Phosphorus Removal Mechanisms in Soil and Slag Media

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ABSTRACT

Excessive phosphorus (P) is one of the major pollutants in natural water that are responsible for algal blooms and eutrophication. P removal by soil and slag is an attractive solution if the P sorption capacity of soil or slag is significant. To design an efficient land treatment facility, basic information on the behaviour of P in the media-water environment is required. In this study, detailed experiments were conducted to study P removal under static and dynamic conditions, and mathematical models were developed to describe these processes.

The kinetic studies on P sorption onto a sandy loam soil from North Sydney, Australia, and dust and cake waste products from the BHP steel industry revealed that P sorption is a slow process. More than 90% of the P was adsorbed within 70, 12 and 60 hours in a mixing system for soil, dust and cake respectively while it was within 240, 24 and 120 hours respectively in a static (no stirring) system. Dust adsorbed P the most, compared to the other adsorbents (220-225 times and 4-5 times of the sorptivity of soil and cake respectively). P sorption in the batch experiments was described better by an equation using the Langmuir isotherm than one using the Freundlich isotherm. The kinetics of P sorption were satisfactorily explained by a static, physical, non-equilibrium sorption model (SPNSM).

The pH of the P solution played a critical role in the extent of removal and the removal mechanisms of P. Removal was at a minimum at pH 2. The effect of pH on P removal varied depending on the type of adsorbents and the initial P concentration. The dominant removal mechanism of P at $pH<8$ was physical sorption, while it was chemical precipitation at $pH>10$. Batch flocculation experiments revealed that the P removal efficiency increased with an increase of adsorbent dose, flocculation (contact) time and mixing rate. P sorption is affected by the presence of NH_4 which competes for available sites on the adsorbents. The amount of P adsorbed by dust and cake in the presence of NH_4 was less than that in a single solute system. The reduction percentage of P for dust ranged from 33 to 57%.

Detailed column experiments conducted with soil, dust and cake as media indicated that dust and cake have much higher sorption capacities than soil. The solid phase P concentrations on dust and cake calculated from batch experimental isotherm constants are substantially higher than those estimated from the dynamic column experiments. A program to fit a generalised, non-linear, advective, dispersion model (MCMFIT) was used to estimate the optimal model parameter values. All the columns exhibited characteristic S-shaped or curvilinear breakthrough curves. The simulated results from a dynamic physical non-equilibrium sorption model (DPNSM), based on Freundlich isotherm constants K and N (obtained from column experimental results) satisfactorily matched the corresponding experimental breakthrough data. P removal under dynamic conditions was explained better as a physical non-equilibrium process than an equilibrium one. The mobility of P is restricted by the adsorbing medium and it is proportional to the sorption capacity of the adsorbents. The DPNSM predictions were better than those of the equilibrium sorption model (ESM). The ESM predictions were similar to DPNSM predictions at high influent P concentrations for dust and cake.

An increase of pH value occurred at the initial stage of P removal. This is due to the liberation of Mg^{2+} and Ca^{2+} ions into the solution from the dust and cake media. The sorption capacity of P in dust and cake columns decreased in the presence of NH_4 due to the competition for sorption sites.

Dust and cake can be applied (i) as an adsorbent in sewage treatment plants, (ii) as a substratum in constructed wetland systems and (iii) as a suppressing material for the release of P from sediments due to their high sorption capacity. The effluent concentrations of heavy metals in the dust and cake column were low enough not to harm any living organisms.

U|T|S

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CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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NOTATION

A	Cross sectional area of column (m^2)
C_r	Courant number
C	Liquid phase concentration (mg/L)
C_f	Liquid phase concentration in the film (mg/L)
C_i	Liquid phase concentration of solute i in the mixture (mg/L)
C_m	Liquid phase concentration in mobile water (mg/L)
C_o	Influent liquid phase concentration (mg/L)
D_s	Dispersion / Diffusion coefficient (cm^2/s)
$D(\Theta)$	Diffusivity as a function of water content
$D_s(\Theta,w)$	Diffusion coefficient as a function of water content (cm^2/s)
$f(C)$	Function of C (sorption isotherm)
H	Column filter depth (cm)
K	Freundlich isotherm constant, [$mg/g(L/mg)^N$]
$K(\Theta)$	Permeability as a function of water content (cm/s)
N	Freundlich isotherm constant (dimensionless)
Q	Flow rate (m^3/d)
R	Solid particle radius (m)
R_d	Retardation factor (dimensionless)
ROH	Ratio of bulk density to porosity
S	Solid phase concentration at any instant (mg/g)
S_1	Solid phase concentration on equilibrium sites (equivalent liquid phase) (mg/g)
S_2	Solid phase concentration on kinetic non-equilibrium sites (equivalent liquid phase) (mg/g)
S_{2e}	Equilibrium solid phase concentration on kinetic nonequilibrium sites (equivalent liquid phase) (mg/g)
S_f	Solid phase concentration in equilibrium with the influent liquid phase concentration (mg/g)
S_m	Maximum capacity of the filter medium to adsorb P solute (mg/g)
S_i	Sorption site i (mg/g)
X	Normalised liquid phase concentration
Y	Normalised solid phase concentration
a	Langmuir isotherm constant (mg/g)
α	Mass transfer coefficient (day^{-1})
α_i	Isotherm fitting parameter (i=1,2,3,4)
α_5	Kinetic sorption rate constant (day^{-1})

α_6	Fraction of the sites available for instantaneous sorption
b	Langmuir isotherm constant (L/mg)
β	Mass of the medium (g)
c(i)	Parameter values, i=1,NVAR.
$c_{max}(i)$	Maximum of the ith parameter
$c_{min}(i)$	Minimum of the ith parameter
d_{max}	Maximum observed concentration (mg/L)
d_{min}	Minimum observed concentration (m/gL)
ε	Porosity
Θ	Amount of liquid (water) (L)
Θi	Initial water content in the column (L)
Θ_m	Water content in the mobile phase (L)
Θ_{im}	Water content in the immobile phase (L)
k_r	Rate constant (day^{-1})
p	Column Peclet number
ρ	Bulk density (g/cm^3)
t	Time (s)
t_1	Pulse period (m)
Δt	Time step (s)
v	Darcy velocity (cm/s)
w	Pore water velocity (cm/day)
w_m	Pore water velocity in the mobile phase (cm/day)
w_s	Pore solute velocity (cm/day)
z	Distance (m)
Δz	Spatial step (m)

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I. INTRODUCTION

1.1 General

Limited water resources and increasing urbanisation require more advanced technology to preserve water quality. One of the important factors affecting water quality is the enrichment of nutrients in water bodies. This causes algal blooms and eutrophication problems. For example, more than 60% of storages which have a capacity of more than 30,000 megaliters in New South Wales, Australia, encounter eutrophication problems. Phosphorus (P) is one of the main nutrients responsible for eutrophication in closed water systems especially in lakes and highly enclosed bays where water is stagnant. The problems caused by phosphorus in waterways are not only introduced by naturally occurring phosphorus - from weathering of rocks and the decomposition of organic materials - but also by extra phosphorus which finds its way into rivers and streams. This additional phosphorus gets into waterways from many different sources such as: (i) agricultural and urban run-off, (ii) sewer overflows and (iii) sewage treatment plant (STP) effluents. The main point source of phosphorus comes from sewage treatment plants. For example, nutrient levels in the Hawkesbury - Nepean River to the west and north of Sydney, Australia are high mainly due to several STP effluent discharges. The present sewage effluent standard for P discharge into waterways is 1.0 mg/L. This effluent standard for P will become more stringent by the year 1996, being reduced to 0.3 mg/L to combat the eutrophication problem (Thomas et al., 1993).

Phosphorus removal consists of its conversion into a solid phase followed by the removal of this phase from the main waste stream. Chemical precipitation, biological removal and land treatment are presently used to remove the phosphorus in sewage treatment plants. Although chemical precipitation is a well established technology which is relatively easy to implement in the existing sewage treatment works, this technique has some major disadvantages due to the cost of chemicals and the need for handling, treatment and disposal of significant additional quantities of chemical sludge (Yamada et al., 1986; Kaneko and Nakajima, 1988; Suzuki and Fujii, 1988; Aulenbach and Meisheng, 1988; Fox et al., 1989; Roques et al., 1991). Biological processes are not attractive due to their sensitivity to environmental changes and pH variation. They cannot be relied upon to effect high removals of phosphorus (>90%) by normal biological uptake mechanisms (Jenkins et al., 1971). In biological treatment processes, the conversion of soluble P to a particulate form is by microbial growth and as a medium for biological growth, most wastewater contains an excess of P. A detailed review of biological P removal is discussed elsewhere (Raper and Barnard, 1994). Thus even those treatment plants adopting biological P removal methods apply chemical treatment as a standby method (Thomas, 1991).

Land treatment is an attractive solution if the particular soil or other media used has significant sorption (a generalised term of adsorption and absorption; definitions of terms and units are presented in Appednix A1) capacity for P (Ebers and Bischofsberger, 1990). The Sydney Water Board (1991) recommended land application of sewage effluent in areas where there are serious eutrophication problems. P removal by soil or slag waste by-products from the steel industry may be a good solution if the media used has a high sorption capacity for P. P sorption in soil and slag has been suggested as a mechanism for P removal in constructed wetland systems which are considered as an appropriate technology for P treatment in many parts of the world (Aulenbach and Meisheng, 1988; Yamada et al., 1987; Mann and Bavor, 1993). The main advantages of this method over a conventional chemical precipitation process are that it does not produce any excess chemical sludge and does not bring about excessive consumption of reagents. Furthermore, P removal by chemical precipitation (for example, lime precipitation) must be done at pHs in the range of 10.5 - 11.0. Consequently effluents require pH correction before being discharged into receiving waters. Lastly, separation of the calcium phosphate precipitate is not always easily accomplished (Roques et al., 1991).

Several researchers have investigated the utilisation of solid reagents for P removal (Yamada et al., 1986; Kaneko and Nakajima, 1988; Suzuki and Fujii, 1988; Aulenbach and Meisheng, 1988; Fox et al., 1989; Ho and Kuruvilla, 1990; Roques et al., 1991; Ho et al.,1992; James et al., 1992; Mann and Bavor, 1993). Few studies, however, have attempted to study P removal mechanisms in soil and slag media to provide basic information for the design of efficient land treatment facilities.

Estimation of the sorption rate and capacity for P in soils and slags is important in the evaluation of the P removal by these media. In order to study the transport and mobility of P in the soil or slag environment, the basic mechanisms for the attenuation of P have to be explored. The dissolved phase of the P is transported in the soil or slag by advection and dispersion in the water in which the P is dissolved (Kjeldsen, 1986). The major mechanisms affecting the transport of P are sorption-desorption, complexation and precipitation-dissolution (Borggaard, 1990; Sanyal and De Datta, 1991). Plants and micro-organisms also take up the P and affect the transport. There are numerous complex compounds and pollutants in landfill leachate, and soil or slag characteristics are very difficult to ascertain, since these media are not homogenous (Bhuvendralingam, 1987). Furthermore, the transport of the P in the solid-liquid environment is determined by the environmental conditions with which they are associated. The simultaneous presence of all elements and compounds can inhibit or accelerate the processes of P sorption, complexation, and precipitation (Crittenden et al., 1986; Kjeldsen, 1986; Bajracharya, 1989; Sanyal and De Datta, 1991)

To understand the transport phenomenon, many geochemical transport models have been developed, but very few experimental data are available to verify them. A number of models accounting for the process of solute sorption are available for saturated flow conditions. Models have also been developed considering the multi-solute sorption process. Crittenden et al. (1986) have developed sorption models incorporating solute mixing, liquid diffusion, competitive sorption etc. and have proposed numerical methods to solve the model equations. Commercial package programs (MYGRT, FASTCHEM etc.) developed by the Electric Power Research Institute, USA (1989) are available. These programs incorporate precipitation-dissolution, sorption-desorption, redox conversions and complexation for modelling chemical attenuation (Bajracharya, 1989).

For the sorption process, there is a basic difference between batch (static) and continuous (dynamic) processes. In the static process, there is a fixed amount of solute and the liquid phase concentration decreases with a corresponding increase in the solid phase concentration. The dynamic process, on the other hand, provides a continuous supply of solution to replace the solute that has been adsorbed from the liquid phase. The P solute needs to be carefully monitored under different conditions. At present, there exist several complex models to predict solute transport involving many model constants. Simple transport models with few coefficients are desirable (Bajracharya and Vigneswaran, 1990).

To design an efficient land treatment facility, basic information on the behaviour of P in the media-water environment is required. This research attempted (i) to study the transport of P in soil and slag (waste by-products from the BHP steel industry) media both under static and dynamic conditions, (ii) to devise mathematical models which can predict the P transport and removal, and (iii) to validate them with experimental data. The model formulation is limited to sorption processes under varying environmental conditions. The model coefficients evaluated from batch and column experiments have been incorporated to predict P transport. P is generally present with high concentrations of ammonium nitrogen (NH_4-N) compounds in most wastewaters. The effects of NH_4-N on the sorption of P in soil and slag have been studied to understand competitive sorption processes under static and dynamic conditions. Field applications of use of slag have also been highlighted.

1.2 Objectives of the Study

The objectives of this study are summarised as follows;

1. To study the kinetics of P, and the effects of pH, precipitation and NH_4-N on P sorption, in selected soil and slag media under static and dynamic conditions.

2. To develop mathematical models which can describe the transport and removal of P in the soil and slag studied under static and dynamic conditions and to verify these results with laboratory scale experiments.

3. To develop the concept of using slag as an adsorbent in sewage treatment, as a substratum in constructed wetland systems and as a suppressing material on the release of P from sediments.

1.3 Scope of the Study

This research included laboratory studies and mathematical modelling. They were performed to study;

1. The kinetics of P sorption in batch experiments using soil and slag under static and mixing systems.

2. The effect of pH, precipitation and foreign material as NH_4-N on P sorption in soil and slag media under static conditions.

3. Effects of influent P concentration, pore water velocity, adsorbent depth, water level above the adsorbent, and foreign material on P sorption onto soil and slag media under dynamic conditions.

4. The development and experimental validation of mathematical models under the static and dynamic conditions to predict the kinetics of P.

5. Preliminary calculations for the design of an extended constructed wetland system using slag as an adsorbent (the toxicity of the slag effluent solution was evaluated from column experiments to study the side effects of using slag in the proposed system).

1.4 Organisation of the Report

Following the introductory chapter which describes the objective and scope of the research in relation to the current status of our understanding of P removal in soil and slag media, Chapter II is devoted to a review of the literature associated with this field. In Chapter III, mathematical models are presented to describe the kinetics of P under static conditions and to predict the transport of P under dynamic conditions. In order to find the optimal model parameters, a program to fit a generalised, non-linear, advective dispersion model is used. The experimental investigations carried out in this study are presented in Chapter IV. Chapter V presents the results and discussions on the experiments and the predictions by the mathematical models. The conclusions and recommendations for future research are given in Chapter VI.

II. LITERATURE REVIEW

2.1 Phosphorus

2.1.1 Nature of Phosphorus

Phosphorus is one of the essential nutrients needed for normal growth in plants and animals. The circulation of phosphorus through the environment can be described by the phosphorus cycle (Figure 2.1). In nature most phosphorus occurs in rocks in the minerals apatite ($Ca_5(PO_4)_3F$), hydroxy apatite ($Ca_5(PO_4)_3OH$), and to a lesser extent, in combination with magnesium (Reiners, 1984). The weathering of these rocks results in the phosphate becoming dissolved in groundwater or streams. The dissolved orthophosphates are the forms that are most readily assimilated by plants (Chiswell and Hammock, 1991). The clearing of forests by man accelerates the weathering process. Mining of phosphate rock for use as fertiliser (eg. superphosphate - $Ca(H_2PO_4)_2$) greatly accelerates the transfer of phosphorus from rocks to plants.

Phosphorus in the form of orthophosphates dissolved in groundwater or streams is readily taken up by plants. Plants convert phosphate to organic forms such as proteins, nucleic acids (DNA and RNA), the energy producing compound adenosine triphosphate (ATP) and its by-product adenosine diphosphate (ADP). Animals obtain their supply of phosphorus by eating plants or other animals. In human beings phosphorus is found in DNA, RNA, proteins, ATP and ADP.

When plants and animals excrete wastes or die, the various forms of organic phosphorus in the decaying matter are mineralised by bacteria to the orthophosphate form (PO_4^{3-}). This becomes dissolved in groundwater or surface water and the cycle continues. A proportion of the orthophosphate dissolved in

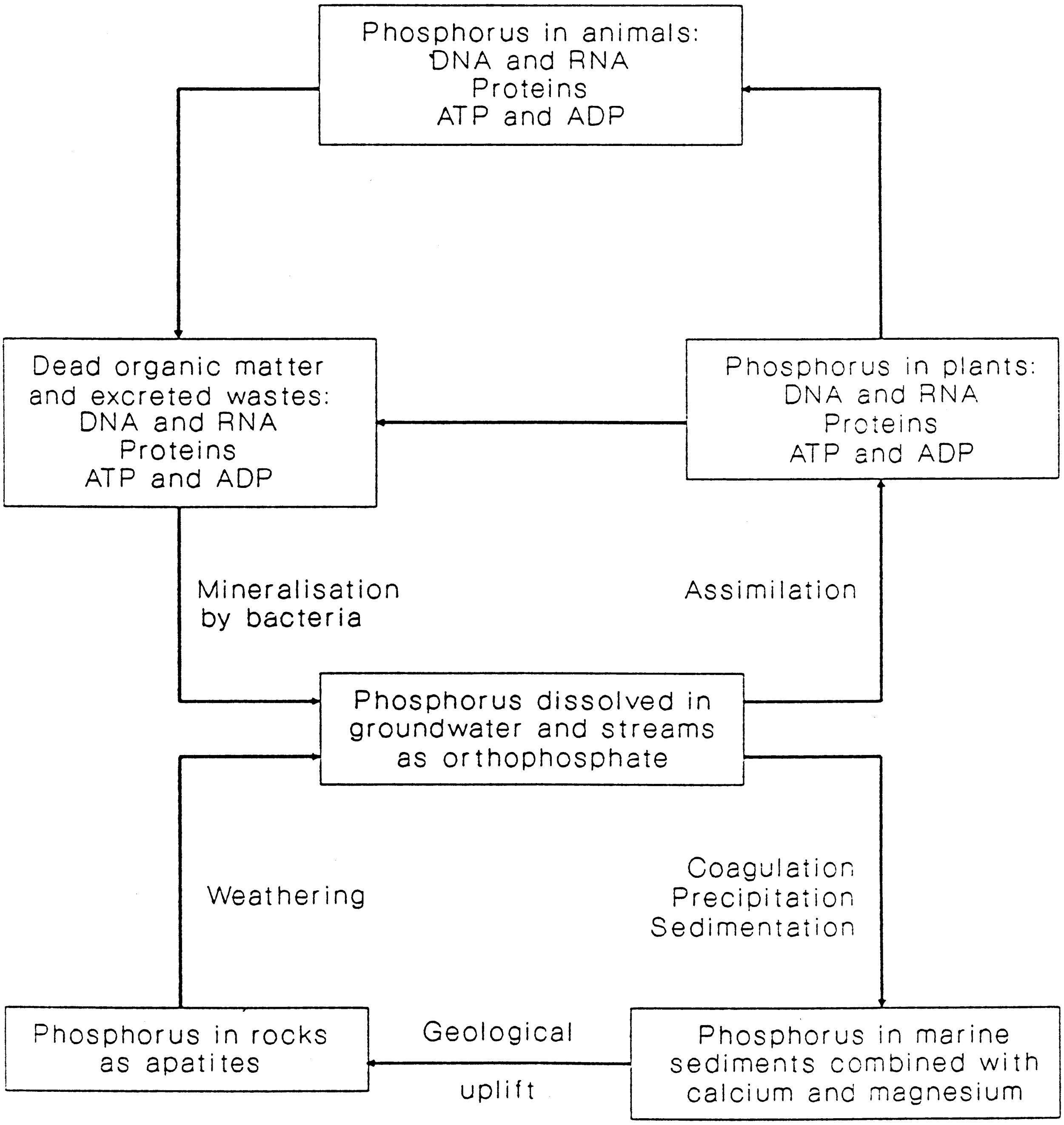


Figure 2.1 The Phosphorus Cycle (Reiners, 1984)

streams is not assimilated but finds its way into the ocean. The abundance of calcium and magnesium counter-ions in seawater causes coagulation, precipitation and sedimentation of the previously dissolved orthophosphate. Geological processes may result in the uplifting of these marine sediments, so that they are exposed to the weathering process again (Reiners, 1984).

Phosphorus is found in wastewater in three forms (US EPA, 1971):

1. Organic phosphorus compounds
2. Condensed phosphates (pyro-, meta-, and polyphosphates)
3. Orthophosphate ions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4)

The actual form of the orthophosphate (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4) is dependent on the wastewater's pH. At the usual pH of municipal wastewater (pH=6.8 to 7.5), the predominant form is HPO_4^{2-}. Domestic wastewater typically contains about 10 mg/L of P. In sewage and other natural waters phosphorus is found in the pentavalent state, tetrahedrally coordinated to oxygen atoms or hydroxyl groups. The phosphate group occurs as ortho-phosphoric acid, as condensed phosphates, in which two or more phosphorus atoms are joined by P-O-P bonds, or as organic phosphates in which P-O-C linkages are present. Each of these forms may exist in solution and as a particulate. Typical concentrations of these species are given in Table 2.1 (Jenkins et al., 1971).

The bacteria that break down organic phosphorus compounds and condensed phosphates to orthophosphate are normally found in sewage. The activated sludge process increases the concentration of these bacteria and therefore speeds up the conversion to orthophosphate. Phosphorus makes up about 2.5% of the cell mass of activated sludge (Metcalf and Eddy, 1991).

Table 2.1 Approximate Concentrations of Phosphate Forms in a Typical Raw Domestic Sewage (Jenkins et al., 1971)

Phosphate Form	P Concentration (mg/L)
Total	10
Ortho	5
Tripoly	3
Pyro	1
Organic	<1

2.1.2 Main Sources of Phosphorus

The main sources of P entering waterways vary from place to place. In metropolitan Sydney the most important P sources are sewage and sewer system overflows (Linforth, 1994). Stormwater runoff is also an important source of P. In the country side, where agriculture and animal husbandry are the main industries, runoff from areas where these activities take place contributes substantial P to soil and water bodies.

2.1.2.1 Agricultural and Animal Husbandry Runoff

This is the main diffuse source of phosphate contamination in Australia. The application of excessive amounts of P fertiliser on agricultural land and the practice of intensive animal husbandry lead to high amounts of P related discharges. The amounts of P not used by crops may accumulate in the soil. Part of this leaches in the percolating soil water to groundwater (van Riemsdijk et al., 1987)

Annual uptake rates of phosphate by crops are of the order of 70 g P_2O_5 /ha /year or 972 mol./ha/year (van der Zee, 1988). It was observed by van der Zee (1988) that soils receiving large amounts of manure formed an almost P-saturated top soil. This is hazardous as it leads to surface water and groundwater contamination in areas such as the Hawkesbury-Nepean catchment in New South Wales, where intensive agriculture and animal husbandry are practiced (Thomas, 1991).

2.1.2.2 Sewer Overflows

Within the Sydney region the second most important source of pollution is sewer overflows. During intense rainfall periods, sewer overflows occur due to excessive inflow and infiltration of stormwater into the sewerage system. Once the hydraulic capacity of the sewerage system is exceeded, sewage may overflow into waterways. During storms, sewer overflows may occur via approximately 3000 designed overflow structures in Sydney, constructed to ensure emergency pressure relief and to protect people from direct exposure to sewage effluent in their homes or property (Linforth, 1994). A large number of surface fitting discharge points, such as manholes, may also overflow during wet weather.

2.1.2.3 Effluents from Sewage Treatment Plant

The main point source of phosphate comes from the effluents in sewage treatment plants. Accelerated eutrophication in many waterbodies in the United States, Europe and Australia has been stimulated by, and has appeared concurrently with, increasing inputs of treated sewage effluents. The amounts of phosphorus remaining after partial removal through treatment in plants are carried along with the sewage effluent when this is discharged into the environment. The New South Wales Clean Waters Act (1970) requires that each sewage treatment plant (STP) has a licence specifying what it may discharge (Thomas, 1991). The licence requirements are set by the EPA after negotiations with water boards and municipalities operating STPs. The major source of phosphorus in municipal wastewater is detergents (Henderson-Sellers, 1984). A commonly used compound in detergents is sodium tripolyphosphate ($Na_5P_3O_4$). Chiswell and Hammock (1991) reported that between 50% and 65% of phosphates in domestic effluents were due to detergents.

2.1.3 Problems Caused by Elevated Phosphorus Concentrations

Eutrophication is a process that involves the ageing of a body of water (Henderson-Sellers, 1984). Natural eutrophication occurs over geological time spans. Of greater concern, however, is the accelerated eutrophication caused by the activities of today's society which increases the nutrient concentration in waterways. Nutrient enrichment in waterways causes increased growth of aquatic plants and phytoplankton. Algal growth in waterways tends to be seasonal and cyclic (Chung, 1990). In summer, higher water temperatures encourage increased rates of biological activity. The cycle that algae blooms follow has a period of rapid exponential growth, and then a period of massive death and decay of the plant material.

Eutrophication is more likely to occur in places where nutrients tend to accumulate, such as lakes, reservoirs, sluggish streams, and poorly flushed estuaries (Barnes et al., 1986). The Hawkesbury-Nepean River, NSW, has a history of problems with eutrophication (SPCC, 1983). These are exacerbated during periods of low flow in the river and high water temperatures during summer.

A specific problem associated with eutrophication is blooming of blue green algae, such as the Microcytes and Cyanophyceae species. Blue green algae discolour the water, cause taste and odour problems, and release toxins which can poison aquatic plants and animals, and terrestrial animals that drink the water (Sydney Water Board, 1991). For example, it was reported in the media that during November 1991, blooms of blue green algae in the Darling River, NSW, caused the death of about 150 cattle and 300 sheep. By killing off competing organisms, the blue green algae becomes the predominant species. From an environmental viewpoint an ecosystem with a low diversity of species is undesirable (Thomas, 1991).

Aquatic plant growth requires a Nitrogen to Phosphorus (N:P) ratio of approximately 16:1. If the N:P ratio is lower than 16:1, then the ecosystem is said to be nitrogen limited. Under these conditions blue green algae can thrive. Blue green algae has an ability to fix nitrogen directly from the atmosphere, whereas most organisms require nitrogen to be in the form of nitrate or ammonia. Therefore, the growth of blue green algae is limited by the availability of phosphorus because they will have an abundant supply of nitrogen from the atmosphere (Henderson-Sellers, 1979).

Blue green algae are primitive photosynthetic organisms which are found in many environments, notably inland waterways, estuaries and the sea. In Australian waters, two genera of blue green algae, Microcystis aeruginosa and Anabaena circinalis, dominate the records of nuisance blooms. For 1991/92 the NSW Blue Green Algae Task Force reported 48 waterways throughout the state with blue green algae blooms, of which 30 were regarded as serious events, having the potential to cause problems with water resources use. Maintaining N:P ratios greater than 16:1 in a waterway is prudent. It appears that the only reliable method of preventing blue green algae blooms is to maintain the phosphorus concentration in the river below 0.05 mg/L (Sydney Water Board, 1991).

2.1.4 Phosphorus in New South Wales Waterways

The challenge facing NSW is to minimise the input of phosphorus to the state's waterways. Various trophic classification models predict that the phosphorus levels in NSW waters can cause significant water quality problems (NSW Blue Green Algae Task Force, 1992). The median levels of phosphorus exceed a nominated desirable level of 0.05 mg/L at 60% of sites sampled throughout the state; with exceedances occurring in all western river basins and some coastal basins. Over the past 18 years, total phosphorus levels have risen by an average rate of 5% per year statewide. There have been significant increases in the Namoi and Hunter valleys. North-western basins generally have the highest phosphorus values (Darling, Intersecting Streams and Border Rivers, Gwydir) or the greatest upward trend (Stevenson, 1993).

According to the report by the NSW Blue Green Algae Task Force (1992), estimates of the total nitrogen to total phosphorus ratio (N:P ratio) for the Darling River at Burtunby from 1978 to 1986 was about 3:1. The N:P ratio less than 29:1 accelerates algal blooms (NSW Blue Green Algae Task Force, 1992). Nitrogen to phosphorus ratios of this magnitude favour the growth of nitrogen fixing blue green algae. In the case of the 1991/92 bloom in the Darling and Barwon Rivers, the total nitrogen to total phosphorus ratio was 5:1. The dominant algae present in the bloom was the nitrogen fixer Anabaena circinalis (Sainty and Jacobs, 1994). The only satisfactory way of changing these ratios will be the selective management of phosphorus sources in the Darling River Basin.

The New South Wales Clean Waters Act (1970) requires that STPs have a licence specifying what they may discharge. The licence requirements are set by the Environmental Protection Authority (EPA) after negotiations with water boards and municipal STP operators. They are set out in probabilistic terms. A fifty percentile and ninety percentile limit for effluent phosphorus discharge is specified. To comply with the fifty percentile licence limit, more than fifty percent of the samples of effluent collected and analysed must be lower than the limit. Similarly, to comply with the ninety percentile licence limit, more than ninety percent of the samples must be lower than the limit. Table 2.2 shows the 1991/92 financial year licence limits, the actual discharges and the loading rates for the Sydney Water Board STPs in the Hawkesbury Nepean Catchment.

