4,5-TCP	2,4,5-trichlorophenol
Atrazine	2-chloro-4-diethylamino-6-ethylamino-*s*-triazine
BTC	Breakthrough curve
CEC	Cation exchange capacity
DCB	Dichlorobenzene
Flumetsulam	(N-2, 6-diflurophenyl-5-methyl-1,2,4-triazolo(1,5a)pyrimidine-2-sulfonamide)
HPLC	High performance liquid chromatography
HSDM	Homogeneous surface diffusion model
Imazaquin	(2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid
Imazethapyr	((±)-[2-4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid)
Linuron	3-(3,4-dichloro-phenyl)-1-methoxy-1-methyl-urea
MCPA	2-methyl-4-chlorophenoxyacetic acid
OC	Organic carbon
ODE	Ordinary differential equation
OM	Organic matter
PCE	Tetrachloroethene

PCOC	*para*-chloro-*ortho*-cresol
PCP	Pentachlorophenol
PCBs	Polychlorobiphenyls
PDE	Partial differential equation
Picloram	4-amino-3,5,6-trichloropicolinic acid
pK_a	Ionization constant
Prometryne	2,4-bis(isopropylamino)-6-methylmercapto-*s*-triazine
TCB	Trichlorobenzene
TCE	Trichloroethene
TeCB	1,2,4,5 tetrachlorobenzene
TTCE	Tetrachloroethylene

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