The Environmental Protection Authority (EPA) asked the Water Board to investigate the technical feasibility of upgrading the Board's twenty three STPs that discharge to the Hawkesbury-Nepean River system, so that they would meet a 90%ile value of 0.3 mg/L for total phosphorus in effluents. Although many STPs comply with their existing licence conditions for nutrient levels in discharges, none of the plants are presently achieving this target effluent quality. In order to achieve the EPA's targets, the Water Board has been reviewing the available technology (Thomas, 1991).

Currently 12 of the 23 Sydney Water STPs that discharge to the Hawkesbury-Nepean River system use chemical phosphorus removal. The chemical process used involves the precipitation of phosphorus by dosing the wastewater with iron salts. Spent pickle liquor (SPL) from steelworks is one of the sources of the iron salts. The SPL commonly contains about 10% (by weight) of iron, most of which is in the ferrous (Fe^{2+}) form (Chung, 1990). The SPL is dosed either before the primary sedimentation tanks or before the aeration tank. The ferrous iron tends to be oxidised into ferric iron (Fe^{3+}) after it is dosed to the sewage (ICI currently produces an iron salt which is used more than the SPL).

Some phosphorus is contained in the suspended organic material and is removed during the primary sedimentation process, while biological uptake of phosphorus occurs during the secondary treatment. The amount of phosphorus commonly removed by biological uptake during secondary treatment is about 2 to 3 mg/L.

Table 2.2 EPA Licence Limits, Actual Effluent Quality and Loading Rate for the Discharge of Phosphorus in the Hawkesbury-Nepean Catchment (Thomas, 1991)

STP	Licence Limits (mg/L)		Actual Effluent Quality (mg/L)		P Loading
	50%ile	90%ile	50%ile	90%ile	(kg/day)
St. Marys	2	4	0.8	3.0	29.5
Quakers Hill	2	4	1.9	4.3	41.0
Penrith	3	5	2.3	5.7	36.6
West Hornsby	2	4	0.9	2.7	8.1
Castle Hill	2	4	0.4	1.4	2.4
West Camden	2	4	1.0	1.1	5.4
South Katoomba	NLL	NLL	1.8	2.7	9.4
Hornsby Heights	2	4	1.2	5.7	5.9
Richmond	NLL	NLL	6.9	9.0	22.8
Winmalee	NLL	NLL	6.4	7.6	19.8
Glenbrook	2	4	1.3	2.4	3.9
Riverstone	2	4	0.5	1.8	0.9
Hazelbrook	NLL	NLL	7.5	9.7	12.0
Wentworth	NLL	NLL	6.4	7.5	9.6
North Katoomba	NLL	NLL	2.2	2.7	2.9
Blackheath	NLL	NLL	6.1	6.9	7.3
Mt. Riverview	NLL	NLL	11.4	13.6	10.3
North Richmond	NLL	NLL	7.4	9.1	5.9
Kellyville	NLL	NLL	9.6	12.9	6.7
Valley Heights	NLL	NLL	6.5	10.7	3.3
Warragamba	NLL	NLL	5.2	8.0	2.6
Round Corner	NLL	NLL	9.3	11.0	2.8
Mt. Victoria	NLL	NLL	3.7	6.1	0.4

NLL: Non Licence Limit

However, during anaerobic digestion of the sludge from these processes, some phosphorus is released back into the supernatant in the form of dissolved orthophosphate (PO_4^{3-}). The digester supernatant is usually returned to the head of the works and unless it is treated, the net phosphorus removal from the wastewater flow stream is reduced (Illungkoo, 1994).

At Penrith STP, a combination of biological and chemical phosphorus removal processes is used. It is the only Water Board STP designed to remove significant amounts of phosphorus biologically. The 50 percentile total phosphorus (TP) concentration in the plant effluent during 1990/91 was 2.3 mg/L (Thomas, 1991).

The median and range of 50 percentile concentrations of total phosphorus in effluent discharged to the river system by STPs with and without SPL dosing are given in Table 2.3. Superior phosphorus removal is achieved at STPs where chemical phosphorus removal is currently used. However, it appears that in order to achieve a 90 percentile TP effluent concentration of 0.3 mg/L (or 50 percentile TP = 0.2 mg/L), chemical dosing prior to the tertiary treatment is also required. If SPL dosing is optimised so that the secondary clarifier effluent has a 50 percentile TP = 1.0 mg/L, then a further 70% removal of phosphorus is required to obtain a final effluent TP = 0.3 mg/L (Illungkoo, 1994).

Table 2.3 Effluent Total Phosphorus Concentration According to Treatment Process (Thomas, 1991)

	Median (mg/L)	Range (mg/L)
With SPL dosing	1.25	0.4 - 6.5
Without SPL dosing	6.90	1.8 - 11.4

The numbers in Table 2.4 show that the Water Board must meet the effluent standard set by the EPA if the EPA is to achieve its aim of improving water quality in the Hawkesbury-Nepean River. In order to meet the EPA target performance levels, the following major changes are required at the Board's STPs; (i) increased plant capacity to allow for projected population increases, and (ii) increased phosphorus removal efficiency to reduce effluent phosphorus concentrations.

Table 2.4 Predicted Future P Loads to the Hawkesbury-Nepean River (Thomas, 1991)

Year		1990/1991	2000
Average Dry Weather Flow (ML/day)		125.4	233.7
P Load (tonnes/year)	STP effluent	119.0	68.2
	Stormwater and Agricultural Runoff	760.0	930.0
	Total	879.0	998.0

2.2 Physico-chemical Phosphorus Removal Process

For technical, economical and environmental reasons, land treatment of wastewater is becoming recognised as a viable alternative to stream discharge. Advanced nutrient treatment methods are costly and may be unreliable in terms of P removal compared with land treatment. With proper management, many soils have a high capacity for removing P from wastewater, and can often reduce it to less than 0.05 mg/L. In land treatment of wastewater, P is usually applied frequently in small amounts, as compared with agricultural fertilisation practices. This is sufficient to cause significant differences in the chemical reactions of P between the two systems. Movement of P in soils is largely dependent on the rate and extent of removal by the soil. The potentially important mechanisms of P removal in land treatment are sorption-desorption and precipitation-dissolution reactions (Sanyal and De Datta, 1991).

2.2.1 Principle of Sorption

Sorption is a surface phenomenon which is defined as an increase in concentration of a particular component at the surface or interface between two phases. In any solid or liquid, atoms at the surface are subject to unbalanced forces of attraction perpendicular to the surface plane. These forces are merely extensions of the forces acting within the body of the material and are ultimately responsible for the phenomenon of sorption. In discussing the fundamentals of sorption, it is useful to distinguish between physical sorption, involving only relatively weak intermolecular forces, and chemisorption, which involves essentially the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent. The sorption of solutes from solution by an adsorbent depends on physical sorption rather than chemisorption. Physical sorption from the liquid phase is invariably exothermic. Physical sorption can be distinguished from chemisorption according to one or both of the following criteria (Samuel and Osman, 1987):

1. Physical sorption does not involve the sharing or transfer of electrons and thus always maintains the individuality of interacting species. The interactions are fully reversible, enabling desorption to occur without changes of temperature, although the process may be slow because of diffusion effects. Chemisorption involves chemical bonding and is irreversible.

2. Physical sorption is not site specific; the adsorbed molecules are free to cover the entire surface. In contrast, chemisorption is site specific; chemisorbed molecules are fixed at specific sites.

2.2.2 Sorption - Desorption

The sorption of phosphorus by soil or slag implies removal from P solution and retention on soil surfaces. If the P is restricted to the surface this is regarded as an "adsorption" reaction. This might be followed by a more or less uniform penetration of P into the solid phase, which is regarded as an "absorption" reaction. Because of the difficulty in distinguishing these two reactions (Glasstone, 1959), the less specific overall term "sorption" is frequently used. The reverse reaction, desorption, describes the release of sorbed P back into solution. For obvious reasons, the balance between sorption and desorption to a large extent influences the concentration of P in the soil solution (Sanyal and De Datta, 1991).

2.2.3 Sorption Equilibrium

Sorption from aqueous solutions involves concentration of the solute on the solid surface. As the sorption process proceeds, the sorbed solute tends to desorb into solution. Eventually, the rates of sorption and desorption will attain at equilibrium state, called "sorption equilibrium". At equilibrium, no change is observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system, the solute, adsorbent, solvent, temperature, pH, and so on. Adsorbed quantities at equilibrium usually increase with an increase in the solute concentration (Samuel and Osman, 1987).

The relationship between the amount of P adsorbed per unit weight of soil or slag and the equilibrium P concentration in solution at a constant temperature has been described by several sets of sorption isotherms. The main motivations for describing sorption curves were (i) to identify the soil or slag constituents involved in sorption (Adams et al., 1987; Loganathan et al., 1987) and (ii) to study the nature of the sorption process to learn more about the mechanism of the process (Barrow, 1987).

The shape of the sorption isotherm relating liquid and solid phase concentrations gives quantitative information about the sorption process and the extent of the surface coverage by the adsorbate. Smooth sorption isotherms are usually obtained because of the presence of a sufficiently large number of sites that may occur in patches of equal energy or randomly distributed sites of unequal energy. Several types of isotherms are used to describe the sorption data. The Langmuir and Freundlich sorption isotherms are the most common ones.

2.2.3.1 Langmuir Sorption Isotherm

The basic assumptions underlying Langmuir's model (the ideal localised monolayer model) are:

1. The molecules are adsorbed on definite sites on the surface of the adsorbent.
2. Each site can accommodate only one molecule (a monolayer).
3. The area of each site is a fixed quantity determined solely by the geometry of the surface.
4. The sorption energy is the same at all sites.

The Langmuir equation was originally derived from kinetic considerations (Langmuir, 1915). Later, it was derived on the basis of statistical mechanics, thermodynamics, the law of mass action, theory of absolute reaction rates, and the Maxwell-Boltzmann distribution law (Young and Crowell, 1962). The Langmuir isotherm is expressed mathematically as follows:

$$S=\frac{abC}{1+bC} \qquad \text{... (2.1)}$$

where, a,b = Langmuir isotherm constants

S = Solid phase concentration (mg/g)

C = Liquid phase concentration (mg/L)

The Langmuir isotherm is an empirical model which cannot explain precipitation reactions or changes in the homogeneity of surfaces. Samuel and Osman (1987) commented that the assumptions in the Langmuir isotherm which include one layer sorption and consistent sorption energy, limit its usefulness. Phosphorus can be energetically adsorbed at different sites on a soil surface or occur in layers on surfaces or precipitate as the phosphate ion (Sanyal and De Datta, 1991).

2.2.3.2 Freundlich Sorption Isotherm

Freundlich sorption equation has been the most widely used mathematical description of sorption in aqueous systems (Freundlich, 1926; Buchter et al., 1989). The Freundlich isotherm is expressed as:

$$S = KC^{1/N} \qquad \text{... (2.2)}$$

where,

K,N = Freundlich isotherm constants

Some researchers tend to attach less significance to the Freundlich equation because it does not provide any measure of a "sorption maximum" in which soil scientists are primarily interested. Nevertheless, the Freundlich coefficient, K, may be regarded as a hypothetical index of P sorbed from a solution having unit equilibrium concentration. In a recent study on P sorption in a number of acid and acid sulphate soils of South and Southeast Asia, a high degree of correlation was found between the Freundlich K and the Langmuir sorption maximum (Sanyal and De Datta, 1991).

More importantly, the Freundlich equation, although originally empirical, was derived rigorously by Sposito (1984). It implies that the affinity (bonding energy) decreases exponentially with the increasing surface coverage, a condition which is perhaps nearer to reality than the assumption of constant bonding energy in the Langmuir equation.

2.2.4 Kinetic Sorption Theory

Sorption of various compounds in aqueous systems onto an adsorbent is a time-dependent process. Figure 2.2 shows that sorption processes occur over a wide range of time scales (micro-seconds to months) compared to the other processes.

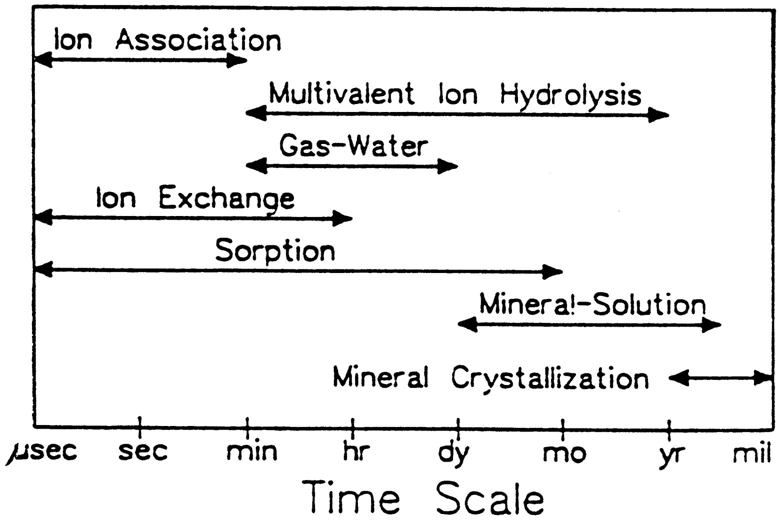


Figure 2.2 Time Scale of Different Processes (Borggaard, 1990)

It is imperative for design to have knowledge on the rate of uptake of solute by adsorbents in different processes such as batch reactors, fixed beds and fluidised beds. It is also important to identify the steps in the adsorptive process, and which of these controls the rate of sorption.

The first step of transport of the adsorbate from bulk solution to the outer surface of the adsorbent granule is by molecular diffusion. This is called external or film diffusion. The concentration gradient in the liquid film around the granule is the driving force for the film diffusion. The second step, termed internal diffusion, involves transport of the adsorbate from the particle surface into interior sites by diffusion within the pore-filled liquid and migration along the solid surface of the pore (surface diffusion) (Keinath and Weber, 1968; Weber, 1972). Because these two transport processes act simultaneously, the more rapid one will control the overall rate of transport. The third step is the sorption of the solute on the active sites on the interior surfaces of the pores. Since the sorption step is very rapid, it does not influence the overall kinetics (Smith, 1968; Weber, 1972). The overall rate of the sorption process, therefore, will be controlled by the slowest step, which would be either film diffusion or internal diffusion. However, control might also be distributed between inter-particle and external mechanisms in some systems (Fritz et al., 1980).

Rates of sorption are usually measured by determining the change in concentration of the solute in contact with the adsorbent as a function of time. Variation of the rate with concentration is not linear, which is expected from diffusion theory. Therefore, the concentration dependence of the sorption rate can be used to identify the rate-limiting step (Samuel and Osman, 1987).

2.2.4.1 Kinetics of Soil and Slag Reactions

The kinetics of P are the time-dependent processes, which are also path dependent (Amacher, 1988). A number of methods have been developed to obtain experimental kinetic data and to analyse the data to arrive at a correct interpretation of the processes responsible for the observed time-dependent phenomena. Some of the methods that have been developed for obtaining and analysing kinetic data for soil and slag systems are: relaxation, batch and flow methods.

Chemical reactions in soils are generally heterogeneous solid-liquid reactions involving a solid component of the soil and the solution. The main chemical processes involved are complexation, ion exchange, dissolution etc. In order to assess the kinetics, one should consider the nature and the rate of the transport processes associated with the chemical reaction: flow and diffusion in the solution, transport across the solid-liquid interface, diffusion in liquid-filled pores and micropores, and surface diffusion penetration into the solid adsorbent (Figure 2.3).

2.2.4.2 Phosphorus Sorption Kinetics

The reaction of P with soil and its kinetics have been studied by Beek and van Riemsdijk (1982). In the non-calcareous, sandy soils the reaction of P is predominantly with the oxides of Al found in the solid phase (Beek, 1979).

The reaction of P with soil was described mathematically using a variety of expressions including the Langmuir and Freundlich isotherms and rate equations (Sibbesen, 1981). Most of the research on the sorption of P to soil particles had been related to wastewater irrigation. Recently there is also an extremely large research and literature on depth related to agricultural/fertiliser/flooded soil dynamics of P and soil interaction. The Freundlich and Langmuir equations describe the initial reactions of solutions containing 20 mg/L or less soluble P in soils (Youssefi, 1978). In the case of P, sorption is slow, so the equation should be used with a kinetic model to predict the mobility of phosphorus.

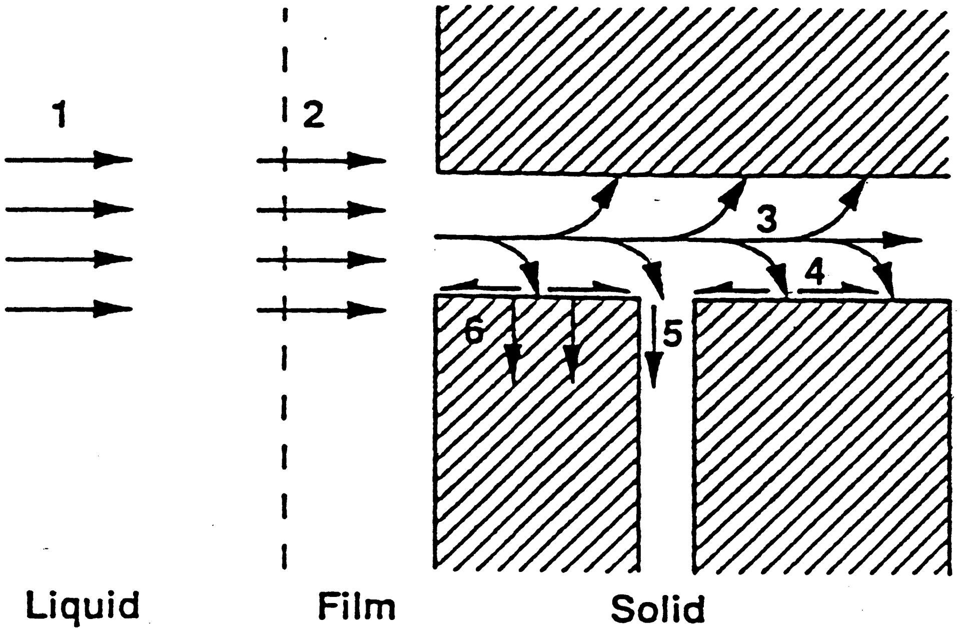


Figure 2.3 Transport Processes in Solid-Liquid Soil Reactions

(A) Nonactivated processes: 1. Transport in the soil solution, 2. Transport across a liquid film at the solid-liquid interface, 3. Transport in a liquid-filled micropore ; (B) Activated processes: 4. Diffusion of a sorbate at the surface of the solid, 5. Diffusion of a sorbate occluded in a micropore, 6. Diffusion in the bulk of the solid (Borggaard, 1990).

2.2.5 Factors Affecting the Rate of P Sorption

Molecules of the solute are removed from solution and taken up by the adsorbent during the process of sorption. The molecules are adsorbed onto the surface area within the pores of adsorbent particle and on the outside surface of the particle.

The transfer of solute from solution to adsorbent continues until the concentration of solute remaining in solution is in equilibrium with the concentration of solute adsorbed by the adsorbent. When equilibrium is reached, the transfer of solute stops. At equilibrium, the distribution of solute between the liquid and solid phases is measurable and well-defined (Samuel and Osman, 1987).

The equilibrium distribution of solute between the liquid and solid phases is an important property of sorption systems and helps in defining the capacity of a particular system (Faust and Aly, 1983). Of equal importance to the sewage engineer are the kinetics of the system which describe the rate at which this equilibrium is reached. The rate of sorption determines the detention time required for treatment and thus the size of adsorbent contacting systems (Samuel and Osman, 1987).

The following factors are considered to influence the rate and extent of sorption reactions (Samuel and Osman, 1987).

2.2.5.1 Hydrogen Ion Concentration (pH)

In general, the H^+ (or OH^-) affects adsorptive processes through dissociation of functional groups on the adsorbate and adsorbent. As an example, a pronounced effect of OH^- was observed on the rate of sorption of 4-chlorophenol onto Columbia LCK carbon (Zogorski, 1976). A sharp decrease in the removal rate above a pH value of 7.5 was observed. The pKa value for this phenol is 9.4, whereupon the anionic form of the phenol is adsorbed at a rate considerably slower than the associated form. However, the rate of sorption at neutral pH values was observed to have no adverse effect in the treatment process.

2.2.5.2 Temperature

The temperature at which a sorption process is conducted affects both the sorption rate and the extent to which sorption occurs. Sorption rates increase with the increase in temperature. As sorption is an exothermic process, the degree of sorption is relatively low at lower temperatures and greater at higher temperatures (Samuel and Osman, 1987). The well-known Arrhenius equation describes this effect of temperature on reaction rate. Some investigators offer this effect as evidence for a diffusion-controlled process (Weber and Morris, 1963).

2.2.5.3 Liquid Phase Concentration

For an experimental study with alkyl benzene sulfonates on activated carbon, removal rates of alkyl benzene sulfonates were observed to increase non-linearly with increasing concentration. The removal rate was increased as the initial concentration of the adsorbate was increased (Zogorski, 1976). Concentration dependence of the rate of sorption is used to define the rate-limiting step in the reaction. When intra-particle transport limits the kinetics of a sorption reaction, the variation in reaction rate is not expected to be linear, whereas the rates of strictly adsorptive reactions and simple diffusion-controlled processes are expected to be proportional to the first power of the adsorbate's concentration (Helfferich, 1962).

2.2.5.4 Molecular Size and Configuration of the Adsorbate

The size of the diffusing molecule affects the overall rate of sorption. The larger the molecule, the slower is the rate at which it diffuses and also the slower the rate of sorption. The sorption experiments with detergent and activated carbon indicated that the length of the aliphatic hydrocarbon chain on the detergent molecule affects the rate of uptake (0.126 mm carbon). The larger the chain and the higher the molecular weight, the slower the rate of sorption (Weber and Morris, 1963; Zoroski, 1976).

Another molecular property to affect the rate of sorption is the configuration of the adsorbate. The effects of this property on the removal rate of sorption of alkyl benzene sulfonates were studied using compounds with the same molecular weight but with different structures by Weber and Morris (1963). They reported that within a homologous series of aliphatic acids, aldehydes, or alcohols, sorption usually increases as the size of the molecules increases.

2.2.5.5 Characteristics of the Waste

The presence of organic and inorganic affects phosphorus speciation. Besides, there is a competition in the type of complex formation. Competing cations like Ca^{2+} in the solution decrease the phosphorus sorption by drastic amounts. The degree of competition for sorption site for various cations varies (Tiwaree, 1989; Bajracharya and Vigneswaran, 1990).

2.2.5.6 Agitation

The rate of sorption is controlled by either film diffusion or pore diffusion, depending on the amount of agitation in the system (Samuel and Osman, 1987). If relatively little agitation occurs between the particle and the fluid, the surface film of liquid around the particle is thick and film diffusion will be the rate-limiting step. Providing adequate mixing, the rate of film diffusion increases to the point that pore diffusion becomes the rate-limiting step (Faust and Aly, 1983). According to Weber (1972), pore diffusion is generally the rate-limiting factor for batch-type contact systems which provide a high degree of agitation.

Film diffusion will be the most likely rate-limiting step for continuous-flow systems.

2.2.5.7 Characteristics of the Adsorbent

Particle size and surface area are the important properties of adsorbents. Sorption rates increase as particle size decreases. The total adsorptive capacity of a adsorbent depends on its total surface area. Characteristics such as cation exchange capacity (CEC), organic content etc. affect the phosphorus retention property of soil/slag matrices. The higher the value of CEC, the higher is the sorption rate. This is also the case with organic matter. The properties of soil influence P sorption by soil minerals and sediments. These include the nature and amount of soil components (eg. clay, organic matter, and hydrous oxides of iron and aluminium); the concentration of the background electrolyte and the valency of the constituent cation; and the pH of the sorption system (Sanyal and De Datta, 1991).

(a) Iron and Aluminium Oxides and Hydroxides

Of the soil properties tested by Buchter et al.(1989), acid ammonium oxalate extractable (amorphous) iron and aluminium proved to be an important criterion for P sorption in several soils. Oxalate extraction is known to dissolve amorphous and poorly crystalline oxides of iron and aluminium while having little or no effect on crystalline iron and aluminium minerals. Crystalline iron oxides are relatively inactive in P sorption (Ryden and Pratt, 1980). The difference in P sorption capacity between fresh soil, and soil after extraction with oxalate showed that a high proportion of P sorption was attributable to poorly ordered minerals (Buchter et al., 1989).

(b) Clay

A significant correlation of P sorption parameters with clay content has been reported by several researchers (Loganathan et al., 1987; Solis and Torrent, 1989; Bennoah and Acquaye, 1989). Clays contributed to P sorption in tropical soils, especially at low pH, when the activity of iron and aluminium is expected to be higher.

Hydrous oxides of iron and aluminium have been found to occur as fine coatings on surfaces of clay minerals in soil (Haynes, 1982). These coatings, characterised by large surface areas, hold an appreciable quantity of P, thereby implying a secondary role of crystalline alumina-silicates (clays) in P sorption (Ryden and Pratt, 1980). Agboola and Ayodele (1983), however, reported no correlation between P sorption maxima and the clay content of soils.

(c) pH and Supporting Electrolytes

There is considerable controversy regarding the effect of pH on P sorption in soils and slags (Barrow, 1987). A decrease in sorption with an increase in pH was reported when dilute solutions of NaCl or KCl was used to measure P sorption. But when a dilute $CaCl_2$ solution was used, P retention by a limed soil increased (Naidu et al., 1990).

It was suggested that the freshly precipitated iron and aluminium oxides (at pH 6.5) were responsible for the increase in P sorption. P sorption on goethite was found to be less dependent on pH when $CaCl_2$ (rather than NaCl) was used as the electrolyte (Parfitt, 1978). Mokwunye (1975) reported a positive effect of pH on P sorption by some soils from the savanna zones of Nigeria. He concluded that this could be associated with the P retention by an activated hydroxy-aluminium species (at pH 5.0) that held P through the surface-exchange of a hydroxyl group. Naidu et al. (1990) reported an increase in P sorption by strongly acidic soils on liming. They attributed this rise to the formation of insoluble Ca-P compounds. Smillie et al. (1987) proposed a chemical association between sorbed P and Ca in soils as an important P retention mechanism. These soils had adequate exchangeable Ca.

(d) Organic Matter

Several researchers have reported on the correlation between organic matter content in soil and P sorption (Bennoah and Acquaye, 1989; Sanyal et al., 1990). Sanyal and De Datta (1991) reported that P sorption by volcanic soils can be correlated with organically bound aluminium, and to a lesser extent, with iron (extracted by sodium pyrophosphate).

Reduction of P sorption by organic matter in soils has been observed by Andereg and Naylor (1988). This can be explained by a possible competitive action between P and organic matter for sorption sites on, for instance, hydrous oxides of iron and aluminium. Earl et al. (1979) noted that citrate, tartrate and acetate were effective (in this order) in reducing P sorption by soils, synthetic iron, and aluminium oxide gels, in contrast with the behaviour of inorganic anions. Ryden et al. (1987) have shown that except for the OH^- ion, inorganic anions have alimented ability to compete with P for sites on hydrous ferric oxide gel. Yuan (1980) also supported the idea that some of the sorption sites for P and organic matter in soils are common. This leads to a competitive effect. In a study conducted by Sanyal et al. (1990), P sorption per unit weight of clay or organic matter was found to increase with a decrease in clay or soil organic matter content.

(e) Free Iron

A correlation between initial P sorption and free iron oxides was reported by Solis and Torrent (1989). Sanyal et al. (1990) obtained significant correlations for iron oxide (active iron) with the Langumir sorption maximum and the Freundlich isotherm constant K. The bonding energy, on the other hand, was not well correlated. Bonding energy was also less strongly correlated with the clay and the organic matter contents of the soils as compared with the above two indexes of P sorption. This indicates that the amount of P sorbed is a function of the number of sorption sites rather than of their bonding energy (Sanyal and De Datta, 1991).

2.2.6 Kinetic Equations

The study of the kinetics of P sorption and release by soils is of considerable interest in soil and environmental science. The time factor is certainly of relevance for P uptake by plants. However, comparisons among soils on the basis of rate constants alone do not seem to be of great practical value, since amounts of P desorbing during any time interval would also depend on the reserve of desorbable P present (Pavlatou and Polyzopoulou, 1988). On the other hand, a better understanding of the energetics of P sorption, based on kinetic studies, may help elucidate mechanisms of P sorption-desorption in soils.

The reaction between P and soils is rapid for the first few hours. It then becomes slow, and continues for a very long time (Bolan et al., 1985; Al-Khateeb et al., 1986). In many cases, it is doubtful whether a true equilibrium is reached within a practicable reaction period, although an apparent equilibrium is possible within a reasonable period. This has led several authors to use a variety of equilibrium isotherms to describe P sorption and desorption by soils.

A number of kinetic equations have been used by several investigators (Table 2.5). Extensive (Sparks, 1986), as well as brief (Pavlatou and Polyzopoulos, 1988) reviews of these kinetic equations have been published to describe P sorption and desorption rates.

Table 2.5 Summary of Kinetic Equations used for P Reaction with Soil Constituents (Bolan et al., 1985)

Equation	Assumptions
First order kinetics $\log C = \log C_o - K_t$	Rate of change in concentration is proportional either to the concentration in solution or to the number of empty sites
Second order kinetics $(1/C_o)-(1/C) = K_t$	Rate of change in concentration is proportional to both the concentration in solution and the number of empty sites
Diffusion equation $X = R\sqrt{t} + b$	Rate limiting step is the diffusion of phosphate ions either from the solution to the surface or from the surface to the interior of the particle
Modified Langmuir equation $X = b_1 + \Delta b_2 + \frac{b_{ii}K_{ii}C}{1+K_{ii}C} + \frac{b_{iii}K_{iii}C}{1+K_{iii}C}$	Rate of sorption is proportional to the concentration in the solution and the number of empty sites
Modified Freundich equation $X = KC^b t^{b1}$	Phosphate reaction in soil system contains three compartments, A,B and C and reacts according to A $\Leftrightarrow$B$\Leftrightarrow$C; rate limiting step is B$\rightarrow$C
Elovich equation $X = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$	Activation energy of sorption increases linearly with surface coverage

Note: Where X is the amount of phosphate sorbed, C_o and C are the initial and final concentrations of phosphate in solution, t is the time, and all other variables are empirical parameters.

In many studies (reviewed by Sparks, 1986), the experimental data were inadequately described by a single first-order kinetic reaction, and were often interpreted as a combination of two or three simultaneous first-order reactions, corresponding to conceptually distinct transformations of different forms of Ca-P compounds (in soil) having varying degrees of crystallites and solubilities. The temperature dependence of P sorption and release by several soils and soil minerals has been found to be generally small, leading to low activated energies of the processes. This tends to show that sorption-desorption processes are diffusion controlled (Sparks, 1986).

Enfield et al. (1976) fitted the P sorption kinetic data to five kinetic models, namely, a linearised first-order sorption, a first-order Freundlich sorption, an empirical function, a diffusion-limited Langmuir sorption, and a diffusion-limited Freundlich sorption. The best fit was obtained for a diffusion-limited model based on the Langmuir or Freundlich equation. The regression coefficients of the models were not correlated with physical and chemical properties of the soils.

2.2.7 Precipitation-Dissolution

The sorption process may be regarded as the one leading to net accumulation at an interface, whereas precipitation is the process that causes an accumulation of a substance to form a new bulk-solid phase. These processes cause loss of material from a solution phase. However, the former is essentially two-dimensional, whereas the latter is inherently three-dimensional (Sposito, 1984). Lin et al. (1983a) proposed that the sorption mechanism prevails at low P concentrations and precipitation prevails at higher P concentrations in soil.

Ryden and Pratt (1980) pointed out a distinction between sorption and precipitation. Sorption requires the structure of sorbent to remain essentially unchanged as the process progresses even though its surface activity decreases. In the precipitation process, however, the surface activity remains constant (Sanyal and De Datta, 1991).

2.2.7.1. Chemistry of Phosphate

The anions of phosphoric acid and the most common condensed phosphates, pyro- and tripoly-phosphate, readily dissociate protons and behave as typical polyprotic acids. Based on the equilibrium constants presented in Table 2.6 and on typical concentrations occurring in raw domestic wastewater, the distribution of ortho-, pyro- and tripoly-phosphate at different pH levels is presented in Figure 2.4. At pH 7.5 the predominant species are $H_2PO_4^-$, HPO_4^{2-}, $HP_3O_{10}^{4-}$, and $HP_2O_7^{3-}$. Because of their complexity, variability and relatively small concentration, the proton and metal ion binding properties of the wide variety or organic phosphates in domestic wastewater are neglected, and phosphates in domestic wastewater can be approximated as a mixture of ortho-, pyro and tripoly-phosphate (Table 2.6), which in some instances (eg., the condensed phosphate complexes of Ca^{2+} and Mg^{2+}) may be sufficiently stable to increase the phosphate solubility significantly, especially in the alkaline pH region (Jenkins et al., 1971).

A number of early research investigations on P chemistry in soil postulated the formation of a variety insoluble inorganic phosphates of Fe, Al and Ca through precipitation reactions (Vacker and Connell, 1967).

Table 2.6 Phosphate Equilibrium (Sillen and Martell, 1964)

Equilibrium	Log equilibrium constant 298°K
$H_3PO_4 = H^+ + H_2PO_4^-$	−2.1
$H_2PO_4^- = H^+ + HPO_4^{2-}$	−7.2
$HPO_4^{2-} = H^+ + PO_4^{3-}$	−12.3
$H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$	−2.5
$H_2P_2O_7^{2-} = H^+ + HP_2O_7^{3-}$	−6.7
$HP_2O_7^{3-} = H^+ + P_2O_7^{4-}$	−9.4
$H_3P_3O_{10}^{2-} = H^+ + H_2P_3O_{10}^{3-}$	−2.3
$H_2P_3O_{10}^{3-} = H^+ + HP_3O_{10}^{4-}$	−6.5
$HP_3O_{10}^{4-} = H^+ + P_3O_{10}^{5-}$	−9.2
$Ca^{2+} + PO_4^{3-} = CaPO_4^-$	6.5
$Ca^{2+} + HPO_4^{2-} = CaHPO_4(aq)$	2.7
$Ca^{2+} + H_2PO_4^- = CaH_2PO_4^+$	1.4
$Ca^{2+} + P_2O_7^{4-} = CaP_2O_7^{2-}$	5.6
$Ca^{2+} + HP_2O_7^{3-} = CaHP_2O_7^-$	3.6
$Ca^{2+} + P_3O_{10}^{5-} = CaP_3O_{10}^{3-}$	8.1
$Ca^{2+} + HP_3O_{10}^{4-} = CaHP_3O_{10}^{2-}$	3.9
$Ca^{2+} + H_2P_3O_{10}^{3-} = CaH_2P_3O_{10}^-$	3.9

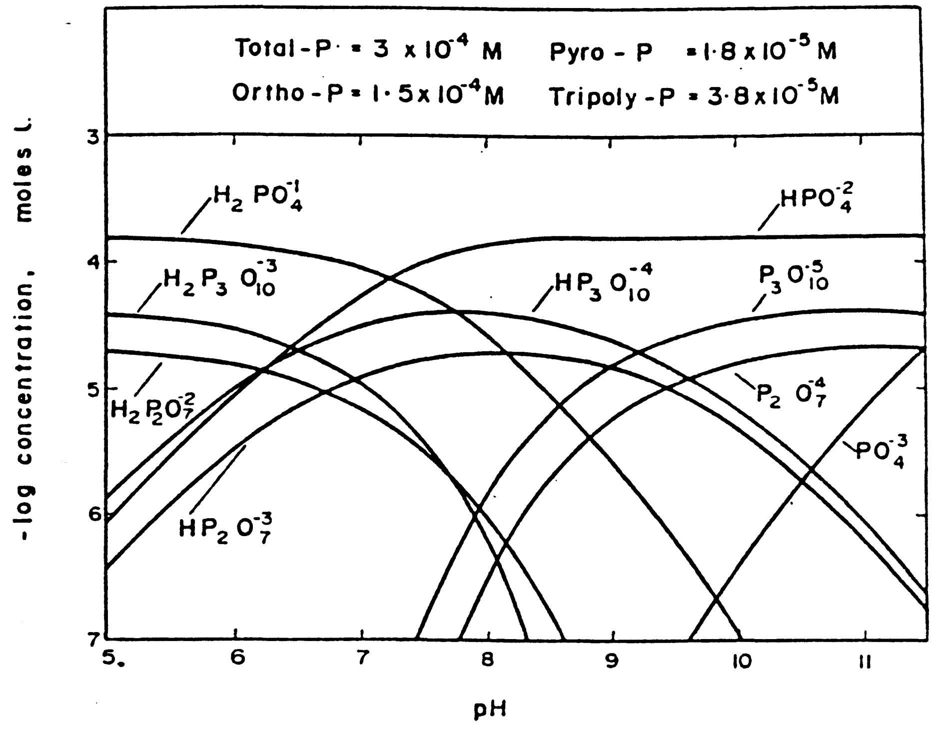


Figure 2.4 pH Concentration Diagram for Phosphate Species of Typical Raw Wastewater (Jenkins et al., 1971)

2.2.7.2 Al Compounds as P Precipitants

Aluminium ions can combine with phosphate ions to form aluminium phosphate as follows:

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \qquad \text{... (2.3)}$$

Equation 2.3 indicates that the mole ratio for $Al:PO_4$ is 1:1. The principal source of aluminium in phosphorus precipitation is 'alum', hydrated aluminium sulfate, having an approximate formula $Al_2(SO_4)_3.14H_2O$ (molecular weight 594). The weight ratio of alum to phosphorus is, therefore, 9.6:1. The optimum pH for the removal of phosphorus lies in the range of 5.5 to 6.5, although some removal occurs above pH 6.5 (Jenkins et. al., 1971).

2.2.7.3 Fe Compounds as P Precipitants

Both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions can be used in the precipitation of phosphorus. With Fe^{3+}, the reaction is similar to that shown earlier for precipitation of aluminium phosphate. The mole ratio for $Fe:PO_4$ is also 1:1. Since the molecular weight of ion is 55.85, the weight ratio of Fe:P is 1.8:1. Just as in the case of aluminium, a larger amount of iron is required in actual situations than the amount calculated from the chemistry of the reaction. With Fe^{2+}, the situation is more complicated and not fully understood. Ferrous phosphate can be formed. The mole ratio of $Fe:PO_4$, in this case, would be 3:2. Experimental results indicate, however, that when Fe^{2+} is used, the mole ratio of Fe:P is essentially the same as that of Fe^{3+} (Jenkins et al., 1971).

A number of iron salts are available for phosphorus precipitation. These include ferrous sulfate, ferric sulfate, ferric chloride, and pickle liquor. Iron salts are most effective for phosphorus removal at certain pH values. For Fe^{3+}, the optimum pH range is 4.5 to 5.0. This is an unrealistically low pH, not occurring in most wastewaters. Significant removal of P can be also attained at higher pH values. For Fe^{2+}, the optimum pH is about 8 and good P removal can be obtained at pHs between 7 and 8 (Illungkoo, 1994).

2.2.7.4 Ca Compounds as P Precipitants

The precipitation of calcium phosphate is strongly influenced both by the kinetics of nucleation and crystal growth and by the chemical composition of the medium. Hydrogen ions, HCO_3^-, Mg^{2+} and F are known to influence both the composition and the activity product of the precipitated calcium phosphate solid (Ferguson, 1970). The precipitation of phosphate from wastewater by calcium has most commonly been conducted by the addition of lime to provide a simultaneous increase in both Ca^{2+} and OH^-. Most calcium phosphate precipitation schemes involve raising the pH of the waste stream to at least 10.5 (and often above pH 11), because at this pH range, experience has shown that low dissolved phosphate residuals are obtained together with a settleable precipitate [possibly due to the simultaneous precipitation of gelatinous $Mg(OH)_2$] (Jenkins et al., 1971).

2.2.8 Surface Interaction between the Solid and Liquid Phase Solution

The solid and liquid phases of soil were treated previously as separate entities. In reality, these phases interact with each other along their plane of contact. This interaction between liquid and solid phases is a very common phenomenon which is related to the difference in atomic structure of both phases on either side of the plane of contact. The materials found for phosphorus precipitation include the ionic forms of aluminium, iron, calcium and magnesium (Bolt,1978).

2.2.8.1 The Surface Charge of the Solid Phase

In ionic soils, the bonds between the different atoms in the lattice are primarily electrostatic in nature. When the polar water molecules are brought in contact with water, they tend to penetrate between the surface atoms, which weakens the binding force between these atoms and may lead to dissociation of surface ions. Clay minerals in particular behave in this manner. The internal structure of the clay mineral has an inbalance of charges due to substitution of Si^{4+} and Al^{3+} ions by other cations of lower valence. The electro-neutrality of the clay particle is then provided by the presence of certain cations (Na^{+}, Ca^{2+}, K^{+}, Mg^{2+}) on the exterior surface. These exterior cations (which are not part of the crystal lattice) dissociate completely from the surface if the latter is in contact with water. As a result, one can conclude that clay minerals in water have a constant surface charge equal in magnitude to the 'substitution charge' of the lattice (Bolt, 1978).

2.2.8.2 Properties of Liquid Layer

In an aqueous environment, a partial dissociation of surface ions takes place imparting an electric charge to the surface of the solid phase. In contrast to partly dissociated molecular acids, where the dissociated H-ions are spread throughout the solution, the ions dissociated from a solid surface tend to remain in the neighbourhood of the charged surface. The cause of this phenomenon is their attraction to the surface charge of the solid phase, preventing them from spreading themselves throughout the system. Depending on the proximity of the charges on the surface, the electric fields of the individual charges reinforce each other, giving rise to a combined electric field in the liquid layer adjacent to the solid surface. This field will attract the dissociated ions (and other ions of the same sign) which will accumulate close to the charged surface. The resulting spatial distribution of charges (eg. a negatively charged surface with an accumulation of positively charged ions close to it) is called a 'double layer'. The accumulated 'counter' ions of the surface can move freely through the solution phase and are subjected to two opposing tendencies: (a) they are attracted towards the surface by the electric field (sorption tendency), and (b) they tend to distribute themselves evenly throughout the solution phase by diffusion (diffusion tendency) (Bolt, 1978).

2.2.9 Ion Exchange

Ion exchange in soil and slag comprises ionic reactions with mixtures of various clay minerals, metal oxides, and variable amounts of organic compounds. It generally involves more than two cations simultaneously. In addition, it is complicated by the presence of sparingly soluble minerals and soluble salts (Tucker, 1983). Basic exchangeable cations include the cations of the alkali and alkaline earth metals (Ca^{2+}, Na^+ and K^+) and Mg^{2+} and NH_4^+. Cations of the trace metals, such as Zn, Cu or Co, may take part in ion exchange reactions but other reactions, such as chelation with these trace metals, are much more important in soil and slag (Tucker, 1983).

Solid phase particles often carry a negative surface charge. The overall electro-neutrality of the system is maintained by the presence of an excess of cations (in comparison to the anions present) in close proximity to the solid surface. This excess of cations cannot be separated from the surface (ie. taken out of the system). It is possible, however, to exchange these cations against others and still maintain the electro-neutrality of the system. To satisfy electro-neutrality, the exchange must be equivalent, eg. two monovalent cations are replaced by one divalent ion. Under favourable conditions, the rate of the reaction is very rapid (occurring in minutes or less) (Tucker, 1983).

2.2.9.1 Cation Exchange Capacity (CEC)

The total amount of cations exchangeable by a unit mass (weight) of soil is termed the cation exchange capacity of the soil, CEC. Unlike that of clays or soil with permanent charge, the CEC of a soil and slag with variable charge is very dependent on the method used for its determination (Parfitt, 1980).

Any method used for a soil with variable charge should indicate the negative charge of the soil as it occurs in the field. Gillman (1979) has tested the validity of various methods, and proposed the following method for soil : saturating the soil with unbuffered $BaCl_2$ (final concentration 0.002 M), displacing it by 0.0015 M $MgSO_4$, and measuring the amount of Mg^{2+} retained and Cl^- displaced. These concentrations were selected because they were close to the upper limit of the ionic strength (0.005 M) for highly weathered Australian soils. The CEC of a soil may sometimes be estimated from its clay and humus content (eg. for illicit clays about 40 cmol (+)/kg and for humus 200-300 cmol (+)/kg). Obviously such estimates are applicable over a limited area in which one knows the type of clay and organic constituents. The specification of the relative amounts of different cations adsorbed by the complex (expressed as percentages of the CEC) is usually referred to as the cationic composition of the sorption complex (Parfitt, 1980).

2.2.9.2 Anion Exchange Capacity (AEC)

The anion exchange capacity (AEC) of soil is the positive charge measured by Cl^- or NO_3^- retention. AEC determinations are less important than those of CEC because relatively few anions are held by simple ion exchange (electrostatic) interactions. However, AEC values indicate whether NO_3^- would be retained by soil or not. For other anions, such as sulphate or phosphate, whose sorption is more complex, AEC is not easily related to the amount adsorbed. Hence it is usually simpler to measure phosphate or sulphate sorption directly (Tucker, 1983).

2.3 Past Studies on P Removal Using Soil

Aulenbach and Meisheng (1988) undertook studies to identify the mechanisms of P removal from secondary treated wastewater in a rapid infiltration land application system consisting of delta sand. Column studies confirmed that P removal is primarily a physico-chemical process rather than a biological one. Sorption, as measured in shaker batch studies, did not account for all of the measured P removal by the sand particles. Sand from a sewage treatment plant rapid infiltration system that had a coating primarily of precipitated $CaCO_3$ was used. Removal of this coating nearly eliminated P removal and its presence was found to play an important role in P removal.

Fox et al. (1989) studied the degree of sorption and release of P from sediments of a river receiving treated sewage effluent. Chemical analysis of the sediment samples showed that the percentages of Fe and Fe-bound P decreased with the increasing distance from sewage treatment plant, whereas the percentage of Ca and solid P increased. P sorption or desorption was rapid initially, and slow at the later stages. They found that P sorption followed a reversible second-order equation. The forward rate constant, k_1, was found to be between 1 and 2 dm^3/mol./minute, and was dependent on pH, calcium and nitrate ion concentrations. They found that the bonding of P was weaker in calcareous sediments compared to iron-containing sediments.

Ebers and Bischofsberger (1990) conducted a series of column experiments with lysimeters for wastewater treatment. They demonstrated that slightly silty sand (under anaerobic conditions) showed better results in eliminating P (86.0 to 99.3%) but has a lower hydraulic loading capacity than fine gravel sand.

Ho et al. (1992) conducted a series of column experiments to examine the removal of P from sewage effluent. The sorption medium used was sand amended with a bauxite refining residue (red mud). An average of 91% P removal was obtained with 30% red mud, 63% removal with 20% red mud and 50% removal with 10% red mud. The decrease in P removal with decreasing red mud content was caused by a decrease in the sorption capacity of the soil and an increase in the infiltration rate. P removal was excellent in the columns packed with 30% red mud both for primary and secondary effluents.

Wakatsuki et al. (1993) studied the application of a Multi-Soil-Layering (MSL) column as an on-site domestic wastewater treatment system to remove P. The MSL unit is composed of a soil layer mixed with 10-25% of metal iron and pelletised jute. The MSL column was piled in a brick pattern at 5 cm vertical and 10 cm horizontal distances, and was surrounded by layers of zeolite. Wastewaters which were pretreated by septic tanks to the level of TP 6-11 mg/L could be treated by this system at a loading rate of 100-850 L/m^2.day without significant clogging. The mean concentrations of treated waters were 0.86 mg/L as TP. The researchers found that metal iron and jute pellets were effective in removing P. The MSL system was found to be capable, not only of purifying wastewater, but also of producing fertile soil during the treatment. They suggested that the soil and zeolite can be recycled in agricultural land to improve soil fertility.

Lam et al. (1993) assessed the feasibility of a soakaway system in treating piggery wastes with five commonly found soils in HongKong. P removal efficiency was higher in volcanic soils than in coarse granitic soils. Most of the P was removed in the top 1 m of the unsaturated zone of the columns. Analysis of the effluent collected at the base of the 3 m columns packed with granitic and volcanic alluvial soil indicated a P removal efficiency of 95%.

2.4 Past Studies on P Removal Using Slag and Other Media

Research has shown that the sorption of dissolved inorganic P depends on pH, temperature and the concentration of coexisting salt (Yamada et al., 1986). These researchers found that sorption was proportional to the porosity of material. The sorption capacity of P was found to be more on soft granulated slag than on hard granulated slag.

Yamada et al. (1987) studied the suppression of P liberation from sediments by using iron slag. The suppression efficiency depended on the amount of slag used. About 85% of P liberation was found to be suppressed by using slag. As for the suppression mechanisms, three effects of suppressing materials were considered. The first was the covering effect of iron slag on the surface of the sediments. The second was the chemical effect of hydrogen sulfide generated in the anaerobic state. The third was the sorption effect.

Kaneko and Nakajima (1988) studied P removal by crystallisation using a granular activated magnesia clinker. From long term pilot-scale studies (2.5 years) at a sewage treatment plant, they found that effluent P concentrations were well below 0.5 mg/L.

Ho and Kuruvilla (1990) investigated P removal from agricultural drainage water (containing P) from the Peel Harvey Estuary in Western Australia using red mud. They conducted batch tests by mixing P solutions with red mud, and with red mud neutralised with phosphogypsum or copperas. Red mud amended with acidic calcium sulphate and ferrous sulphate had up to 18 times the sorption capacity of untreated red mud. Experiments were conducted by equilibrating the P solution with red mud for 24 hours. P removal was observed up to 97%.

Roques et al. (1991) studied the possibility of P removal by fixation with half-burned dolomite grains. Semi-burned dolomite is a commercial product employed in water treatment processes for water neutralisation and for the removal of Fe and Mn species. This was obtained from the thermic dissociation of dolomite $[(Ca, Mg (CO_3)_2]$ at 650 -750 °C resulting in a material containing equal molars of MgO and $CaCO_3$. They found that the fixation occurred as a superficial precipitate of a (nonstoichiometric) badly crystallised calcium phosphate. The equilibrium phase between the solid and P solution could be quantified using the Freundlich isotherm ; $S = 1.19 C^{0.353}$ (where S and C are the amount of P adsorbed per unit mass of grain, and the concentration of P solution respectively). The precipitation reaction was sufficiently rapid and near equilibrium conditions were rapidly attained. The fixation capacity for P was approximately 20 mg/g for solids with a particle mean diameter of 0.5 mm. They suggested that this treatment could be used in the tertiary stage of a wastewater treatment.

James et al. (1992) conducted a series of laboratory studies to evaluate the feasibility of adding iron oxides or steel wool to peat and sand to increase P sorption. Langmuir type batch isotherms and column leaching studies showed that rust and untreated steel wool markedly increased P sorption. Estimated useful lives for the iron-amended materials ranged from zero years for unamended sand to several years for steel wool-amended peat, depending on the quantities of iron materials added. The results suggested that steel wool offers a low cost, efficient amendment for peat and sand beds designed for P removal from wastewater.

Mann (1992) investigated the importance of the solid matrix substratum in P removal efficiency in two large-scale, constructed wetlands which received secondary treated sewage effluent. Two PVC-lined systems were studied, a gravel filled "control" trench and a simulated wetland, comprising alternate areas of unplanted gravel, gravel planted with Typha species and open water. The trench systems removed at best 60 to 80% of the applied P during the first two months of operation and then showed considerably lower performance. Although P removal in the studied systems involved the immobilisation and removal of P through chemical precipitation, bacterial action, plant uptake and related physico-chemical pathways, the sorption capacity of the gravel substratum mediated most of the removal. The P removal efficiency observed in full-scale systems corresponded closely to results obtained in the laboratory. These results showed that the P sorption capacity of a constructed wetland system may be estimated, prior to construction, through use of conventional ion exchange capacity studies.

Mann and Bavor (1993) investigated the P removal efficiency of three gravel based constructed wetland systems (CWS) in which secondary sewage effluent was treated. The constructed wetland system, 100 m x 4 m x 0.5 m with an impervious liner, comprised an unplanted gravel "control" trench and gravel trenches planted with non-culture (natural) stands of either Typha orientalis or Schoenoplectus validus. P sorption in the large-scale gravel systems was variable and ranged from -40% to 40%. Ion exchange experiments have been used to evaluate the gravel and industrial conglomerates, with a view to improve P immobilisation through substratum selection and effluent flow management. The maximum sorption capacity of regional gravels ranged from 0.026 to 0.048 mg/g compared to blast furnace slag (0.16 to 0.42 mg/g) and fly ash (0.26 mg/g).

2.5 Constructed Wetland Systems (CWS)

Treatment of wastewater in a wetland system is an environmentally friendly, easily operated and cost effective treatment option for a wide variety of wastewaters. Basically, wetlands are of two types : Natural and constructed (artificial) wetlands. Constructed wetlands use the same treatment mechanism of a natural system, but the process takes place in a more controlled environment. Both natural and constructed wetland systems have shown considerable potential for wastewater treatment although the technique is still in the development stage. Some wetland systems use only soil or gravel as media whereas others use aquatic vegetation in addition to soil or gravel media to assist in treatment of wastewater. Pollutant removal mechanisms in this process are complex, and includes physical, chemical and biological mechanisms. Direct pollutant removal mechanisms include filtration of suspended solids and pathogen by media, sedimentation of suspended solids in void spaces, sorption of heavy metals, nutrients and dissolved solids, precipitation of metals and phosphorus and bacterial metabolism processes - nitrification and denitrification (Mohanathansan et al., 1991).

Practical applications have demonstrated that artificial wetland systems can form a highly efficient and adaptable wastewater treatment option with a potential to treat domestic effluents to secondary and tertiary standards; to upgrade conventional oxidation-stabilisation ponds and secondary treatment systems to meet high effluent standards, and to treat a range of industrial effluents including those from abattoirs, pulp and sugar mills, acid mine drainage, leachate, animal wastes and urban and stormwater runoff (Mackney, 1993).

2.5.1 Factors Contributing to Efficiency of Constructed Wetland Systems

Wastewaters passing through wetland systems go through bacterial metabolism and physical sedimentation as do those in conventional wastewater treatment plants. The fundamental difference between conventional and wetland systems is that in the former, wastewater is treated rapidly in highly managed energy-intensive environments (ie. reactors) whereas in wetland systems, treatment occurs at a comparatively slow rate in essentially unmanaged, ecological environments (Wood, 1993).

2.5.1.1 Plant Species

The direct role of the aquatic plants (macrophytes) in wastewater treatment in wetlands is the provision of surfaces for bacterial growth, the filtration of solids, the translocation of oxygen to the plants and the improvement of soil permeability. The oxygen flux to the root of reeds is a species-related phenomenon. The common reed, *phragmites australis*, has been accepted worldwide as a candidate species for wetland wastewater treatment facilities. This is principally due to its production of deep roots and rhizomes (1.5 m or more) which create a great volume of active aerated root zone per surface area of reed bed. Other suitable plants are *scirpus mucronatus* and *typha* species. The lower root penetration of *typha* has encouraged simultaneous nitrification and denitrification and provides conditions conductive for sulphate removal from acid mine drainage (Wood, 1988).

The other major function of the reeds is to increase and stabilise the hydraulic permeability of the substrata in which they are planted and through which the wastewater flows. Wood (1993) has reported that percolation through soils is improved by the presence of roots and rhizomes of *phragmites*. As the roots and rhizomes penetrate through the soil, they loosen it, increasing porosity by forming pores of tubular shape. Upon decay, the roots and rhizomes will leave horizontally interconnected channels behind. According to Kickuth (1980) these channels will stabilise the hydraulic conductivity in the rhizosphere at a level equivalent to coarse sand within 2 to 5 years regardless of the initial porosity of the soil.

The aquatic plants (reeds) also play a role in water management. Water losses to the atmosphere from a wetland occur from water and soil (through evaporation), and from the emergent portions of the plants (by transpiration). The combination of the two processes is termed evapotranspiration. In denser beds, the shelter and higher humidity caused by the reeds may reduce overall evapotranspiration compared with open water (Bernatowicz and Leszcznska, 1976).

2.5.1.2 Substrata

The substrata in which the reeds are established provide a stable surface area for microbial attachment, a solid substrate for plant growth, and function directly in the purification of the wastewater by way of physical and chemical processes. The substrata affect retention time, contact opportunities for organisms with the wastewater, and the availability of oxygen, all of which relate directly to treatment capabilities (Brix, 1987; Good and Partick, 1987; Steiner and Freeman, 1989). To provide maximum permeability of the bed in which the reeds are to be grown, it is necessary to select a soil or substratum which has a composition from which a stable structure can evolve through channels created by dead and decaying rhizomes. Studies by Cooper and Boon (1987) indicated that soils classed as sandy clay loam, clay loam, silty clay and the lighter part of the clay, may be suitable, if gravel, river sand, or waste ash is not available.

Initially, the hydraulic conductivity of the replaced soil should be about 10^{-3} to 10^{-5} m/s, with a long term operational permeability of 10^{-3} m/s. However, it is not advisable to design a wetland on the expectation of permeability improvement. Experiences in Europe have indicated that systems where soil hydraulics were not adequately considered actually have a low hydraulic conductivity (2-3 x 10^{-6} m/s) during the first years of performance and function basically as surface flow systems. This results in channelling and poor vegetation growth in some areas due to lack of water (Brix, 1987; Cooper, 1986; Davies, 1988; Steiner and Freeman, 1989).

2.5.1.3 Microorganisms

Microorganisms, which may be either attached to the macrophyte root and stem structures or free living in the water, form the basic physiological mechanisms by which pollutants are removed from wastewaters. Although the reeds will be translocating oxygen to the root zone, the extent of the aerobic region will be determined by the oxygen demand within the vicinity of the roots, as well as the photosynthetic and free diffusion characteristics of the reeds. The aerobic zone extends no further than a few millimetres from the site of oxygen release, and processes for the oxidation of carbonaceous and nitrogenous materials occur in this zone. As ammonia is nitrified to nitrate by nitrification, the nitrate acts as terminal electron acceptor for denitrification through facultative aerobes in adjacent anoxic zones. In the absence of oxygen and nitrate, and as the redox potential decreases, anaerobic degradation processes occur using energy from SO_4^{2-}, Mn^{4+}, Fe^{3+} and CO_2 (Wood, 1993).

It is evident that the presence of such a diverse ecological environment leads to the occupancy of a wide spectrum of micro-organisms capable of degrading the variety of organic and inorganic compounds in wastewaters. While the readily biodegradable portions of wastewaters are decomposed rapidly, fractions may also be incorporated into the organic sediment to be anaerobically degraded over an extended period, extending the overall retention time available for pollutant removal (Cooper and Boon, 1987; Wood, 1993)

2.5.1.4 Temperature

Variations in the temperature of wastewaters appear to have little effect on effluent quality because the total number of active bacteria in the soil and rhizosphere increase in winter months. This allows increased concentrations of substrate away from the inlet end of the bed, with the effect that the concentrations of bacteria increase in the middle and outlet zones of a bed (Cooper, 1986). There are a number of factors which will help to maintain a relatively high temperature in the rhizosphere during winter:

- Insulating effect from plant cover and litter on the surface
- Production of heat from microbial activity in the rhizosphere
- Influent wastewater temperature.

These factors should prevent the infiltration areas and the rhizosphere from freezing during winter (Brix, 1987).

2.5.2 Phosphorus Removal in CWS

P removal in a wetland is achieved through plant uptake and the biological and physico-chemical storage of P in the substrata. Aquatic plants supplied with sewage effluent tend to show increased growth, and usually have increased tissue P concentrations. However, P adsorbed in rooted emergent vegetation and algae is released back into the water body and settles after tissue death.

The mechanism of P sorption to the substrate involves the exchange of a phosphate ion with an OH^- of a metal hydroxide, MOH, where M = Fe or Al, and is thought to be essentially irreversible at iso-pH, constant ionic strength, and in the absence of competing ions. The saturation of the sorption complex is positively linked to the desorption of P. Phosphorus is also precipitated within the substrata as salts of the metal ions present. The distinction between sorption and precipitation reactions has appreciable practical significance. Sorption theory dictates that the P concentration in solution largely determines the amount of P sorbed, with surface 'activity' changing accordingly. Precipitation theory, however, dictates that the P concentration controlled by the solubility product of the least concentration maintained in solution is greater at high adsorbent saturations than at low adsorbent saturations. This is directly relevant to wastewater disposal (Swindell and Jackson, 1990).

It has been observed that soils have the capacity to regain, and in some cases enhance, their adsorptive capacities after apparently having reached saturation and subsequently been allowed to rest (Ellis and Erickson, 1969). The phenomenon is explained by the slow dissolution of aluminium and iron compounds creating new sites for sorption of P with time.

Average soils can be expected to contain 2-4% iron and 5.0-7.5% aluminium. Thus, if all iron and aluminium were dissolved and converted to iron and aluminium phosphates, nearly 1000 tonnes of P could be precipitated per hectare m^3 (1 hectare area x 1 m deep). However, under normal conditions, ie. near-neutral pH, and moderate temperatures, iron and aluminium are both slow to dissolve, and only a fraction of the possible capacity of the soil to precipitate P will be realised in the short term (Swindell and Jackson, 1990).

2.5.3 Past Studies on P Removal in CWS

Swindell and Jackson (1990) reported that a 494 ha constructed wetland operating since mid-1987 in Orlando, Florida, U.S.A. produced an effluent in 1989 with average concentrations of 0.08 mg/L as TP. Influent flows were approximately 0.58 m^3/s. Most of the P was removed in the early stage of the system. P removal efficiency peaked at a detention time of 5 days. P uptake during 1989 across the same area was 0.41 kg/ha.day. The fixation of P in bacteria and algae cells and the eventual storage of these cells in the sediments were thought to be the primary removal mechanisms. Because of a design that allows for more control over internal flow rates than most other constructed wetlands, the system was able to provide an effluent with consistently low P concentrations.

Mohanathansan et al. (1991) studied on the removal mechanisms and design criteria in wetland treatment plants. They found that the main factors influencing the design of wetland systems are hydraulic considerations, substrate media, vegetation, design configuration and the operating procedure of the system. Water depth and frequency of flooding are important because they may influence the light penetration and photosynthesis. Influent wastewater quality parameters such as turbidity, pH, dissolved oxygen and salt concentration affect the plant species selection. Media size and type affect the physical and chemical treatment mechanisms and the selection is based on the cost, degree of treatment and design requirements. The overall configuration of a wetland system may affect water velocity, water depth and fluctuation, detention time and distribution patterns.

Batchelor et al. (1991) reviewed a constructed wetland research program in South Africa. Their research indicated that artificial wetlands established in different substrates and subjected to various domestic wastewaters at different application rates could effectively reduce P levels, provided that certain design criteria were met. Under the experimental conditions employed, satisfactory wetland performance could be achieved at relatively high loading rates (up to 2700 L/m^2.day) and shallow (0.2 m) substrate depths. Serial arrangement of wetlands using ash and soil substrates resulted in efficient P removal.

Wood (1991) considered the application of constructed wetlands to be a reliable and realistic alternative treatment option, particularly suited to small and medium-sized communities, agriculture and industries in sparsely populated and developed areas. In South Africa, there are presently approximately thirty systems either in operation, under construction or in the planning stages.

Masters (1993) designed a low cost treatment system to reduce the water pollution potential of dairy waste. It incorporates three stages; a sump in which anaerobic actively occurs; an aerobic vegetated filter with a base of permeable P adsorbing material; and an irrigated plantation or crop using water that has passed through the system. Recent work by West Australian companies and government departments has shown that a range of materials with a high P Retention Index (PRI) is available to accomplish this. While high PRI materials include natural materials such as loams and clays, waste products generated by mineral processing industries in the South West of Australia are also suitable. Red mud in particular is physically and chemically suited for use as a P adsorbing material.

III. THEORETICAL CONSIDERATIONS

This chapter has been divided into two sections. The first section deals with the mathematical formulation of P sorption under static conditions. The second section discusses the mathematical modelling of saturated column experiments.

3.1 P Transport in Static Systems

Transport of reactive solutes through soil profiles into groundwater is a major environmental concern. Over the past three decades, numerous researchers have endeavoured to quantify the processes governing the interactions with soil of various solutes like pesticides, nutrients, heavy metals, and other toxic substances. The transport and ultimate disposition of phosphorus in groundwater systems are mainly affected by sorption-desorption and precipitation-dissolution reactions between groundwater and aquifer materials. There are two aspects of sorption reactions that must be quantified and modelled in this context: first, the form or character of the equilibrium distribution between liquid and solid phases toward which a particular solute of concern in the system is thermodynamically driven, and second, the rate at which this distribution is approached (Weber and Miller, 1989).

Numerous models exist to explain the kinetic behaviour of solutes. Amacher et al. (1988) stated that single-reaction models did not describe retention release reactions in soils adequately. They considered that multi-reaction models predict observed kinetics better but involve too many model parameters, which usually must be evaluated by curve fitting techniques. Complicated models, involving many parameters (which are difficult to evaluate), are likely to induce more error while estimating those parameters. Independent methods for their estimation are usually unavailable. The method applied in evaluating the parameters in multi-reaction multi-site models is usually the curve fitting technique. Hence, simple models which involve fewer parameters are desirable (Bajracharya, 1989). The single reaction model has been found to explain the kinetic behaviour of P sorption adequately in this study.

3.1.1 Kinetic Non-equilibrium Sorption

Non-equilibrium models used to predict concentrations at different times can be categorised into two classes: kinetic non-equilibrium and physical non-equilibrium models. The kinetic non-equilibrium model simply incorporates a reaction with rate constant (k_r) and does not explain what actually takes place (Bolt, 1979). An exponentially parabolic sorption kinetics equation can be stated as follows,

$$S_t = S_e(1 - e^{-k_r t}) \qquad \ldots (3.1)$$

where, S_t = Solid phase concentration at time t (mg/g)

S_e = Solid phase concentration at equilibrium (mg/g)

k_r = Rate constrant (day^{-1})

t = Sorption time (day)

3.1.2 Static Physical Non-equilibrium Sorption Model (SPNSM)

A simple Static, Physical, Non-equilibrium Sorption, Model (SPNSM) has been used in this study to describe the kinetics of P sorption. The model makes use of isotherm constants and one other parameter (termed a film transfer constant) to completely describe the rate of P sorption with time in the static system. The model has been tested with the data of P sorption in the experimental soil (a sandy loam soil from North Sydney, Australia) and slag (waste by-products from the BHP steel industry such as dust and cake). The model is based on the assumption that the particles of adsorbent are surrounded by an immobile water layer and that the liquid phase concentration of P in this layer exists in equilibrium with the solid phase concentration on the adsorbent surface (film diffusion model). The classical film diffusion equation may be referred to in any Chemical Engineering Handbook (eg. Perry and Chilton, 1978).

It was assumed that there is no concentration gradient within the immobile layer or in the bulk solution. At any instant the transfer of solute takes place across the film and the rate at which sorption takes place is proportional to the difference between the concentration of the bulk P solution and the immobile layer P concentration at that instant. The constant of proportionality involved is usually known as the film transfer constant and this factor is denoted as α. When the bulk solution and the film layer concentrations become equal, there is no more transfer of solute and the equilibrium point is said to be reached. Initially the solid phase concentration is assumed to be zero. At any instant, the mass balance yields,

$$C_o = C + (\beta/\theta)S \qquad \text{... (3.2)}$$

where, C_o= Initial bulk concentration of P (mg/L)

C = P concentration in the bulk solution at any instant (mg/L)

S = Solid phase concentration at any instant (mg/g)

β = Mass of adsorbent (g)

θ = Volume of P solution (L)

The rate at which sorption is taking place can be written as;

$$-\frac{dS}{dt} = \alpha(\theta / \beta)[C - C_f] \qquad \text{... (3.3)}$$

The following equation is obtained from the classical film diffusion equation,

$$\frac{dC}{dt} = -\alpha[C - C_f] \qquad \text{... (3.4)}$$

where, α = Film transfer constant (day^{-1})

C_f = P concentration in the fixed film layer in equilibrium with the solid phase concentration (mg/L)

The film diffusion constant can be computed by several methods. One method is by plotting (-dC/dt) against [C-C_f]. The slope of the plot is the value of α. The value of C_f is computed from the amounts which have been adsorbed at that instant ie., by making use of Eqn. 3.6. The isotherm parameters can be used for the evaluation of C_f since equilibrium exists at all times between the film layer and the solid phase concentration.

The other method to compute α is from the slope of the curve in a flat of concentration, C versus time at t=0. At t=0, from Eqn. 3.4 the value of C_f is zero and the value of α is given by

$$\alpha = \frac{dC}{C_o\, dt}\Big|_{t=0} \qquad \text{... (3.5)}$$

In this study the film transfer constant (α) was approximated from the kinetic data itself. To estimate the most suitable film transfer constant at different initial concentrations, the α value which provides the best simulation to the experimental data by SPNSM was taken as the optimal value. The FORTRAN list of estimating the optimal film transfer constant is presented in Appendix A2.

The Freundlich isotherm (Eqn. 3.6) is used in this study.

$$S = KC_f^{1/N} \qquad \text{... (3.6)}$$

where, K, N = Freundlich isotherm constants

For N = 1, using Eqns 3.2 and 3.6, Eqn 3.4 is expressed in normalised form as

$$\frac{d(C/C_o)}{dt} = \frac{\alpha\theta}{\beta K}[1 - \{(\beta K/\theta) + 1\}\frac{C}{C_o}] \qquad \text{... (3.7)}$$

Integrating Eqn. 3.7 between the limits of initial bulk concentration and the concentration at any instant t, one obtains

$$\frac{C}{C_o} = \frac{1 + (\beta/\theta)K\exp[-\alpha\{1 + \theta/(\beta K)\}t]}{1 + (\beta/\theta)K} \qquad \text{... (3.7.1)}$$

When N is not equal to 1, Eqn. 3.3 in combination with Eqn. 3.6 becomes non-linear and cannot be solved analytically. Consequently the combined equations (Eqns 3.3 and 3.6), and Eqn. 3.2 were solved numerically in sequence using the finite difference technique. The numerical scheme in sequence is as follows:

$$S_{i+1} = -\alpha\,(\theta/\beta)\,\delta t\,\{C_i - (S_i/K)^N\} + S_i \qquad \text{... (3.8)}$$

$$C_{i+1} = C_o - (\beta/\theta)S_{i+1} \qquad \text{... (3.9)}$$

where, i = time index

δt = time step (days)

In this study the solid phase concentration of P at any time step was approximated from the difference of the bulk and the equilibrium liquid phase concentrations at the previous time step. The liquid phase concentration was computed from Eqn. 3.9. The solid and liquid phase concentrations then march forward in time based on the initial liquid and solid phase concentrations. The time step should be chosen carefully to avoid oscillations. The requirement of effective time step is only for the intermediate period when the system has not reached the equilibrium state. A large time step gives rise to stability problems. The smaller the time interval, the better the result. The validity of the numerical method was checked by solving the problem numerically for N=1 and then comparing its results with the analytical solution of the ordinary linear equation (Bajracharya, 1989). The analytical and numerical solutions for N=1 for an initial P concentration of 20 mg/L are shown in Figure 3.1. The constants used in computations are shown in the same figure. The FORTRAN listing of SPNSM is presented in Appendix A3.

3.2 P Transport in Dynamic Systems

Understanding solute transport mechanisms through soils is a requirement for making correct decisions on waste disposal. The extent of aquifer contamination by pollutant discharges has to be assessed and proper remedial measures have to be taken. An enormous growth in the development and use of solute transport modelling has been witnessed in the last three decades.

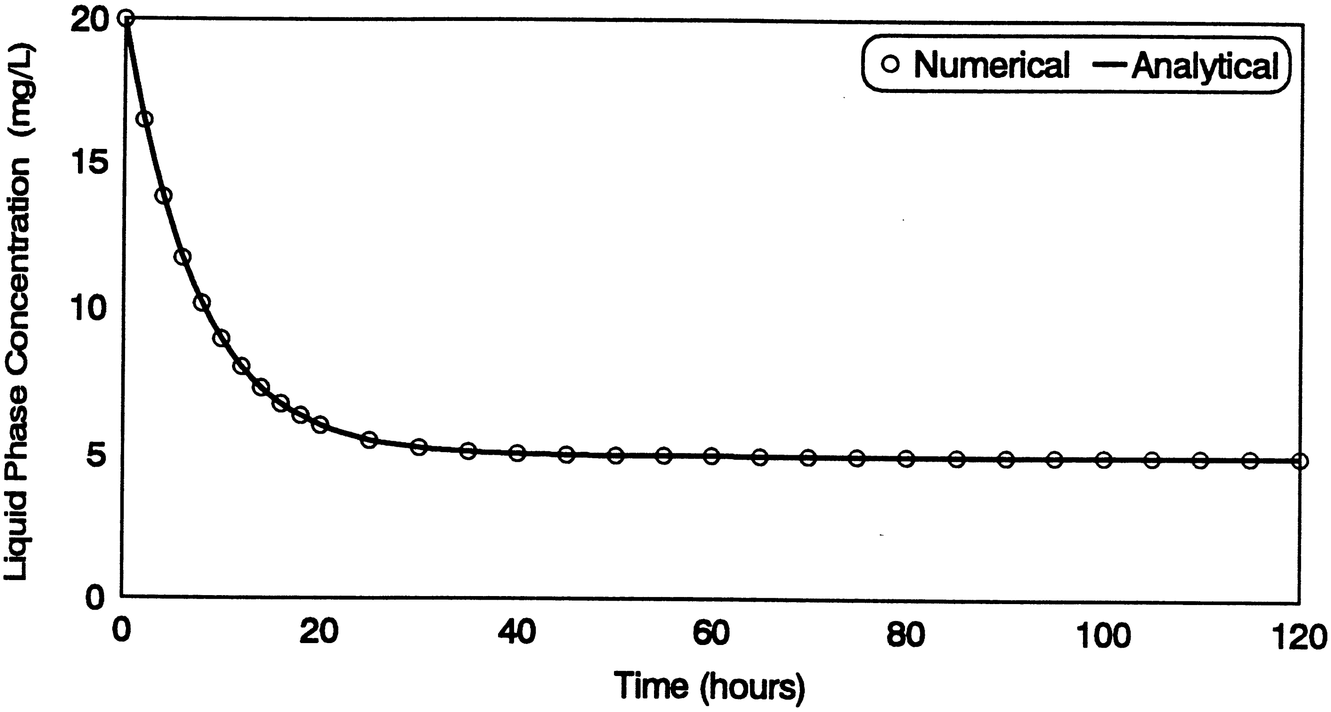
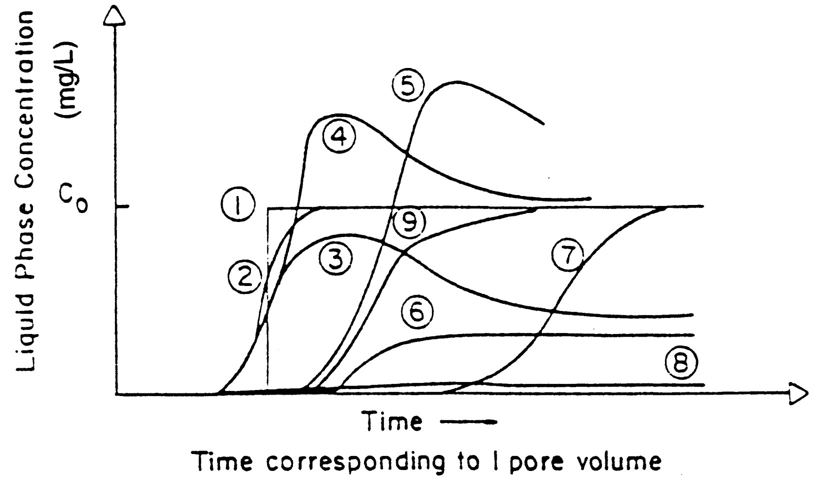


Figure 3.1 Comparison of Numerical (Eqns. 3.7 &3.8) and Analytical (Eqn.3.6) Solutions of Sorption Kinetics for Freundlich Isotherm Constant N=1

Numerous theoretical models are found in the literature (Rible and Davis, 1955; Nielsen and Bigger, 1962, 1963; Rubin and James, 1973; van Genuchten and Parker, 1984; van Genuchten and Wierenga, 1976, 1977; Rao et al., 1979; Jennings, et al., 1982; Rubin, 1983; Valocchi, 1985; Christensen, 1984, 1985, 1987; Crittenden et al., 1986; Bajracharya and Vigneswaran, 1990; Mahinthakumar and Vigneswaran, 1991). Recent modifications of the basic models simply incorporate additional model coefficients. Most of the models developed lack experimental verification.

Soils, unlike synthetic resins, are not specific, well defined entities. Hence, a simple, general theory, adequate to broadly describe the behaviour of many soils and slags is desirable. This study uses simple models which involve a few coefficients that are easy to evaluate experimentally.

The mechanisms which determine the rate at which chemicals are transported through soil are diffusion/dispersion, sorption-desorption, decay and intra-aggregate diffusion (Bolt, 1979). These mechanisms affect the shape of the breakthrough curves which depict effluent concentrations versus time. The results of effluent sample analysis are usually presented in this form. A qualitative interpretation of breakthrough curves is usually carried out based on the shape of the curves. The different types of curves caused by different governing mechanisms are shown in Figure 3.2.



1) Advective transport (without dispersion)
2) Advective transport + dispersion
3) Advective transport + degradation + dispersion
4) Advective transport + dissolution/desorption + dispersion
5) Advective transport + dissolution + sorption + dispersion
6) Advective transport + precipitation + sorption + dispersion
7) Advective transport + sorption (fairly mobile) + dispersion
8) Advective transport + sorption (less mobile) + dispersion
9) Advective transport + sorption (film diffusion) + dispersion

Figure 3.2 The Shape of Breakthrough Curves (Kjeldsen, 1986)

Pollutants subject to several simultaneous mechanisms of a more complex nature may exhibit other, often non-interpretable results (Kjeldsen, 1986). The present study, however, was conducted to observe sorption process only. Conditions were maintained such that sorption was the major governing process.

Sorption processes can be assumed to take place instantaneously or at a certain rate. The instantaneous sorption concept gives rise to an equilibrium sorption model, and the rate controlled process gives rise to a non-equilibrium sorption model. Non-equilibrium sorption is further classified as kinetic equilibrium and physical non-equilibrium. In this study, a Dynamic, Physical, Non-equilibrium, Sorption Model (DPNSM) was used to predict the P transport in saturated column experiments.

The usual method of obtaining isotherm constants is from batch experiments. The isotherm constants obtained by this procedure are used to predict the concentration history curve in the dynamic system. This method is generally unsatisfactory (Tiwaree, 1989; Bajracharya and Vigneswaran, 1990). The isotherm constants obtained from column experiments describe the observed breakthrough better than the isotherm constants obtained from batch experiments (Bajracharya, 1989; Bajracharya and Vigneswaran, 1990). Thus, in this study, isotherm constants obtained from column experiments were used to predict the concentration history curve.

Models belonging to the two classes of sorption reaction equilibrium are discussed in section 3.2.3 and are tested for their validity from the column experimental results conducted under various conditions.

Exact analytical solutions can be obtained for linear sorption. For non-linear isotherms, numerical techniques are used to arrive at approximate solutions.

These approximate solutions are adequate for practical purposes considering the uncertainties in the accuracy of the model parameters involved.

3.2.1 Equilibrium Sorption Model (ESM)

Many models have been developed in recent years for describing solute movement in soils. Mostly the one dimensional solute transport equation has been used to simulate the movement of contaminant in a soil matrix theoretically or experimentally. The one dimensional solute transport equation with reactions is given by (eg., Bajracharya and Barry, 1993a),

$$\frac{\partial C}{\partial t} + \frac{\rho}{\varepsilon}\frac{\partial S}{\partial t} = D_s\frac{\partial^2 C}{\partial z^2} - w\frac{\partial C}{\partial z} \qquad \text{... (3.10)}$$

where,

S = Solid phase concentration of the solute (mg/g)

C = Liquid phase concentration of the solute (mg/L)

D_s = Dispersion coefficient (cm^2/day)

w = Pore water velocity (cm/day)

ε = Porosity

ρ = Bulk density (g/L)

t = Time co-ordinate (day)

z = Spatial co-ordinate (cm)

In developing the Eqn. 3.10 for saturated flow conditions, the following assumptions are applicable.

- The flow is unidirectional.
- The flow is steady and the process is isothermal.
- The porous media is homogenous.

- The porosity, specific surface and pore size distribution of the medium do not change with time.
- The medium has constant water content and density. The density and viscosity of the fluid do not change with time and space.
- Only the dissolved solute and a few small precipitates are mobile and other solid associated chemical species are immobile.

Depending on boundary and initial conditions, Eqn. 3.10 can have different solutions. The left hand side of the equation represents the amount of mass accumulated per unit time in the elementary system considered. The first and second terms on the right hand side represent the transport rates by dispersion and advection respectively.

In order to solve the problem, the rate of sorption has to be specified by a certain function. A common assumption that can be made in groundwater systems is that the equilibrium of sorption reaction is reached quickly. Therefore, the expressions of the equilibrium isotherms can be used to quantify the partitioning between the liquid and solid phases.

In the case that processes such as sorption and ion exchange are very fast compared to the bulk fluid flow rate, then reversible sorption reactions can be assumed to be in a state of local equilibrium (Valocchi, 1985). In this model, the sorption process is assumed to be very fast or instantaneous, as diagrammatically shown in Figure 3.3. Having made this local equilibrium assumption, the model introduces the Freundlich isotherm for the sorption of P.

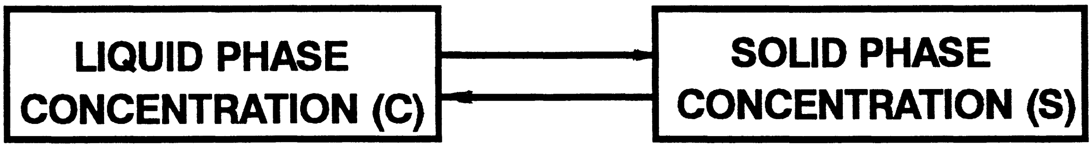


Figure 3.3 Equilibrium Sorption Process

The Freundlich isotherm for P sorption is given by Eqn. 3.6. By differentiating this equation with respect to C, one can obtain,

$$\frac{\partial S}{\partial C} = (K\theta)C^{(\theta-1)} \qquad \text{... (3.11)}$$

where, $\theta=1/N$

By substituting Eqn. 3.11 into Eqn. 3.10 and neglecting the dispersion term, the following equation is obtained:

$$-\frac{\partial C}{\partial t}/\frac{\partial C}{\partial z} = \frac{w}{1 + (\rho/\varepsilon)K\theta C^{(\theta-1)}} \qquad \text{... (3.12)}$$

where, $w_s = -\frac{\partial C}{\partial t}/\frac{\partial C}{\partial z}$ = Pore solute velocity (cm/day)

$R_d = 1+(\rho/\varepsilon)K\theta C^{(\theta-1)}$ = Retardation factor

The denominator term in the right hand side of Eqn. 3.12 is called a retardation factor (R_d). This means that the solute velocity (w_s) is retarded by a factor R_d. The relative solute Darcy velocity (w_s/w) in Eqn. 3.12 can be calculated by substituting proper values of ρ, ε, K, N, and C in Eqn. 3.12. The values of ρ, ε and C can be estimated from the soil or slag medium and solute used, while K and N can be obtained from equilibrium batch experiments involving the pertinent adsorbent and solute. Basically, Eqn. 3.12 expresses the relative solute pore velocity, which for saturated flow conditions is identical to the relative solute Darcy velocity.

3.2.2 Dynamic Physical Non-equilibrium Sorption Model (DPNSM)

The second term on the left hand side of Eqn. 3.10 describes the reaction process. When the reaction process is insufficiently fast, an additional differential rate equation must be used to solve Eqn. 3.10. This results in the non-equilibrium sorption model. Sorption kinetics can be expressed mathematically as:

$$\frac{\partial S}{\partial t} = \alpha_5[f(C) - S] \qquad \ldots (3.13)$$

where,

$$S_e = f(C) \qquad \ldots (3.14)$$

The factor α_5 is the rate constant. The solute transport equation is coupled with the rate equation and then solved for the liquid and solid phase concentrations using MCMFIT (Mixing Cell Model FIT). The MCMFIT is briefly described in the following section.

3.2.3 MCMFIT: A Program to Fit a Generalised Non-linear Advective-Dispersion Model

Recently Bajracharya and Barry (1995) developed a fitting program from an improved mixing cell model to estimate the parameters of transport models. This code, MCMFIT, makes use of non linear least-squares fitting to find optimal parameter values by matching improved mixing cell model predictions with column experimental data. The optimum values of the dispersion coefficient (D_s) and kinetic mass transfer coefficient (α_5) in column experiments were obtained by the fitting program.

In MCMFIT, a two site sorption model (Selim et al., 1976; Cameron and Klute, 1977; Rao et al., 1979) was used to consider equilibrium and non-equilibrium sorption simultaneously. Sorption on the medium surface is assumed to take place at two sites. One site is controlled by time dependent sorption reaction and the other site exhibits instantaneous sorption. The distribution of such sites is determined from the observed data.

At equilibrium, sorption on both the equilibrium and the non-equilibrium sites is described by a non linear isotherm given by:

$$S_1 = \alpha_6 \, f(C) \qquad \text{... (3.15)}$$

and

$$S_2 = (1-\alpha_6)f(C) \qquad \text{... (3.16)}$$

where, S_1 = Solid phase concentration on equilibrium sites (mg/g)

S_2 = Solid phase concentration on kinetic non-equilibrium sites (mg/g)

α_6 = Fraction of the total number of sites

Total sorption ie., ($S_1 + S_2$) is calculated using Eqn. 3.14 at equilibrium. The two site model is then given by:

$$\frac{\partial C}{\partial t} + \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} = D_s \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} \qquad \text{... (3.17)}$$

with the non-equilibrium sorption process defined by:

$$\frac{\partial S_2}{\partial t} = \alpha_5 \left[(1-\alpha_6) f(C) - S_2\right] \qquad \text{... (3.18)}$$

This process can be mathematically attributed to the large heterogeneities in microscopic pore water velocities (van Genuchten, 1981). Two site sorption processes have been efficiently solved using mixing cell models in MCMFIT. When $\alpha_6 = 1.0$ and $\alpha_5 = 0$, the two site model reduces to equilibrium model. This model reduces to dynamic non-equilibrium model when α_6 equals to zero.

A general S-curve isotherm has been incorporated in the MCMFIT. The following equation was used in the development of the fitting program due to its versatility:

$$S = \alpha_1\{1-[1+(\alpha_2 C)^{\alpha 3}]^{\alpha 4}\} \qquad \text{... (3.19)}$$

Eqn. 3.19 reduces to the Freundlich equation when $\alpha_1 = -1.0$ and $\alpha_4 = 1.0$. When $\alpha_1 = -1.0$, and $\alpha_3 = \alpha_4 = 1.0$, it reduces to linear form. It reduces to the Langmuir type when $\alpha_4 = -1.0$ and $\alpha_3 = 1.0$.

A FORTRAN program to carry out the non linear least-squares fitting of the general non linear transport model to experimental data was developed by Bajracharya and Barry (1995). It was based on the maximum neighbourhood method of Marquardt (1963) as implemented by van Genuchten (1980, 1981), Parker and van Genuchten et al. (1984), and Barry et al. (1988). Program descriptions of MCMFIT and its operation are briefly summarised at the Appendix A4.

3.2.4 Effect of Model Parameters on Breakthrough Curve

The effects of pore water velocity (w), dispersion coefficient (D_s), kinetic mass transfer coefficient (α_5), K and N Freundlich isotherm constants, fraction of equilibrium site (α_6), and influent P concentration (C_o) were studied using MCMFIT. The effects of these parameter values on the breakthrough curve are shown in Figures 3.4 to 3.10. Figure 3.4 shows simulated breakthrough curves for different pore water velocities. The breakthrough curves are nearly S-shaped with more spreading and longer breakthrough times as the pore water velocity decreases. This effect may be due to the increase of residence time in the column for lower pore water velocities, thus increasing the diffusion of the phosphorus solute into the medium. Figure 3.5 shows that the increase in the dispersion coefficient (D_s) delays the breakthrough time. For the higher dispersion coefficients (D_s>2) the simulated S-shaped breakthrough curve turns out a curvilinear pattern.

The effect of the kinetic mass transfer coefficient (α_5) is shown in Figure 3.6. A lower kinetic mass transfer coefficient (α_5<0.05) is found to be valid for the adsorbing media which have less sorption capacity. The effect of Freundlich isotherm constant K is shown in Figure 3.7. Slight changes in the Freundlich isotherm constant N have a significant effect on the breakthrough time (Figure

3.8). The smaller the N value, the more P sorption in the adsorbing media is achieved. Figure 3.8 shows that the smaller N values correspond to shorten breakthrough times. Figure 3.9 shows the breakthrough curve for the equilibrium (α_6=1, α_5=0) and non-equilibrium (α_6=0) processes.

The effect of influent P concentration is shown in Figure 3.10. Since P is favourably adsorbed in the medium, higher P concentrations diffuse faster in mobile phase than lower P concentrations, because of stronger partitioning into the solid phase as shown in the breakthrough curves. The concentration gradient within the adsorbing phase becomes larger with increases in P concentration. Then the rate of mass transfer into the solid phase increases, resulting in an earlier equilibrium state.

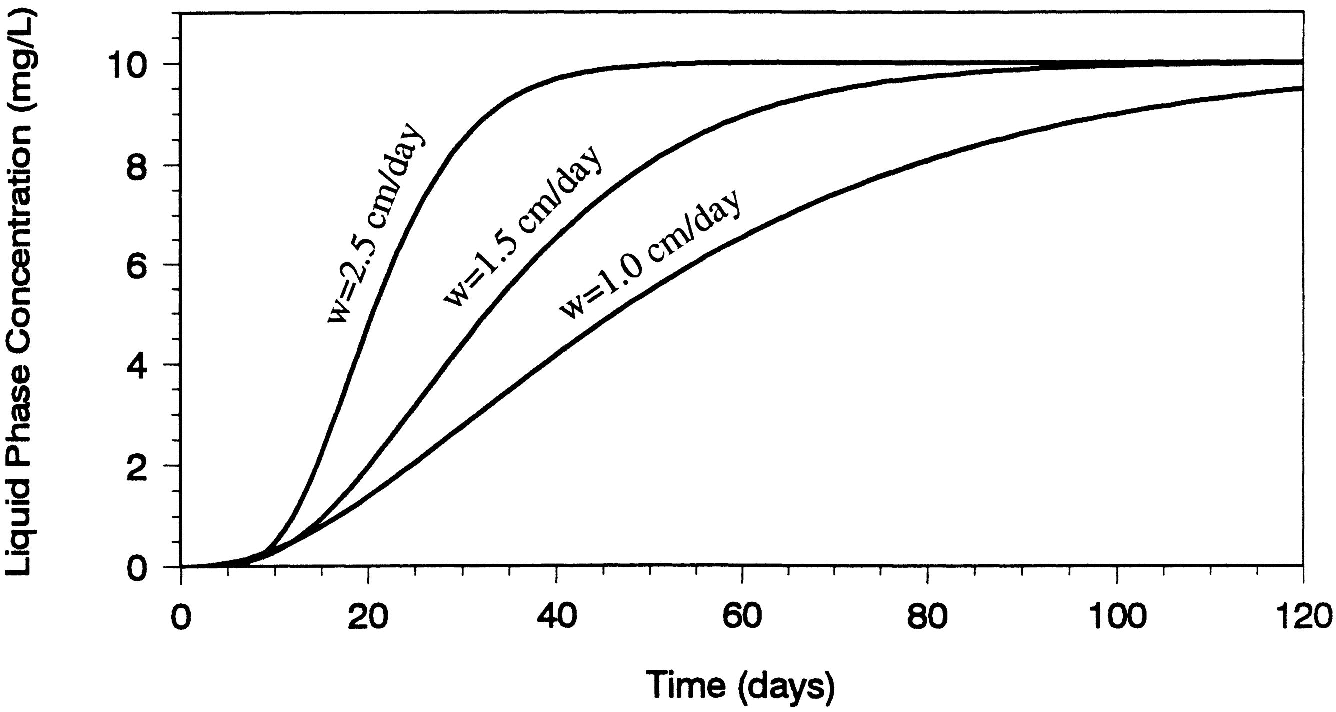


Figure 3.4 Effect of Pore Water Velocity (w) on the Breakthrough Curve (K=4.26 mg/g(L/mg)^N, N=1.11, D_s=1.20 cm^2/day, α_5=0, α_6=1.0, ROH=3.00 g/cm^3, C_o=10 mg/L, H=5 cm)

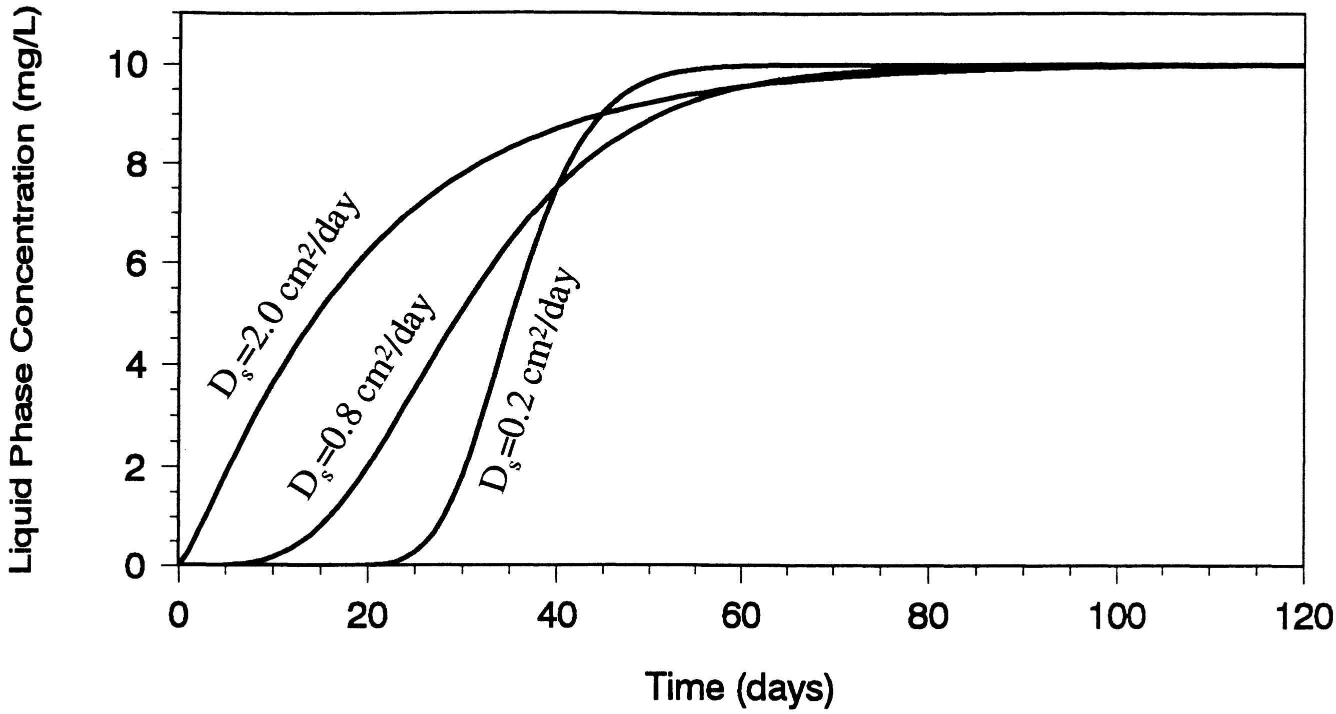


Figure 3.5 Effect of Dispersion Coefficient (D_s) on the Breakthrough Curve (K=4.26 mg/g(L/mg)^N, N=1.11, w=1.50 cm/day, α_5=0, α_6=1.0, ROH=3.00 g/cm^3, C_o=10 mg/L, H=5 cm)

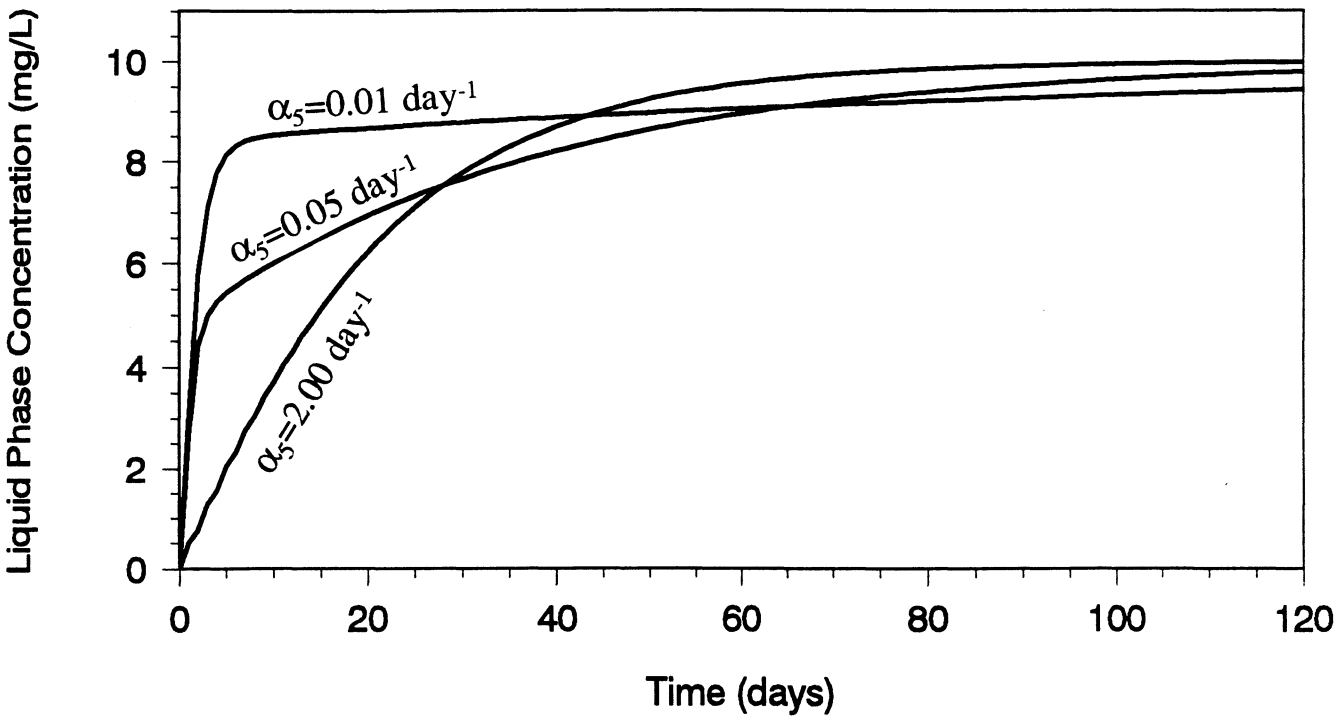


Figure 3.6 Effect of Kinetic Mass Transfer Coefficient (α_5) on the Breakthrough Curve (K=4.26 mg/g(L/mg)^N, N=1.11, w=1.50 cm/day, D_s=1.20 cm^2/day,α_6=0, ROH=3.00 g/cm^3, C_o=10 mg/L, H=5 cm)

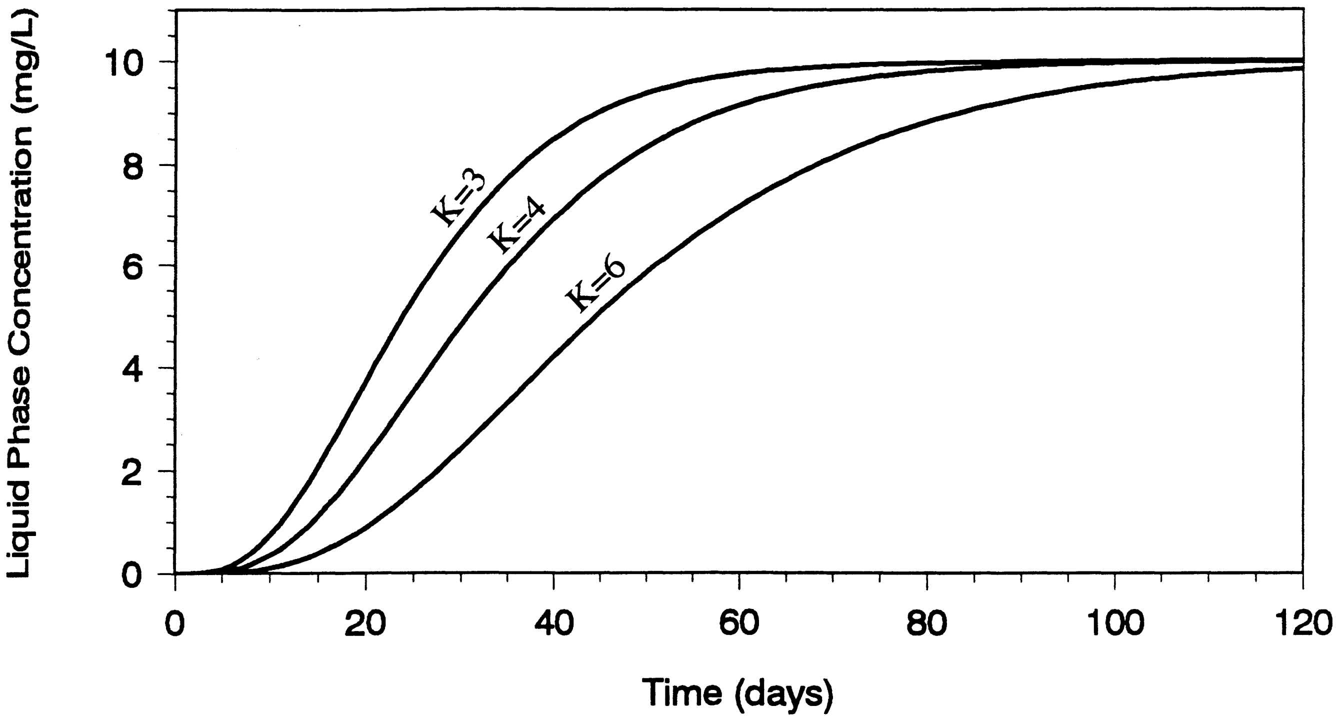


Figure 3.7 Effect of Freundrich Isotherm Constant K on the Breakthrough Curve ($N=1.11$, $w=1.50$ cm/day, $D_s=1.20$ cm^2/day, $\alpha_5=0$, $\alpha_6=1.0$, ROH=3.00 g/cm^3, $C_o=10$ mg/L, $H=5$ cm)

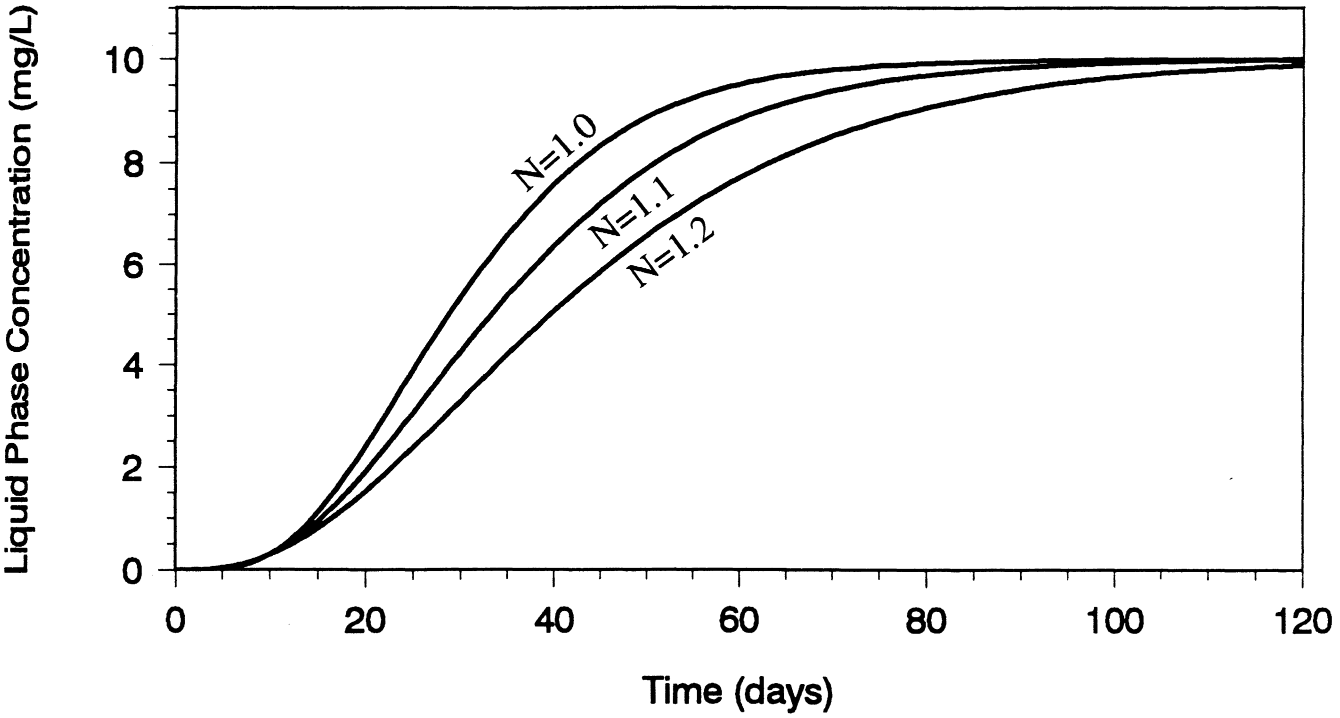


Figure 3.8 Effect of Freundrich Isotherm Constant N on the Breakthrough Curve ($K=4.26$ mg/g(L/mg)^N, $w=1.50$ cm/day, $D_s=1.20$ cm^2/day, $\alpha_5=0$, $\alpha_6=1.0$, ROH=3.00 g/cm^3, $C_o=10$ mg/L, $H=5$ cm)

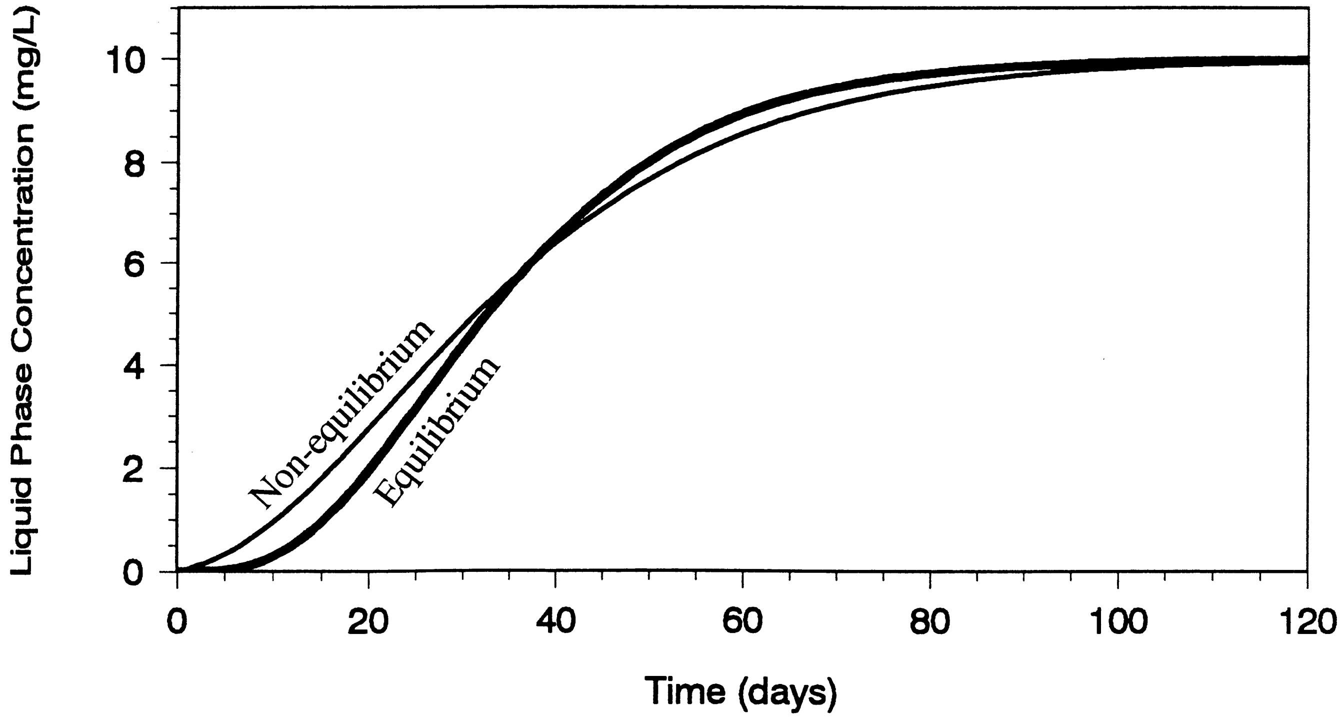


Figure 3.9 Effect of Fraction of Equilibrium Site (α_6) on the Breakthrough Curve (K=4.26 mg/g(L/mg)^N, N=1.11, w=1.50 cm/day, D_s=1.20 cm^2/day, ROH=3.00 g/cm^3, C_o=10 mg/L, H=5 cm)

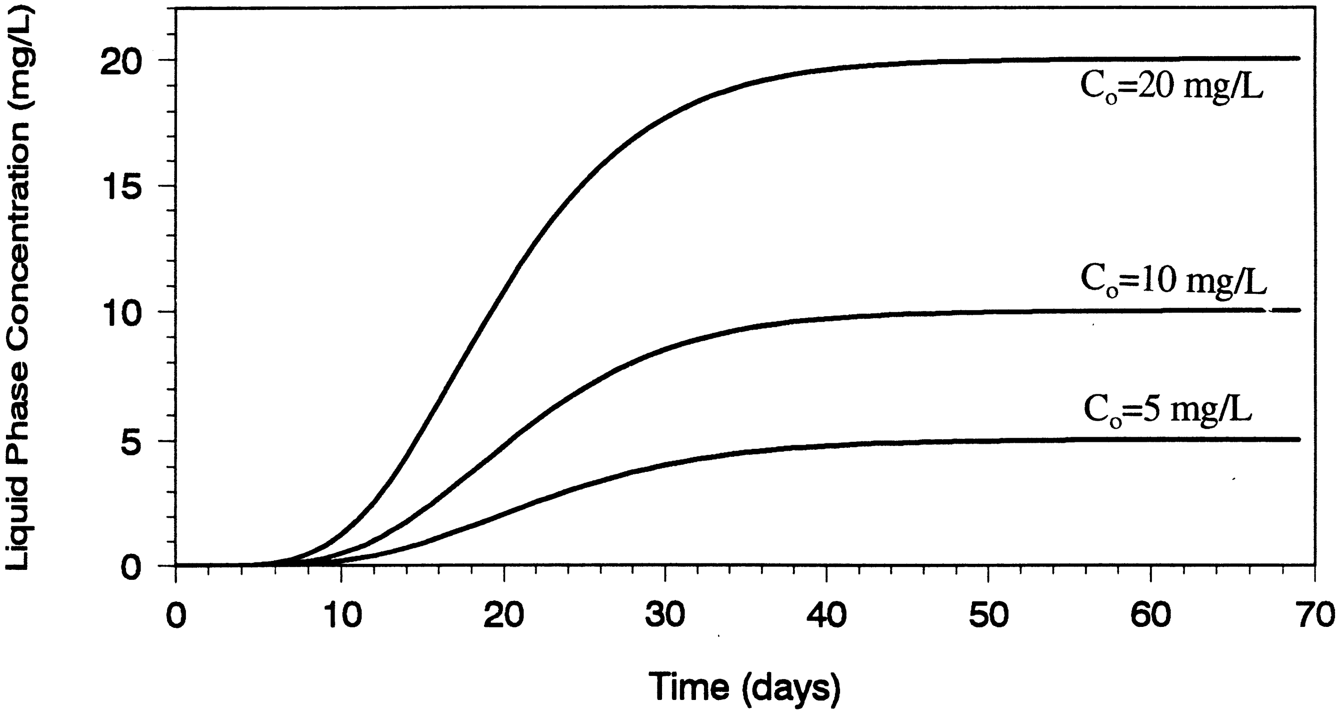


Figure 3.10 Effect of Influent Concentration (C_o) on the Breakthrough Curve (K=4.26 mg/g(L/mg)^N, N=1.11, w=1.50 cm/day, D_s=1.20 cm^2/day, α_5=0, α_6=1.0, ROH=3.00 g/cm^3, H=5 cm)

IV. EXPERIMENTAL INVESTIGATION

The experimental investigations carried out in this study can be divided into two parts: batch and column sorption studies.

4.1 Materials Used

4.1.1 Adsorbents Analysis

A sandy loam soil obtained from North Sydney, Australia, and slag waste materials such as dust and cake obtained from the BHP steel industry were used as the adsorbents in batch and column experiments for P transport in this study. Since the main emphasis of this study was on the investigation of mechanisms of P removal, the soil used was chosen arbitrarily. The dust was taken from the secondary bag house used to control fugitive emissions from vessels in the steel industry. The cake is gas scrubbing slurry from the blast furnace. In the steel production process, converter slag (dust) and blast furnace slag (cake) are produced independently, and they have different natures.

Soil samples were taken at different depths and places to represent the area sampled. They were air dried at 105 °C for 24 hours and the media of less than 2 mm size fraction obtained through sieving were used in the experiments. The coarser fractions (>2 mm) and plant debris of the soils were removed by dry sifting in an acid cleaned sieve with a 2 mm brass mesh. Soil samples were mixed well and air dried at room temperature before being used in the experiments. Figure 4.1 shows the soil texture classification. The relative properties of clay, silt and sand particles in a soil are referred to as the mechanical or particle size composition of soil. This is used to determine the soil textural class based on certain arbitrary divisions. The terms sand, silt and clay denote not only primary soil particles but also designate a soil type (U.S. Department of Agriculture, 1964). From the analysis, it was evident that the test soil is mainly composed of medium sized sand and can be classified as a sandy loam soil.

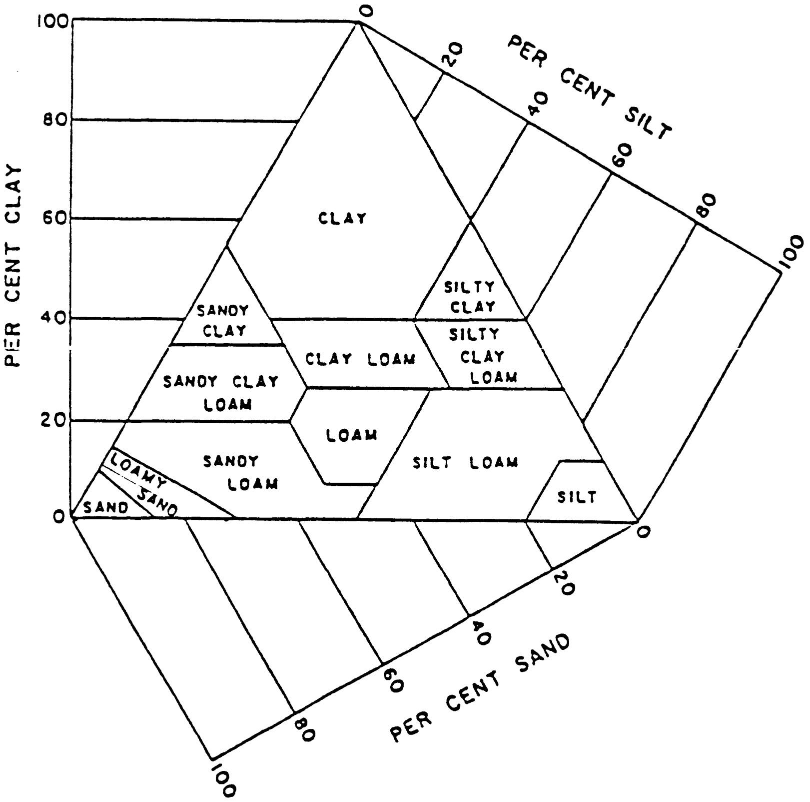


Figure 4.1 Soil Texture Classification (U.S. Department of Agriculture, 1964)

Steel industry dust was taken from the secondary bag house deducting system used to control fugitive emissions from vessels in the steel industry. Cake is gas scrubbing slurry from the blast furnace. In the steel production process, converter slag (dust) and blast furnace slag (cake) are produced independently, and they have different natures.

The characteristics of soil, dust and cake were analysed by standard procedures (Klute et al., 1986). Percent sand, silt and clay were determined by the hydrometer method. The pH of suspensions in water was measured by a HI8314 Membrane pH Meter. The pycnometer method was used to determine particle density. Permeability was determined by the constant head method. Total element concentrations in soil, dust and cake were determined in an acidified solution by ICPAES (Inductively Coupled Plasma Atomic Emission Spectrometer). The analytical methods to study the physical and chemical properties of soil, dust and cake are summarised in Tables 4.1 and 4.2.

Table 4.1 Analytical Sources of Physical Properties of Soil, Dust and Cake

Constituents	Analytical Sources
1. Classification of Soil	Based on the textural triangle and nomenclature developed by the U.S. Soil Conservation Service (1951)
2. Soil Texture	Australian Standard Method AS.1289. C6.1-1977
3. Specific Gravity and Bulk Density	Australian Standard Method AS.1289.E1.1-1977
4. Particle Density	Water Treatment Hand Book by Degremont (1991)
5. Porosity	Natural Systems for Waste Management and Treatment by Reed (1988)

Table 4.2 Analytical Sources of Chemical Properties of Soil, Dust and Cake (NSW Department of Agriculture, 1994)

Constituents	Analytical Sources
1. pH	Method No. EEC 101
2. Cation Exchange Capacity (CEC)	Method No. EEC 101, ICP 301
3. Total Nitrogen (TN)	Method No. ETN 101
4. Total Phosphorus (TP)	Method No. EMD 101, ICP 101, ICP 201
5. Organic Matter	Wakely Black
6. Exchangeable Cations (Ca, Na,Al)	Method No. EEC 101, ICP 301
7. Heavy Metal (Fe)	Method No. EMD 101, ICP 101, ICP 201

4.1.2 Chemicals Used in Preparing Synthetic Wastewater

Various concentrations of P solution were prepared to study the degree of P removal. Known amounts of solid Na_2HPO_4 were mixed with distilled water to prepare P solutions in the range of 5 mg/L to 50 mg/L. The measurement of P was done according to the Standard Methods for Examination of Water and Wastewater (1985). P concentration was determined by Stannous Chloride method using a Milton Roy Spectronic 20D spectrophotometer. The effect of P sorption in the presence of foreign materials were studied using known concentration of P and NH_4 solutions. Reagent grade chemicals were used in preparing standard solutions as given in Standard Methods for the Examination of Water and Wastewater (1985). The pH value of the solution was initially adjusted by sodium hydroxide (NaOH) solution and hydrochloric acid (HCl) using a HI8314 Membrane pH Meter. Synthetic wastewater was prepared to study the effect of foreign materials on P sorption in batch experiments. Table 4.3 shows the characteristics of the synthetic wastewater.

Table 4.3 Characteristics of the Synthetic Wastewater (Stock Solution)

Constituent	Quantity (g)
Glucose (Commercial Grade)	10.00
Urea (")	7.15
KH_2PO_4 (Analytical Grade)	0.85
K_2HPO_4 (")	2.18
Na_2HPO_4 (")	1.77
NH_4Cl (")	0.17
$MgSO_4.7H_2O$ (")	2.25
$CaCl_2$ (")	2.75
$FeCl_2.H_2O$ (")	0.03
Distilled Water	to 1 L

4.2 Design of Batch Experiments

The batch sorption experiments conducted have been classified into three different categories as discussed below: Batch sorption experiments in the mixing system, batch sorption experiments in the static system and batch flocculation experiments. In the case of the mixing system, a known amount of adsorbent was mixed thoroughly with the P solution for 1 minute using a magnetic stirrer at 120 rpm. The sorption was allowed to continue without any mixing afterwards. On the other hand, the batch experiments under the static system did not involve any mixing even at the initial stage of P sorption.

4.2.1 Batch Sorption Experiments of P in the Mixing System

The batch reactors were 250 mL conical glass flasks. In each flask, 200 mL of a known concentration of P solution was mixed with the known amount of adsorbent. Preliminary batch experiments were conducted to determine the optimum amounts of soil, dust and cake as adsorbents. It was difficult to observe an equilibrium state for amounts of adsorbents less than 30 g for soil, 0.05 g for dust and 0.5 g for cake within 240 hours, especially for the high initial P concentrations (more than 30 mg/L of P). In addition, it was impossible to estimate the solid phase concentrations at various initial concentrations for amounts of adsorbents more than 100 g for soil, 2 g for dust and 5 g for cake. When the amount of adsorbents was more than 100 g for soil, 2 g for dust and 5 g for cake respectively, the equilibrium liquid phase P concentration was almost zero within 24 hours for the initial P concentration of 5 to 15 mg/L. Eventually the amount of adsorbents used for batch sorption experiments was determined so as to avoid the above two drawbacks. Reactors were thoroughly cleansed in nitric acid and distilled water. They were oven dried before they were used. The batch sorption experimental set up in the mixing system is shown in Figure 4.2.

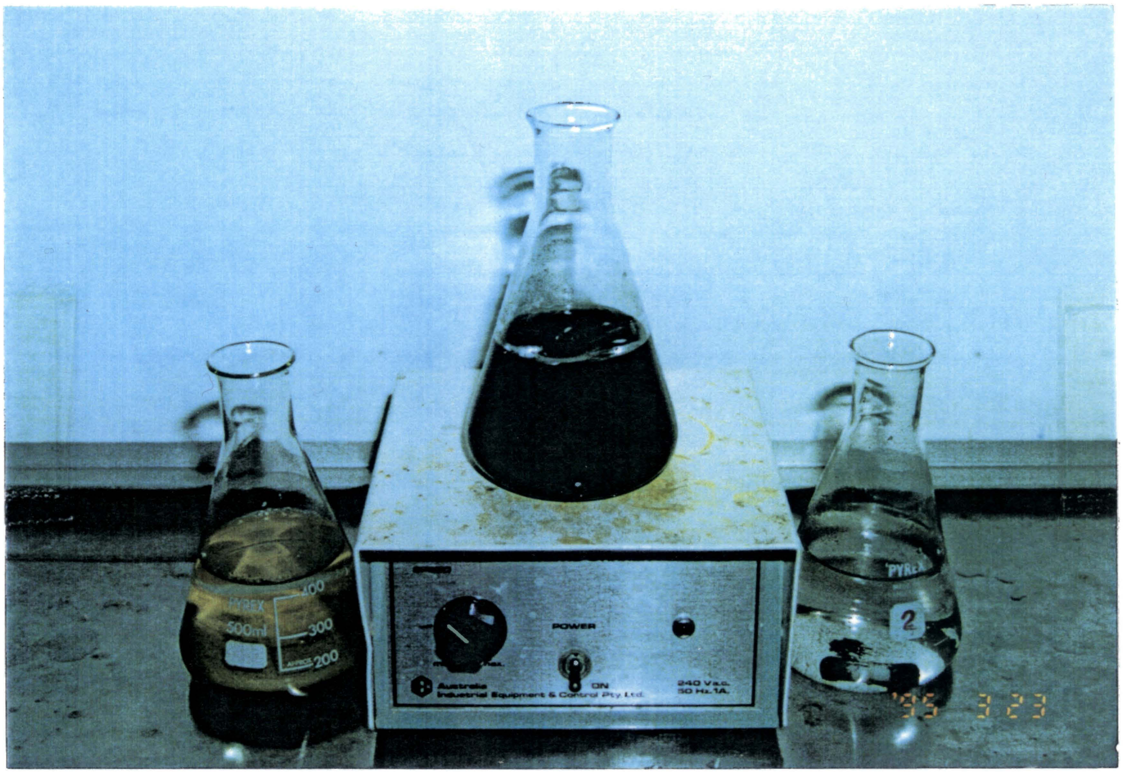


Figure 4.2 Batch Sorption Experimental Set-up in the Mixing System

4.2.1.1 Experiments to Study the Kinetics of P Sorption

The purposes of these experiments are to investigate the P removal process with time and to find the equilibrium P concentration. P sorption was characterised by the Freundlich and Langmuir isotherm constants. Standard P solutions were prepared by dissolving Na_2HPO_4 in distilled water. Sorption experiments for P were carried out at various initial P concentrations and the supernatant concentrations of P were determined with the increase of time interval (15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours and up to 120 hours). A known amount of the adsorbents (50 g for soil, 0.1 g for dust and 1.0 g for cake respectively) was thoroughly mixed for 1 minute using a magnetic stirrer (with the mixing velocity of 120 rpm). Standard P solutions had various initial concentrations ranging from 5 to 40 mg/L. The details of the experiments are summarised in Table 4.4.

Table 4.4 Experiments on Kinetics of P Sorption in the Mixing System

Adsorbent Type	Amount of Adsorbent (g)	Volume of P Solution (mL)	Initial P Concentration (mg/L)
Soil	50.0	200	5,10,15,20 25,30,35,40
Dust	0.1	200	5,10,15,20 25,30,35,40
Cake	1.0	200	5,10,15,20 25,30,35,40

Equilibrium sorption experiments were duplicated to confirm the accuracy of the results. For the determination of liquid phase concentration, the supernatant was filtered and the P (as orthophosphate) concentration was measured by the visible light spectrophotometer. The solid phase concentration was computed from the following relation (the intrinsic amount of P in the adsorbents was not added to the solid phase concentration):

$$S = \frac{(C_o - C_f).\Theta}{\beta} \qquad \text{... (4.1)}$$

where, C_o = Initial liquid phase concentration (mg/L)

C_f = Final equilibrium concentration (mg/L)

S = Solid phase concentration (mg/g)

Θ = Amount of solution (L)

and β = Amount of adsorbent (g)

Equilibrium sorption isotherm constants in the mixing and static systems were evaluated from equilibrium batch sorption experiments. The experiments involved equilibration for a period of 120 hours. The sorption was quantified using both Freundlich and Langmuir isotherms. The Freundlich isotherm is expressed as:

$$S = KC^{1/N} \qquad \text{... (4.2)}$$

where, S = Solid phase concentration (mg/g)

C = Liquid phase concentration (mg/L)

K = Freundlich isotherm constant [mg/g(L/mg)^N]

N = Freundlich isotherm constant (dimensionless)

Taking 'logarithms' on both sides of Eqn. 4.2,

$$\log S = \log K + (1/N) \log C \qquad \text{... (4.3)}$$

Eqn. 4.3 gives a straight line plot, when 'log S' is plotted against 'log C' with the intercept as 'log K' and gradient as '1/N'.

The Langmuir equation is based on kinetic principles and the monolayer concept. Langmuir regarded the surface of solid as an array of sorption sites, each site being capable of adsorbing a molecule of adsorbate. The Langmuir isotherm is of the form,

$$S = \frac{ab\,C}{1 + bC} \qquad \text{... (4.4)}$$

where, a,b = Langmuir isotherm constants

Eqn. 4.4 gives a straight line plot when 'C/S' is plotted against 'C' with the intercept as '1/ab' and gradient as '1/a'.

4.2.1.2 Batch Sorption Experiments at Different pH Levels

A series of batch sorption experiments of P was conducted at different pH levels in the same manner. The initial pH of the P solution ranged from 2 to 12. The pH of P solution was adjusted only at the initial stage of experiment and no adjustments were made thereafter when sorption was taking place. The details of the experiments at different pH levels are summarised at Table 4.5.

Table 4.5 Batch Sorption Experiments of P at Different pH Levels

Adsorbent Type	Amount of Adsorbent (g)	Volume of P Solution (mL)	pH	Initial P Conc. (mg/L)
Soil	50.0	200	2,4,6,8,10,12	20
Dust	0.3	200	2,4,6,8,10,12	20

4.2.1.3 Batch Precipitation Experiments at Different pH Levels

Chemical precipitation experiments were conducted to verify the predominant mechanism for P removal at different pH levels. Fixed amounts of soil and dust (50.0 g and 0.3 g respectively) were separately added to 200 mL of distilled water and then thoroughly mixed for 1 minute. The supernatant of the mixed solution was decanted and this decanted solution was used to prepare the standard P solution. The amount of P removed by precipitation at different pH levels was compared with that by sorption. The details of the batch precipitation experiments at different pH levels are summarised in Table 4.6.

Table 4.6 Batch Precipitation Experiments at Different pH Levels

Adsorbent Type	Volume of P Solution (mL)	pH	Initial P Conc. (mg/L)
Soil	200	2,4,6,8,10,12	20
Dust	200	2,4,6,8,10,12	20

4.2.1.4 Batch Sorption Experiments in the Presence of Foreign Material

As wastewater contains NH_4-N in addition to P and both compounds are adsorbed normally by soil and slag media, the effects of NH_4-N on the sorption of P were studied. Dust and cake were used as the adsorbents. The batch reactors were 250 mL conical glass flasks. The initial P concentrations in this solution were 5, 10, 15, 20, 25, 30, 35 and 40 mg/L and the concentration of NH_4 was maintained at 40 mg/L. A known amount (0.1 g for dust and 1.0 g for cake respectively) of the adsorbents was thoroughly mixed with the solution for 1 minute at a mixing speed of 120 rpm and no mixing occurred afterwards. The details of the experiments are described in Table 4.7. Two batch sorption experiments were also conducted to study the sorption behaviour of P in the presence of other foreign materials using synthetic wastewater with the characteristics shown in Table 4.3. The experimental conditions are presented in Table 4.8.

4.2.2 Batch Sorption Experiments of P in the Static System

Another series of batch sorption experiments was conducted to study the P sorption in the static system. The batch reactors used were 500 mL conical flasks. In each flask, 400 mL of a known concentration of P solution was mixed with a known amount of adsorbent (100.0 g for soil, 0.4 g for dust and 2.0 g for cake respectively).

Table 4.7 Batch Sorption Experiments of P in the Presence of NH_4

Adsorbent Type	Amount of Adsorbent (g)	Volume of Solution (mL)	Initial P Conc. (mg/L)	NH_4-N Conc. (mg/L)
Dust	0.1	200	5,10,15,20 25,30,35,40	40
Cake	1.0	200	5,10,15,20 25,30,35,40	40

Table 4.8 Batch Sorption Experiments of P in the Synthetic Wastewater

Adsorbent Type	Amount of Adsorbent (g)	Volume of Solution(mL)	Initial P Conc. (mg/L)
Dust	0.1	200	10,20,30,40
Cake	1.0	200	10,20,30,40

The standard P solution and the adsorbents were kept in a completely static (no stirring or mixing) condition throughout the experiments. The experiments were carried out at various initial concentrations (5 to 30 mg/L of P). The liquid phase concentrations were determined at different times (1, 2, 4 hours and up to 170 hours for dust and up to 480 hours for soil and cake). The pH of the P solution was measured at various times to study pH changes as P sorption proceeded. Figure 4.3 shows the batch sorption experimental set-up in the static system. The details of batch sorption experiments to study the kinetics of P sorption in the static system are summarised in Table 4.9.

4.2.3 Batch Flocculation Experiments

The jar test is a batch experiment which is not practical at most wastewater treatment plants. While a wastewater treatment plant treats flows of the order of

100 L/s, the jar test is conducted with 1 litre of wastewater. Thus batch flocculation experiments may not perfectly simulate full scale wastewater treatment processes. Despite this limitation, however, the jar test is recommended for assessing coagulation and flocculation (Barnes et al., 1986; WPCF, 1977, 1991).

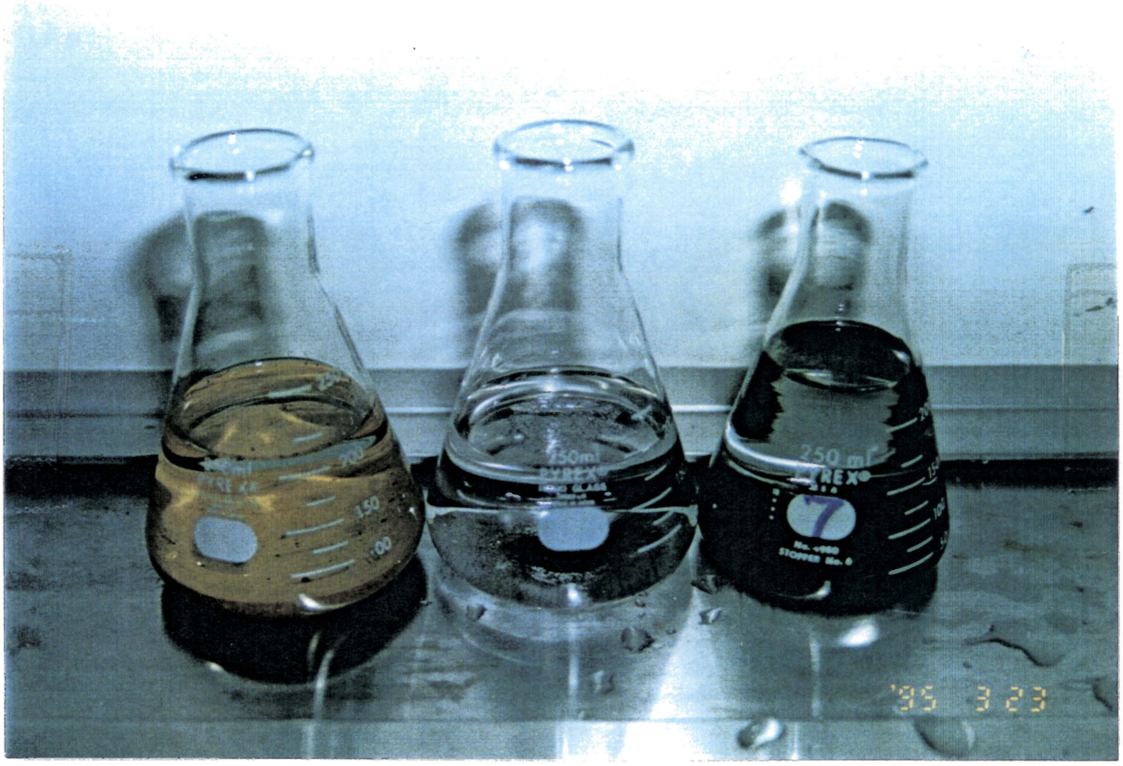


Figure 4.3 Batch Sorption Experimental Set-up in the Static System

Table 4.9 Experiments on Kinetics of P Sorption in the Static System

Adsorbent Type	Amount of Adsorbent (g)	Volume of P Solution (mL)	Initial P Concentration (mg/L)
Soil	100.0	400	5,10,15 20,25,30
Dust	0.4	400	5,10,15 20,25,30
Cake	2.0	400	5,10,15 20,25,30

A series of batch flocculation experiments was conducted to investigate the effect of flocculant dose, flocculation time and mixing rate. Dust was used as an adsorbent throughout the batch flocculation experiments because it proved to be the most effective in the removal of P among the three adsorbents tested. The batch flocculation experimental apparatus consists of a set of six vertical paddles lined up with a common horizontal drive shaft. The paddles are motor driven with a variable speed control and speed indicator. The reactors were one litre beakers. In each beaker, 1000 mL of a known concentration of P solution was mixed with a known amount of dust. The mixing speed was fixed throughout the experiments. Samples were decanted from each beaker at different contact times. The experimental set-up and its sketch are shown in Figures 4.4A and 4.4B respectively. The percentage of P removal was quantified under various conditions. The experimental conditions of the batch flocculation experiments are presented in Table 4.10.

4.3 Design of Column Experiments

The field conditions were simulated in the laboratory by packing a column with the same soil, dust and cake media used in the batch experiments. The column experiments were carried out mainly to validate the mathematical models and to find the breakthrough pattern under various conditions.

The experimental set-up consisted of perspex columns packed with the adsorbent. A phosphorus solution was supplied to the columns under gravity from overhead containers (each with a capacity of 20 litres). The constant head was ensured by providing an overflow tube above the adsorbents. The effluent flow was controlled by a flow meter.

Table 4.10 Summary of Batch Flocculation Experiments

	Amount of Dust Added (g)	Initial P Conc. (mg/L)	Mixing Speed (rpm)	Contact Time (minutes)
Effect of Dust Dose at Different Initial P Conc.	5,10,20 30,50,100	10,20,30	60	30
Effect of Dust Dose at Different Contact Time	5,10,20 30,50,100	20	60	10,30,60
Effect of Contact Time at High Dust Dose	30	10,20,30	60	10,20,30 40,50,60
Effect of Contact Time at Low Dust Dose	2	5,10	60	10,20,30 40,50,60
Effect of Mixing Velocity	30	10,20,30	20,40 60,80	30

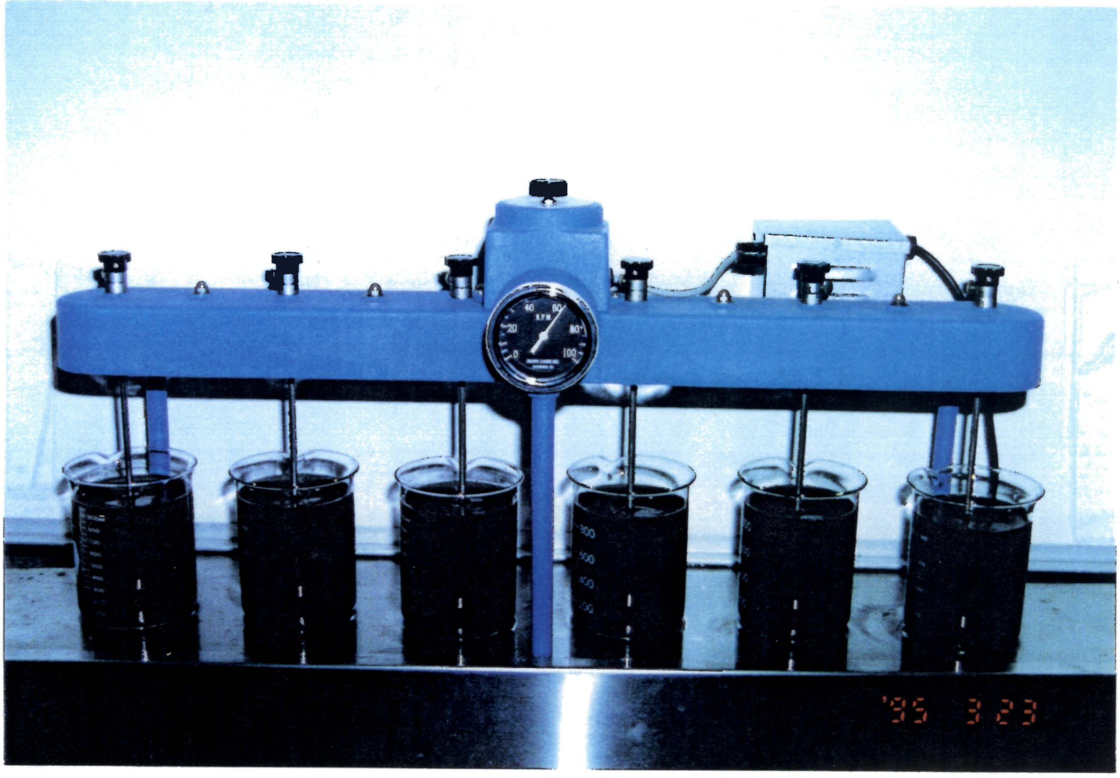


Figure 4.4A Batch Flocculation Experimental Set-up

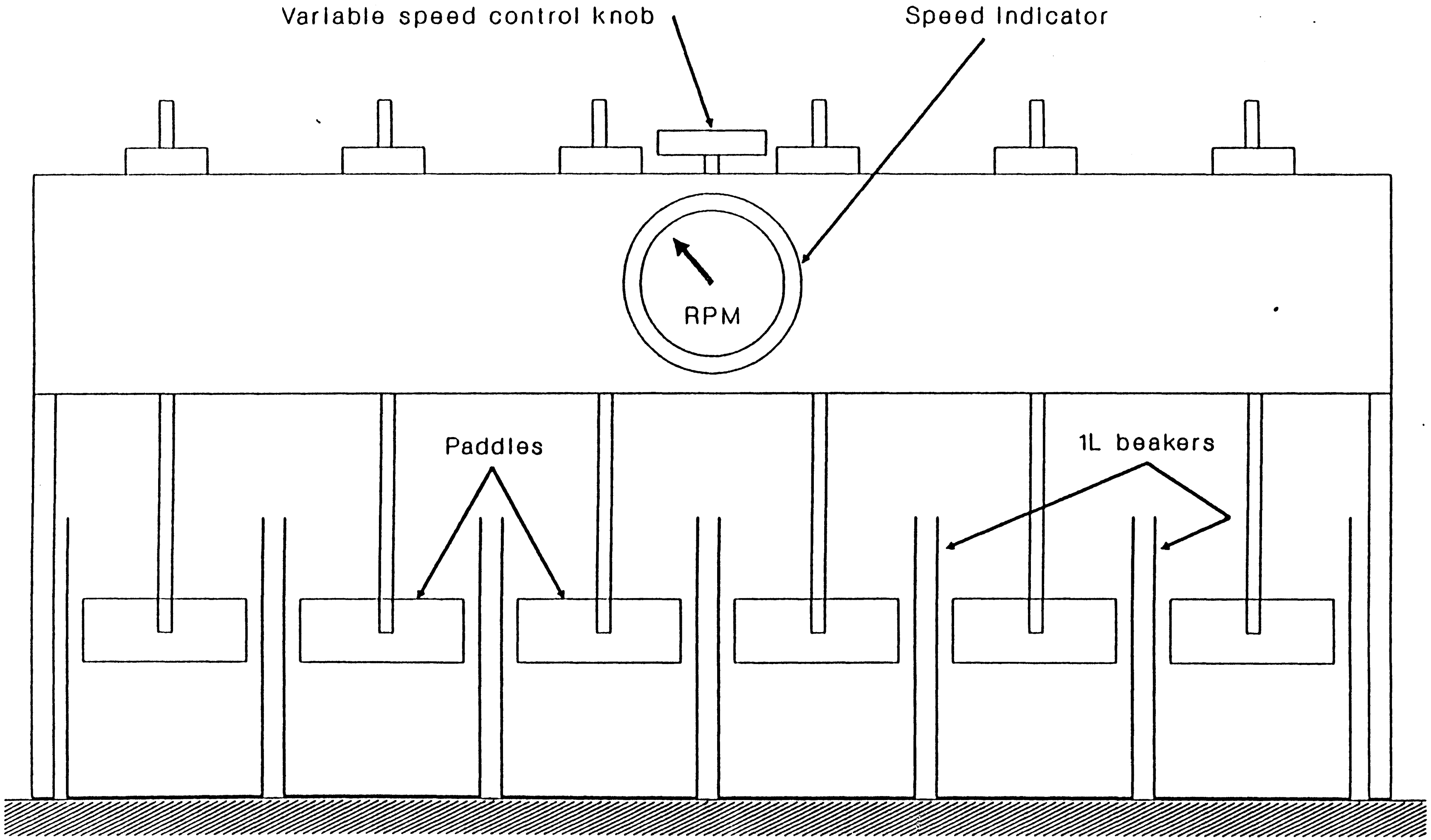


Figure 4.4B Sketch of Batch Flocculation Experimental Set-Up (Not to Scale)

A sketch of the experimental set-up is shown in Figure 4.5. Figure 4.6 shows the details of column structure. Pre-wetting of the adsorbents was ensured by putting them into a tap water column. The concentration of PO_4-P in the tap water was less than 0.05 mg/L. Care was taken not to allow any air bubbles in the under drainage section and in the media layer. The bulk density was computed from the volume and weight of the media packed in the column.

It is evident that the solid phase concentration (S) and the liquid phase concentration (C) must co-exist in equilibrium at the breakthrough point. This is the principle on which the isotherm constants have been evaluated. The pH of the P solution in the influent was maintained in the range of 6 to7. The solid phase concentration was estimated in the equilibrium state. Six columns of 9 cm diameter were packed with the adsorbents to thicknesses of 1 to 5 cm (H). In a few cases a 30 cm diameter column was used to investigate whether there is any significance of the column diameter. The depth of the media was maintained shallow at 1-5 cm to achieve an early breakthrough. The entire effluent concentration history curve was recorded. To estimate the solid phase concentration, the soil, dust or cake in the column was taken out for air drying at the equilibrium stage of each column. It was further dried in an oven at a temperature of 105 °C for 24 hours. Then the pre-weighed amount of the adsorbents was extracted by using nitric acid. After extraction, it was diluted by adding a required volume of distilled water and the solution was decanted. Then the samples were analysed for P concentration by using a spectrophotometer. Mathematically, the solid phase concentration can be expressed as:

$$S = \frac{CV}{\beta} \qquad \text{... (4.5)}$$

where, C = Liquid phase concentration (mg/L)

S = Solid phase concentration (mg/g)

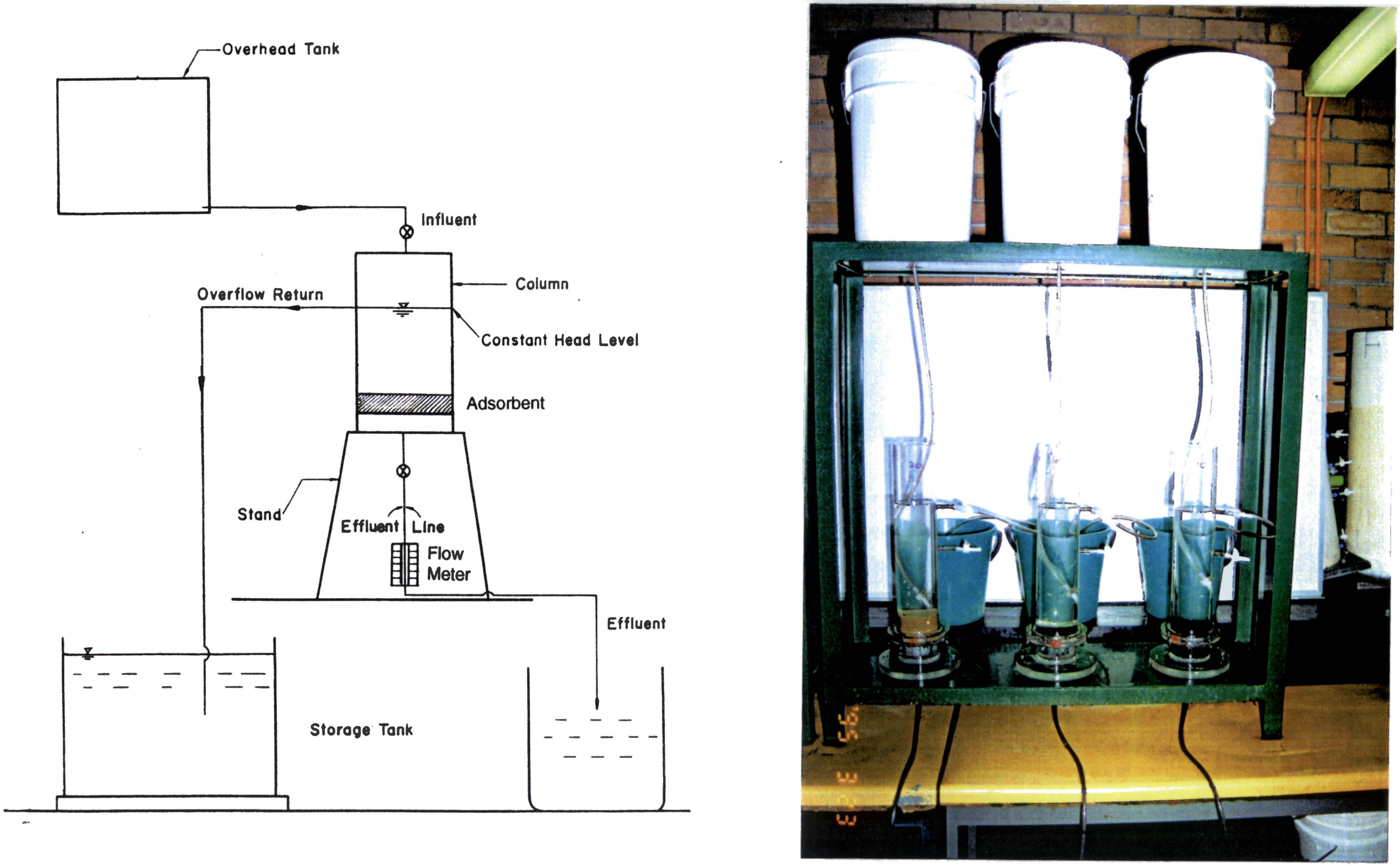


Figure 4.5 Column Experimental Set-up (Not to Scale)

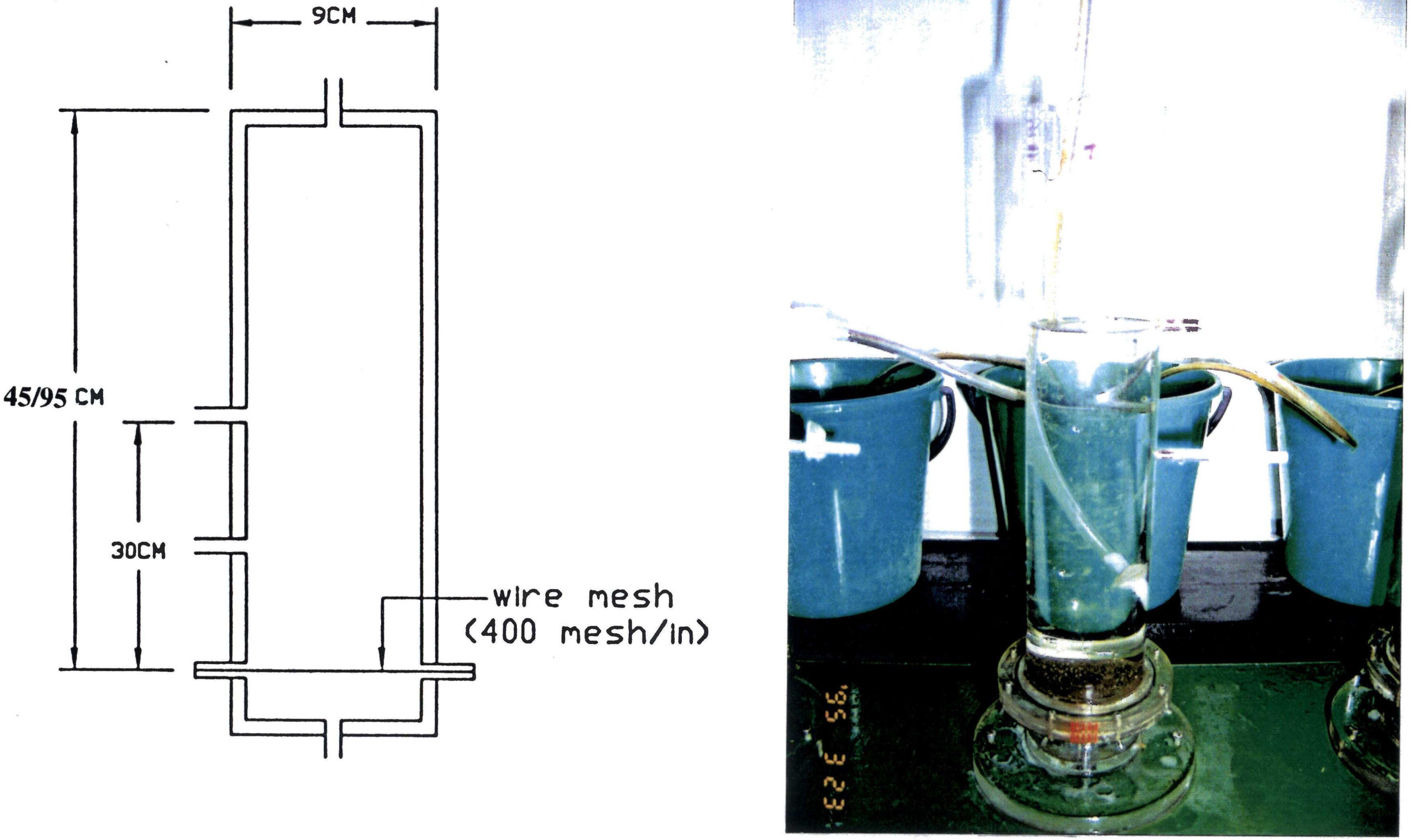


Figure 4.6 Details of Column Texture (Not to Scale)

V = Volume of solution (L)

β = Amount of the adsorbent (g)

4.3.1 Column Experiments with Soil

A series of four soil column experiments were conducted varying the influent concentration, pore water velocity, adsorbent depth and the water level above the soil. The influent P concentration ranged from 10 to 40 mg/L and the soil depth was maintained at 5 cm of depth. It was difficult to maintain the velocities exactly equal in all the columns. The pore water velocities reported are the average values during the experimental run time. The pore water velocity range studied was 1.53 to 5.14 cm/day. Columns of two different diameters (9 and 30 cm) were used to enable the collection samples of sufficient quantity within a short time interval. Wire mesh (400 meshes/in) was placed below the adsorbent to distribute effluents uniformly. Each column was flooded with a known concentration of P solution. Forty litres of P-free water was infiltrated through the soil column prior to the introduction of the P solution to ensure a uniform compactness of soil. The effluent P concentration was measured till the effluent concentration was equal to the influent P concentration.

Another series of column experiments were carried out at different pore water velocities (w) to investigate the effect of pore water velocity on P removal. Soil depth and water level above the adsorbent were kept constant while pore water velocitis were controlled by a flow meter.

A set of column experiments was also conducted varying the soil depth (1, 2, 3, 4 and 5 cm) to investigate the effect of soil depth on P removal. Water levels above the soil medium and pore water velocities were varied at different soil depths.

Finally a series of the column experiments were conducted varying the water level (5, 15 and 25 cm) above the soil medium to study the effect of water level on P removal. Soil depth was kept constant at different water levels. The experimental conditions of the soil column experiments are summarised in Table 4.11.

Table 4.11 Summary of Soil Column Experiments

	Influent P Conc. (mg/L)	Pore Water Velocity (cm/day)	Adsorbent Depth (cm)	Water Level (cm)	Column Diameter (cm)
Effect of Initial Conc. of P	10,20 30,40	1.5, 2.1 2.9, 5.1	5	25	9
Effect of Pore Water Velocity	30	1.0, 1.6, 2.3	5	25	9
Effect of Filter Depth	50	38.0, 11.8 9.1, 5.0	2,3,4,5	25	9
Effect of Water Level	30	1.2, 1.9, 2.9	5	5,15,25	30

4.3.2 Column Experiments with Dust

Column experiments were conducted with dust of 1 cm depth. A high pore water velocity (w=305 cm/day) was maintained for the influent concentrations of 5, 10, 20 and 30 mg/L to achieve early breakthrough times. The pore water velocity was maintained low (w=37 and 43 cm/day) for the high influent concentrations of 40 and 50 mg/L to observe the breakthrough pattern in detail (It took only a few hours to reach at breakthrough stage for the influent concentrations of 40 and 50 mg/L and the high pore water velocity of 305 cm/day). The shallow depth of dust (1 cm) was adopted to shorten the breakthrough time and to reduce the possible effect of chemical precipitation of P. Precipitation may occur with the increase in contact time between the P solute and the dust particles. Forty litres of P-free water were infiltrated through the dust column prior to the introduction of P solution to ensure the uniform compaction of dust. The pH change of the P solution in the influent concentrations of 40 and 50 mg/L was also estimated.

The other series of dust column experiments was conducted to study the effect of foreign material containing NH_4-N on P removal. The conditions of the dust column experiments is presented in Table 4.12.

Table 4.12 Summary of Dust Column Experiments

	Influent P Conc. (mg/L)	NH_4-N Conc. (mg/L)	Pore Water Velocity (cm/day)	Adsorbent Depth (cm)	Water Level (cm)
Effect of Influent P Conc.	5,10,20,30 40,50	0	305 37, 43	1	29
Effect of Foreign Material	20	0,10,20	305	1	29

4.3.3 Column Experiments with Cake

Column experiments with a cake medium packed to 3 cm deep were performed for different influent concentrations of P (5, 10, 20, 30, 40 and 50 mg/L). The pH was maintained at 6-7. Pore water velocities ranged from 10 to 60 cm/day at different influent concentrations. Forty litres of P-free water was also infiltrated through the cake column prior to the introduction of P solution to ensure the uniform compaction of cake. The pH change of the P solution in the influent concentrations of 40 and 50 mg/L was measured.

Another series of cake column experiments was conducted to study the effect of NH_4-N on P removal. Influent NH_4-N concentration was maintained at 30 mg/L. The conditions of the cake column experiments are presented in Table 4.13.

Table 4.13 Summary of Cake Column Experiments

	Influent Conc. of P (mg/L)	NH_4-N Conc. (mg/L)	Pore Water Velocity (cm/day)	Adsorbent Depth (cm)	Water Level (cm)
Effect of Influent P Conc.	5,10,20 30,40,50	0	10,10,16 46, 54, 60	3	27
Effect of Foreign Material	20	0,30	890	1	29

V. RESULTS AND DISCUSSION

The experimental results obtained from this study are presented in this chapter with qualitative and quantitative interpretations. They have been grouped into six sections. The first section presents the physical and chemical characteristics of the adsorbents used such as soil, dust and cake. The next three sections discuss the batch experiments and the fifth section covers the column experiments conducted. Practical aspects of the field application of dust and cake are discussed in the sixth section.

5.1 Characteristics of the Media

Since P transport from the liquid phase to the solid phase is influenced by the intrinsic characteristics of the media, the physical and chemical properties of soil, dust and cake need to be investigated for proper interpretation of P sorption. The details of the analytical methods used are given in Chapter IV (Section 4.1.1).

5.1.1 Physical Characteristics of the Media

The grain size analysis for the soil is presented in Figure 5.1. Sieve analysis showed that the average soil particle size (0.3 mm) was in the range of a fine to medium sand fraction. The physical characteristics of soil, dust and cake tested are presented in Table 5.1. The soil is composed of higher sand fractions than the dust and cake. The permeability of the soil was the highest and was in the moderate permeability class. The value of the permeability of soil (2.1×10^{-3} cm/s) shows that this type of soil can be used in rapid infiltration systems in land applications of wastewater (Reed et al., 1988). For rapid infiltration, a sand or gravel of high permeability is recommended as a substratum (Steiner and

Freeman, 1989). The degree of compaction also affects the permeability of the soil. From the compaction test (Figure 5.2), the maximum dry density of the soil is estimated as 2.01 g/cm^3 and its optimum moisture content is 9.7%. Permeability of the media depends on the available pore space and the degree of clogging of the pores by extraneous solids and by the formation of biomass within it (Illungkoo, 1994). Cohesive clay media in the substratum have an advantage for P removal by physico-chemical reactions (Wood, 1993). However, they can produce hydraulic problems due to low permeability. Hydraulic conductivity has been a continual problem in vertical flow artificial wetlands (Brix, 1987; Mackney, 1989). Raised temperature, increased pH, decreased dissolved oxygen and other factors are reported to be unfavourable for the sorption of P. P release takes place through diffusion processes, physical turbulence, and metabolisms in the adsorbent (Choi and Chung, 1995).

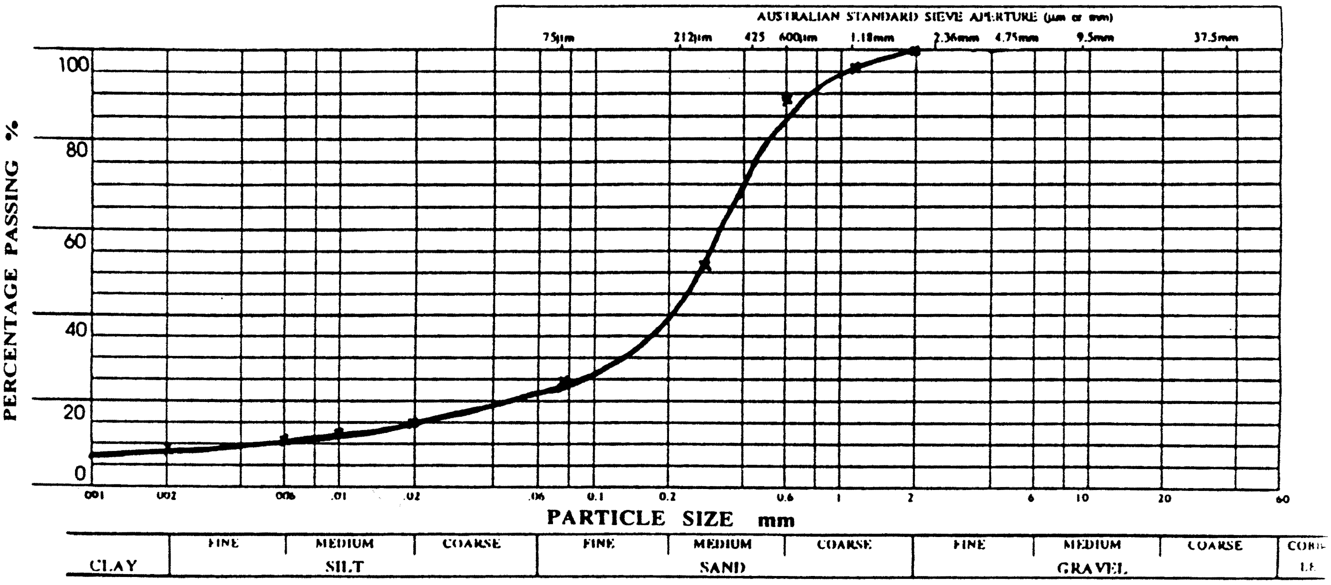


Figure 5.1 Particle Size Distribution of Soil

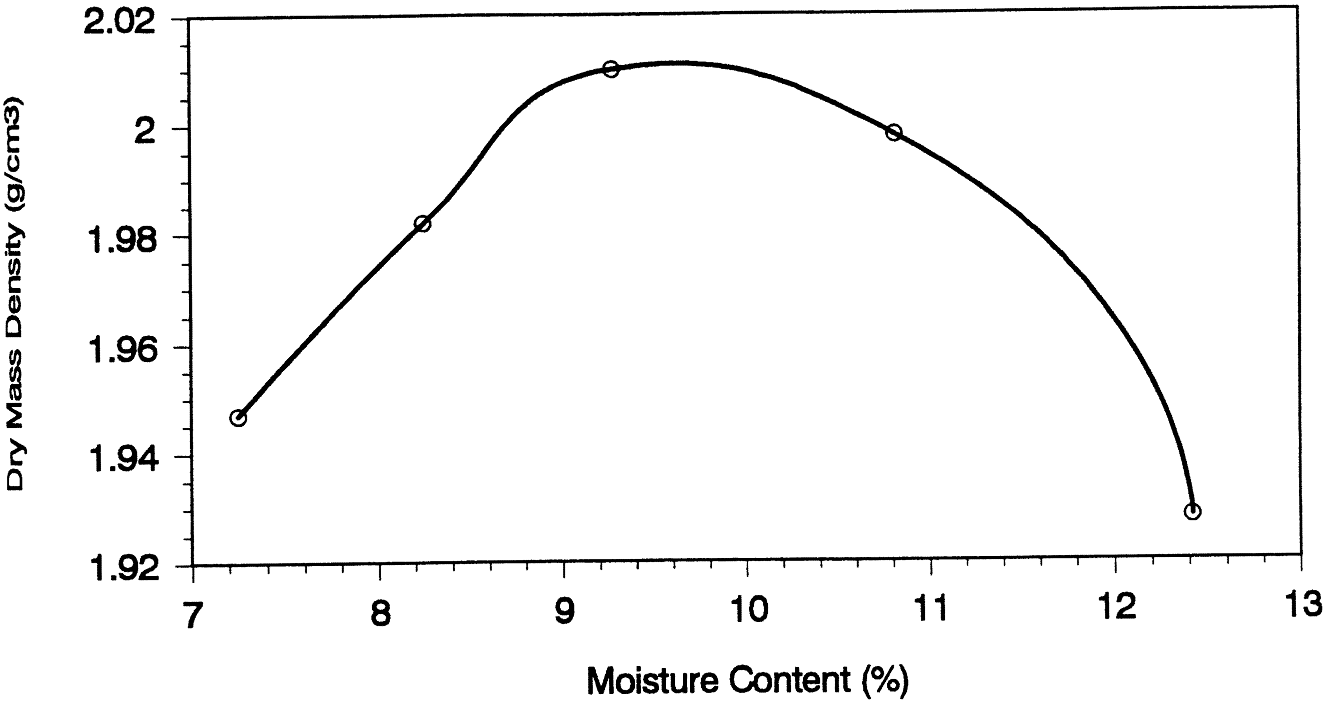


Figure 5.2 Compaction Test for Soil (Blows/Layers=25, No. of Layers=3, Mass of Hammer=2.7 kg, Mould diameter=10.5 cm, Mould height=11.5 cm, V=1 L)

Table 5.1 Physical Characteristics of Soil, Dust and Cake

Parameter	Soil	Dust	Cake
Sand % < 2 mm	78.0	2.5	11.8
Silt % < 0.06 mm	13.2	83.5	87.8
Clay % <0.002 mm	8.8	14.0	0.4
Particle density (g/cm^3)	2.38	2.78	2.27
Permeability (cm/s)	2.1×10^{-3}	1.8×10^{-5}	3.2×10^{-5}
Bulk density (g/cm^3)	1.42	1.01	0.76
Porosity	0.47	0.63	0.61
P Retained (mg/g)	2.5×10^{-2}	1.3×10^{-3}	3.6×10^{-3}

5.1.2 Chemical Characteristics of the Media

Table 5.2 shows the chemical composition of dust and cake. The chemical properties of soil, dust and cake are presented in Table 5.3. The pH of the soil, dust and cake used are all alkaline in nature, and the amount of calcium ion present in them was observed to be proportional to the pH. The effective cation exchange capacity (CEC) values for soil, dust and cake are 7.0, 73.4 and 97.1 cmol (+)/kg respectively (Table 5.3). The major contributing factors for CEC are calcium for soil (4.5 cmol(+)/kg) and dust (68.0 cmol(+)/kg), and sodium for cake (46.9 cmol(+)/kg). Dust and cake contain high percentages of iron (17.7% and 34.4% respectively), aluminium, calcium and other exchangeable cations, which assist P removal by chemical precipitation. Large proportions of iron, calcium and other metal ions may enhance ion exchange and precipitation of P.

Table 5.2 Chemical Composition of Dust and Cake

Parameter	Composition of Dust (%)	Parameter	Composition of Cake (%)
Fe	40.30	Fe_2O_3	67.50
CaO	12.50	CaO	7.10
MgO	5.00	ZnO	5.50
Zn	2.20	SiO_2	4.10
SiO_2	1.90	MgO	3.80
Na	0.92	Mn_3O_4	1.37
Al_2SO_4	0.88	Al_2O_3	1.15
Mn	0.78	Na_2O	0.87
F	0.70	SO_3	0.46
TiO_2	0.20	P_2O_3	0.19

Table 5.3 Chemical Properties of Soil, Dust and Cake

Constituents	Soil	Dust	Cake
pH[1]	7.50	11.80	9.00
Organic Matter[2] (%)	0.50	16.80	13.40
Total Nitrogen[3] (%)	0.03	0.05	0.14
Exchangeable Cations[4] (c mol(+)/kg)			
Al	<0.01	0.22	<0.01
Mg	1.14	0.32	20.92
Ca	4.50	67.96	27.53
K	0.18	1.88	1.80
Na	1.17	3.00	46.88
CEC (Cation Exchange Capacity)	7.00	73.40	97.10
Total Elements[5] (%)			
P	0.01	0.07	0.05
Al[6]	0.35	0.19	0.21
Fe[6]	1.00	17.70	34.40

[1] pH of a 1:5 w/v soil suspension in 0.01 m $CaCl_2$ at 25 ^{o}C

[2] Organic matter, calculated as total carbon (Walkely Black) divided by 0.57

[3] Total N determined by combustion (Leco)

[4] Exchangeable cations in a 0.01 M $BaCl_2$ leachate, determined by ICPAES (Inductively Coupled Plasma Atomic Emission Spectrometer). Exchangeable Al is determined only if pH < 5.04

[5] Total elements determined by acid digestion and ICPAES

[6] Al and Fe are not fully removed in the acid digestion.

5.2 P Removal in Batch Experiments

Batch experiments were conducted to study (i) the extent of P sorption under equilibrium conditions and (ii) the kinetics of P sorption. The results are discussed under two headings: mixing and static (no stirring or mixing) systems with adsorbents. The batch experiments with initial mixing for 1 minute are referred to as mixing systems for convenience.

5.2.1 P Sorption in the Mixing System at Equilibrium

A series of batch experiments were conducted to observe the P sorption with time in soil, dust and cake media. A standard P solution and the adsorbents were thoroughly mixed for 1 minute to measure the effect of agitation on the P solution. Batch equilibrium experiments were conducted by equilibrating the known amount of media with P sorption for a period of 120 hours. It was observed that more than 90% of the P was adsorbed by soil, dust and cake within 70, 12 and 60 hours respectively. Over a pH range of 5-6, a significant amount of P was adsorbed on all three absorbing media. Among the three media tested, dust adsorbed P the most (225 and 4 times of that of soil and cake respectively for an initial P concentration of 40 mg/L). The sorption profile of P is presented in Table 5.4 and Figures 5.3A to 5.5B. The equilibrium concentration of P at different initial concentrations of P solution is presented in Table 5.4. The amount of P adsorbed on the adsorbents increased rapidly at the initial stage and then it decreased gradually. It is clear from the physical characteristics of the adsorbents that the particle size of slag (dust and cake) is smaller than that of soil (Table 5.1). This led to a high sorption capacity of P in the slag (both dust and cake).

Although the chemistry of slag (dust and cake) was not studied in detail in the present work, past studies on this topic are of some relevance to show why slag has high P removal capacity. It has been reported that the inorganic P combined with aluminium, iron and calcium are retained in sediments as insoluble compounds under aerobic conditions (Hosomi and Sudo, 1979; Hosomi et al., 1982).

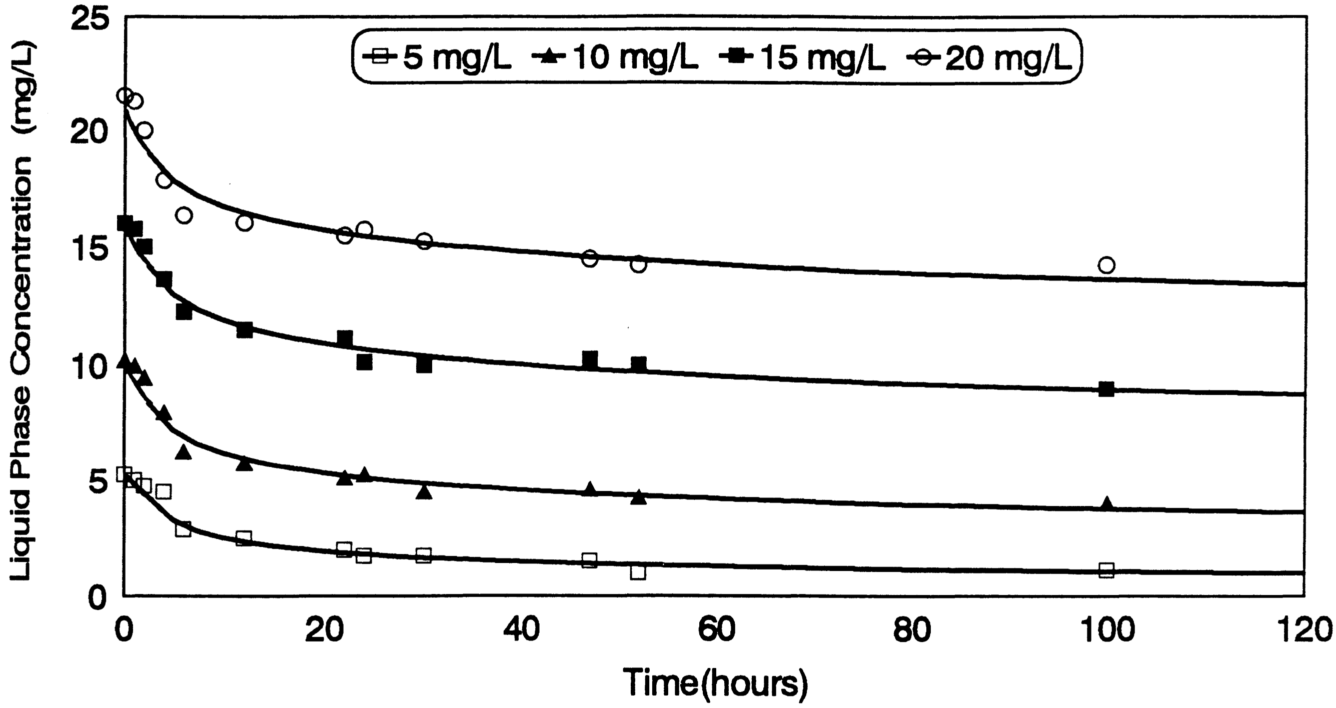


Figure 5.3A Kinetics of P Sorption in Soil in the Mixing System
(C_o = 5,10,15 and 20 mg/L, β=50.0 g, V=200 mL, pH=5-6)

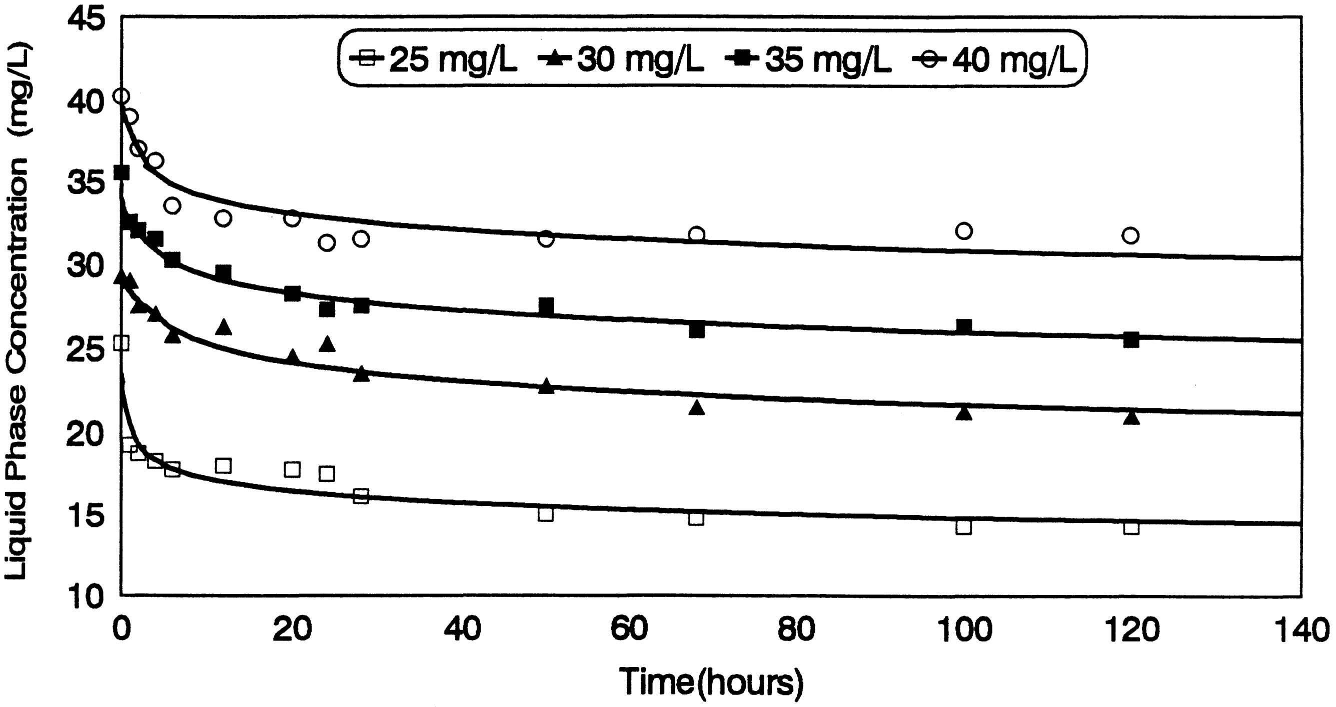


Figure 5.3B Kinetics of P Sorption in Soil in the Mixing System
(C_o = 25,30,35 and 40 mg/L, β=50.0 g, V=200 mL, pH=5-6)

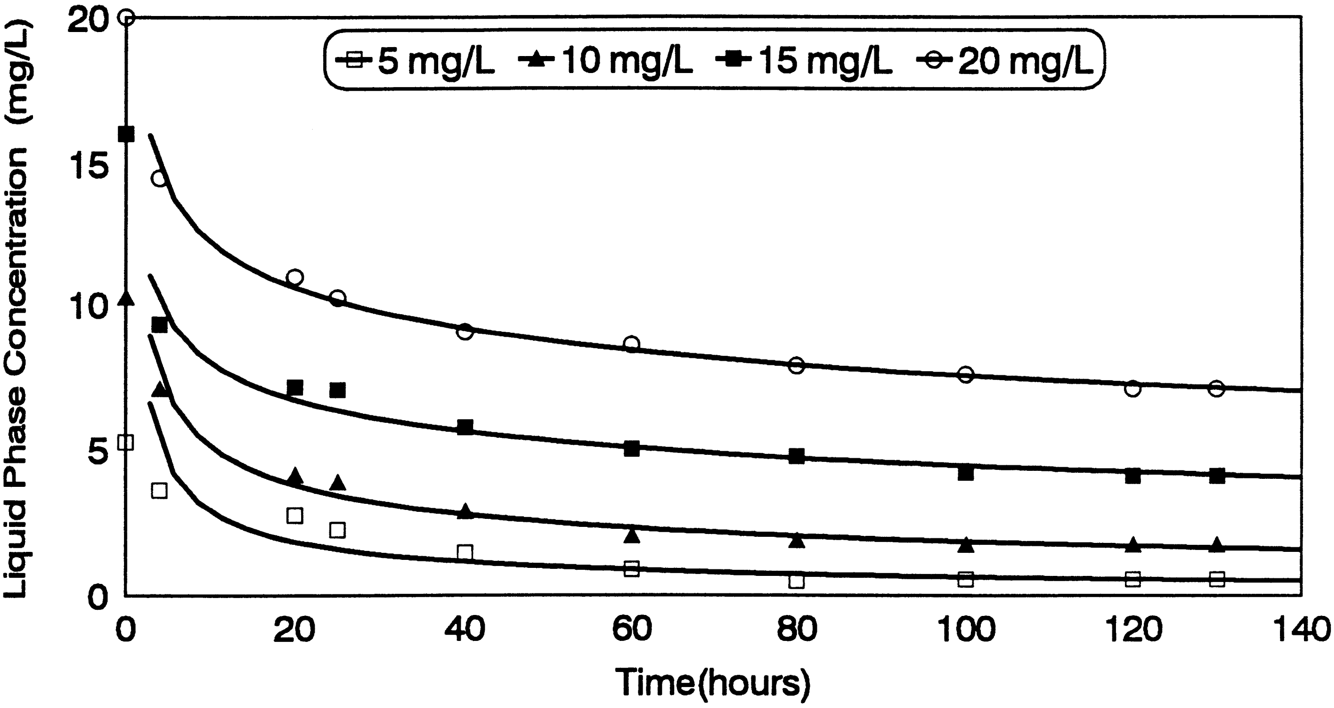


Figure 5.4A Kinetics of P Sorption in Dust in the Mixing System
(C_o = 5,10,15 and 20 mg/L, β=0.1 g, V=200 mL, pH=5-6)

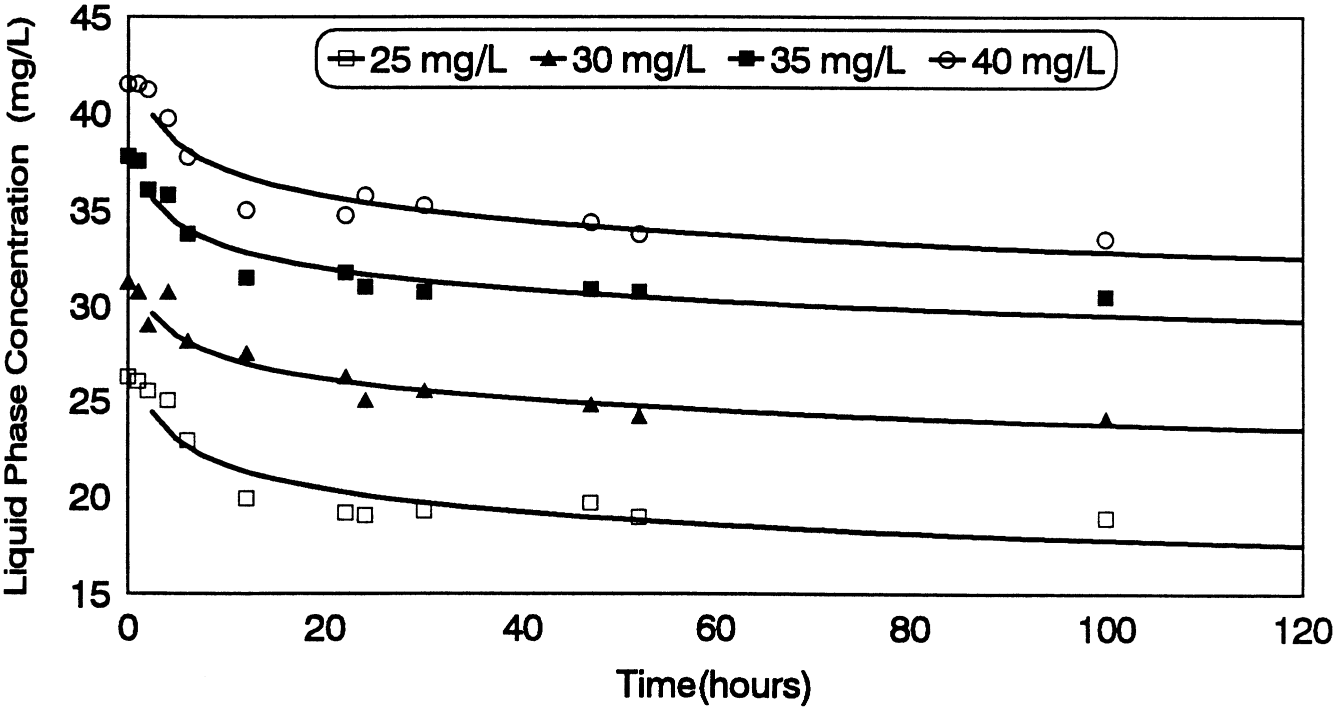


Figure 5.4B Kinetics of P Sorption in Dust in the Mixing System
(C_o = 25,30,35 and 40 mg/L, β=0.1 g, V=200 mL, pH=5-6)

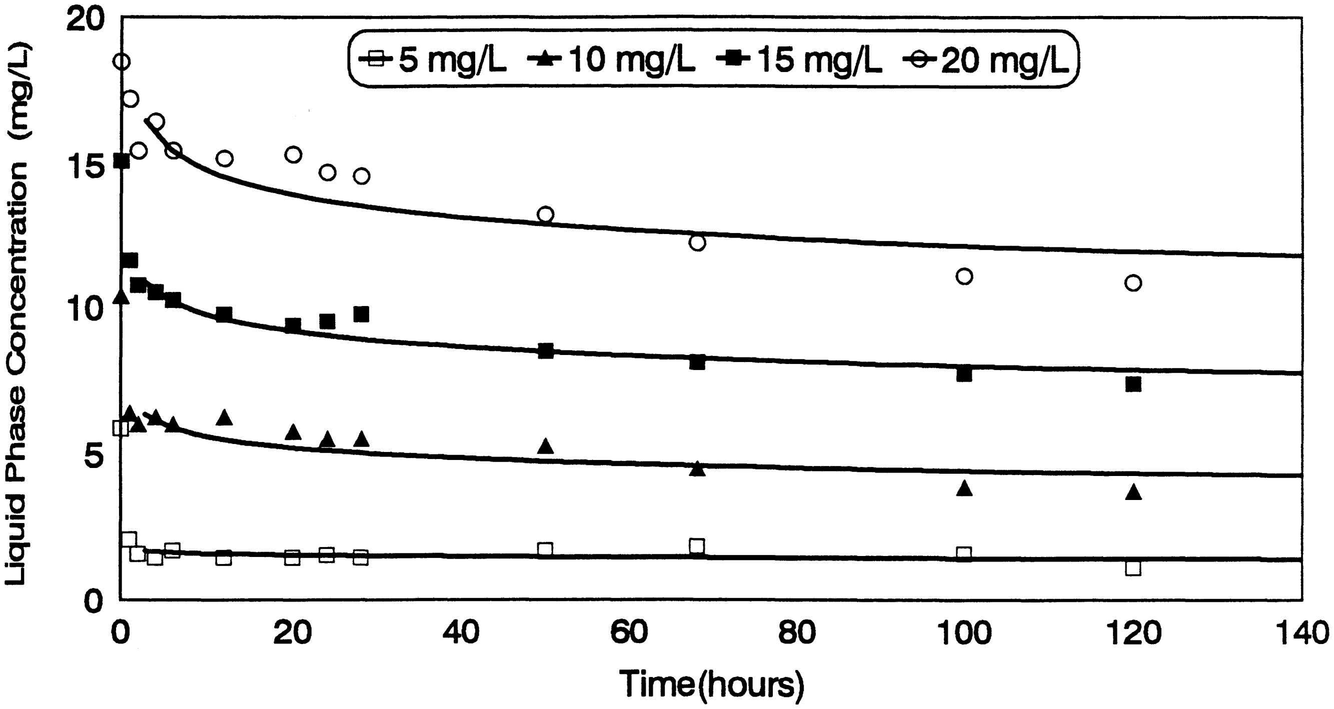


Figure 5.5A Kinetics of P Sorption in Cake in the Mixing System
(C_o = 5,10,15 and 20 mg/L, β=1.0 g, V=200 mL, pH=5-6)

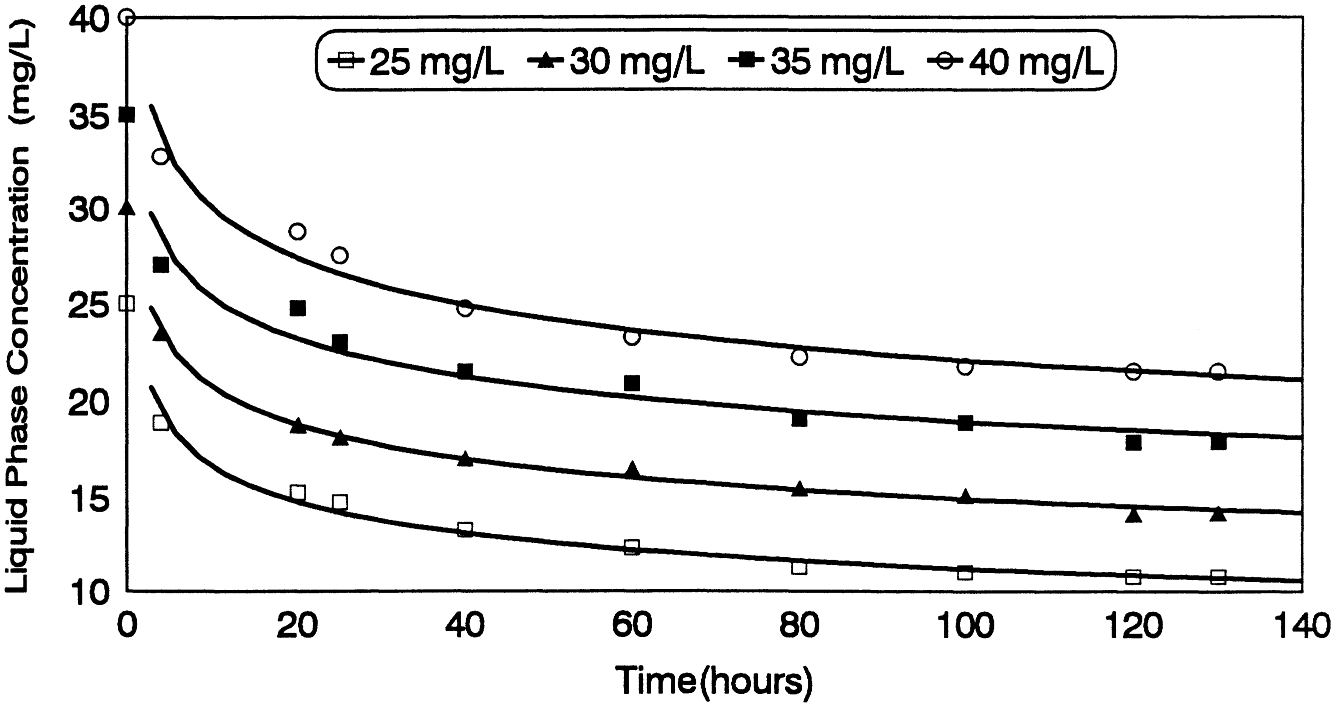


Figure 5.5B Kinetics of P Sorption in Cake in the Mixing System
(C_o = 25,30,35 and 40 mg/L, β=1.0 g, V=200 mL, pH=5-6)

Under anaerobic conditions, aluminium phosphate and iron phosphate (which is found in an insoluble state under aerobic conditions) are dissolved, and the inorganic phosphate is released from sediment (Joh, 1983). The slag (ie. dust and cake) contains large amounts of calcium which adsorbs the dissolved inorganic P. Sorption of P also takes place due to the presence of other elements such as aluminium, magnesium, iron, manganese and titanium exposed on the surface of slag. Yamada et al. (1986) concluded from their studies that calcium hydroxide adsorbed large amounts of P, followed by magnesium hydroxide, ferrous oxide, magnesium carbonate and aluminium hydroxide. They also observed that the sorption site of P was coincident with the site of calcium, magnesium, aluminium and silicon compounds located on the surface of the slag. Among the authentic compounds, calcium hydroxide played an important role in the sorption of P on the slag surface (Yamada et al., 1986). The complex compounds on the surface of dust and cake might be constituted by calcium, aluminium, silicon and magnesium during production of granulated blast furnace slag in the steel industry. From an X-ray energy spectrogram of the slag reacted with P, it was proved that P was adsorbed on the surface of calcium, magnesium and aluminium compounds (Yamada et al., 1986). The large amounts of P sorption in dust may be due to the sorption of calcium on the surface of dust (67.96 cmol (+) /kg as an exchangeable cation of Ca).

Sorption is usually characterised by the coefficients of sorption isotherms. The Freundlich isotherm is the oldest and it has been shown to explain phosphorus sorption better in most soils than the more widely used Langmuir isotherm (Fitter and Sutton, 1975). The use of the latter equation was deprecated by Barrow (1978) because of its complexity and its failure to confirm with current mechanistic theory of ion sorption, particularly in relation to the effect of sorption on surface charge (Bowden et al., 1973). For these reasons it was suggested that the Freundlich isotherm may be more appropriate for describing the routine application of phosphorus sorption processes in soil (Barrow, 1978). In general, the Langmuir isotherm has been preferred to the Freundlich equation from a theoretical point of view because the terms involved in the Langmuir isotherm have physico-chemical significance, representing the extensive (sorption capacity) and intensive (affinity) properties of the adsorbent. Holford (1982), however, concluded that the Freundlich isotherm K was highly correlated with sorptivity (which reflects the sorption capacity and affinity) while the reciprocal exponent (N) proved to be an affinity parameter, and was most useful in this role for soils of similar sorption capacity.

Table 5.4 Equilibrium Concentration of P in the Mixing System for Various Initial Concentrations (V=200 mL, pH=5-6)

	Soil (50 g)		Dust (0.1 g)		Cake (1.0 g)	
C_o (mg/L)	C_e (mg/L)	S_e (mg/g)	C_e (mg/L)	S_e (mg/g)	C_e (mg/L)	S_e (mg/g)
5	1.13	0.019	1.12	8.26	0.55	0.89
10	3.75	0.027	4.00	12.50	1.75	1.65
15	7.38	0.031	9.00	14.00	4.10	2.18
20	10.88	0.031	14.25	14.50	7.10	2.58
25	14.25	0.044	18.88	14.74	10.75	2.85
30	21.00	0.033	24.05	14.90	14.13	3.17
35	25.50	0.040	30.50	14.50	17.88	3.42
40	31.75	0.034	33.50	15.50	21.50	3.70

In the present study, the sorption of P was quantified by using Freundlich and Langmuir isotherms. The coefficients of the Freundlich and Langmuir isotherms obtained from the experimental results are tabulated in Tables 5.5A and 5.5B respectively. It is clear from these results that the Langmuir isotherm gives a better correlation for P sorption with all the three adsorbents used than the Freundlich isotherm. This observation was not in accordance with past researchers' observations on the sorption of heavy metals. Most of the sorption experimental results for heavy metals have been found to fit well with the Freundlich isotherm (Bajracharya, 1989).

Table 5.5A Freundlich Isotherm Constants (K, N) in the Mixing System

Adsorbing Media	Soil	Dust	Cake
K [mg/g(L/mg)^N]	0.02	8.99	1.22
N	5.00	6.09	2.72
R^2 (Correlation coefficient)	0.76	0.88	0.98

Table 5.5B Langmuir Isotherm Constants (a, b) in the Mixing System

Adsorbing Media	Soil	Dust	Cake
a (mg/g)	0.04	15.50	3.34
b (L/mg)	0.90	1.02	0.65
R^2 (Correlation coefficient)	0.96	0.99	0.99

Table 5.6 shows the correlation coefficient (R^2) of the Freundlich and Langmuir isotherm constants obtained from the fitting data of the batch experimental results of Mann and Bavor (1993). In both cases, the Langmuir isotherm described well the P sorption for the gravel and soil from North Sydney, Australia. However, the experimental results with the slag are fitted better by the Freundlich isotherm. The high percentage error in the calculation of the Freundlich and Langmuir isotherm constants was attributed to the high initial concentration of the solution used (more than 25 mg/L of P). According to Murphy et al. (1983), accurate isotherm constants have been determined for low initial concentrations (less than 20 mg/L) of P solution.

Table 5.6 Correlation coefficients (R^2) for the Freundlich and Langmuir isotherm constants for various adsorbents (Amount of adsorbent = 20 g, C_o=5,10, 20, 50 and 100 mg/L at room temperature) (Mann and Bavor, 1993)

Adsorbents	Correlation of Freundlich Isotherm (R^2)	Correlation of Langmuir Isotherm (R^2)
R gravel	1.00	0.92
G gravel	0.37	0.46
GBF slag	1.00	0.77
BF slag	0.01	0.62
Fly ash	0.01	0.77

5.2.2 Kinetics of P Sorption in the Mixing System

Experiments were conducted to see how fast the equilibrium stage for P was reached in the mixing system. It was observed that P sorption is a slow process, usually taking a few hours to adsorb more than 90% of the total amount adsorbed at equilibrium. Figures 5.3A to 5.5B show the temporal variation of P sorption on different types of the adsorbent at an initial pH range of 5 to 6.

The experimentally observed kinetic data of P sorption on soil, dust and cake were used to check the validity of the proposed mathematical model (SPNSM). The simulated curves are presented along with the observed data in Figures 5.6A to 5.8B for different initial concentrations of P. The values of the film transfer constant (α) computed at various initial P concentrations for soil, dust and cake are shown in Table 5.7. The values are computed based on the Freundlich isotherm. High fluctuations of the film transfer constants was observed for soil (α ranging from 2.88 to 0.65 day^{-1}) as compared to dust (α ranging from 1.20 to 0.36 day^{-1}) and cake (α ranging from 1.18 to 0.38 day^{-1}). It was observed that the initial concentration of P affected the film transfer constant. The film transfer constants gradually decreased as the initial concentration of P increased. This was coincident with the fact that equilibrium stage was reached slowly as the initial P concentration increased. Limited sorption capacity of the adsorbents could be attributed to the decrease of the film transfer constant as the initial P concentration increased.

Table 5.7 The Film Transfer Constant (α) of the Adsorbents for Various Initial P Concentrations in the Mixing System

C_o (mg/L)	Soil (day^{-1})	Dust (day^{-1})	Cake (day^{-1})
5	2.64	1.13	0.82
10	2.88	1.20	1.18
15	2.21	0.67	1.10
20	1.44	1.10	0.84
25	0.84	0.55	0.55
30	0.72	0.79	0.55
35	0.65	0.38	0.43
40	0.74	0.36	0.38

5.2.3 P Sorption in the Static System at Equilibrium

A series of batch experiments were also conducted to observe the P sorption in the completely static (no mixing) system for the same adsorbents. The P solution and the adsorbents were kept under static conditions (no stirring or mixing) throughout the experiments. Depending on the initial P concentrations, more than 240, 24 and 120 hours were taken to adsorb more than 90% of the P for soil, dust and cake, respectively. With this information, batch equilibrium experiments were conducted by equilibribrating the P solution in soil and cake for a period of 480 hours, and 170 hours with dust. Here too, dust adsorbed the P the most (220 and 5 times more than that of soil and cake respectively for an initial P concentration of 30 mg/L) (Table 5.8 and Figures 5.9A to 5.11B).

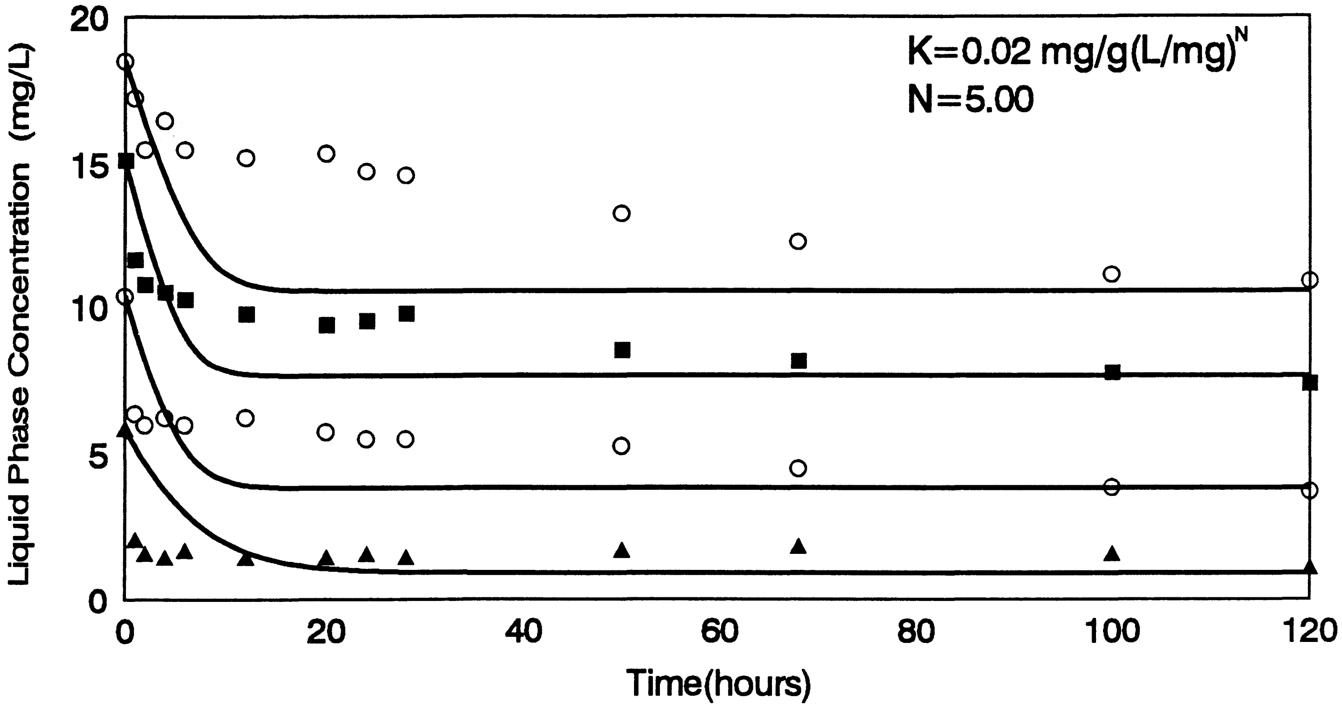


Figure 5.6A Observed and Predicted Kinetics of P Sorption in Soil in the Mixing System (C_o = 5,10,15 and 20 mg/L, β=50.0 g, V=200 mL, pH=5-6)

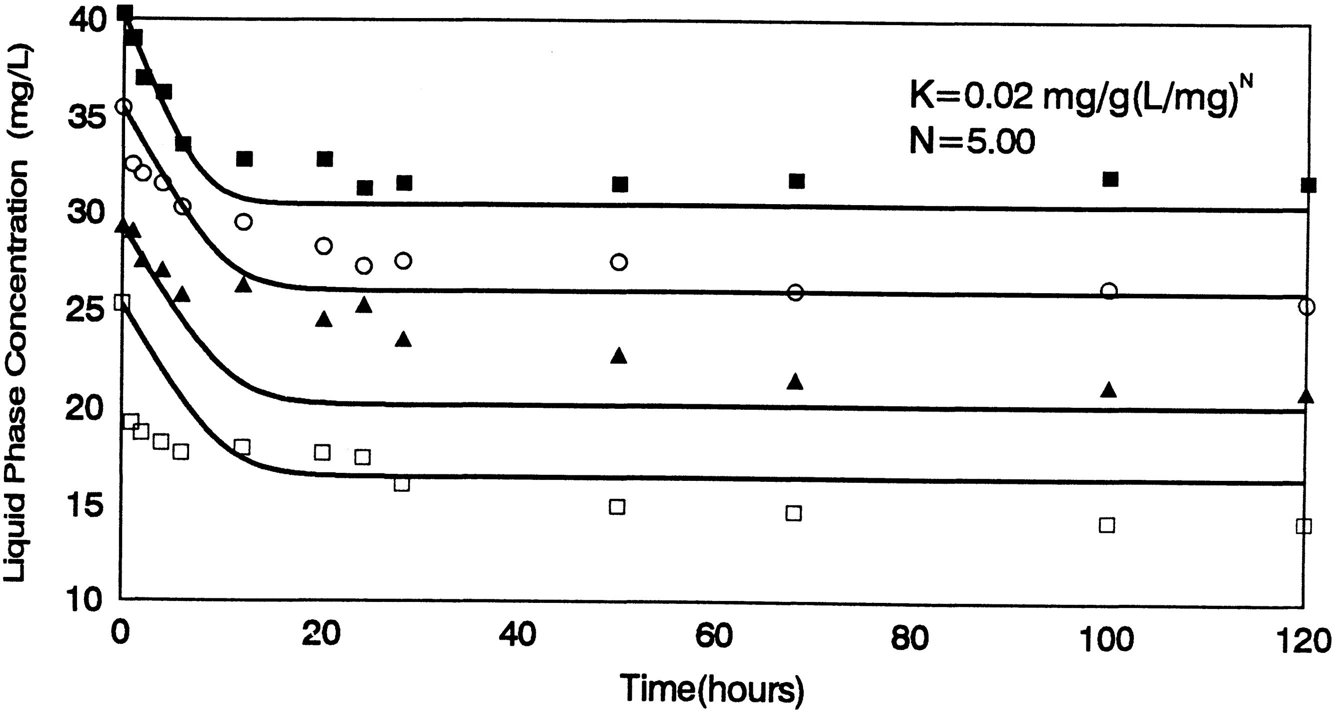


Figure 5.6B Observed and Predicted Kinetics of P Sorption in Soil in the Mixing System (C_o =25,30,35 and 40 mg/L, β=50.0 g, V=200 mL, pH=5-6)

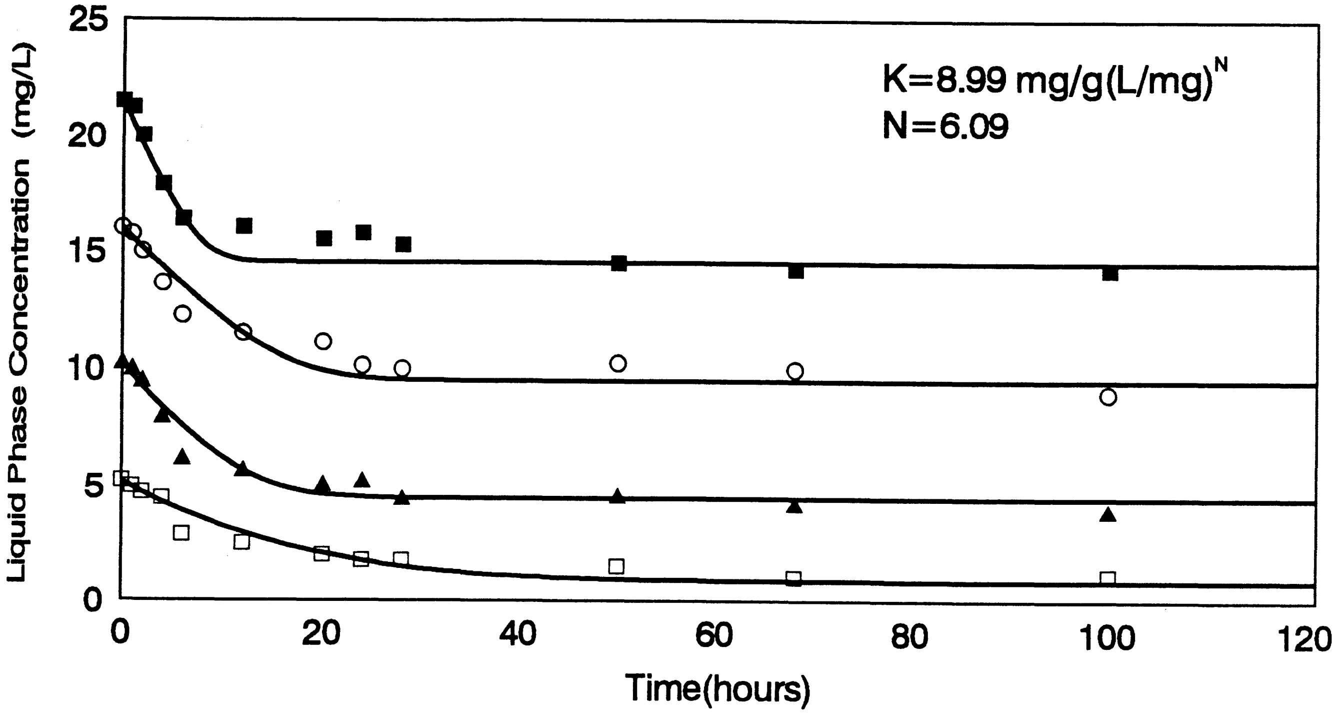


Figure 5.7A Observed and Predicted Kinetics of P Sorption in Dust in the Mixing System (C₀ = 5,10,15 and 20 mg/L, β=0.1 g, V=200 mL, pH=5-6)

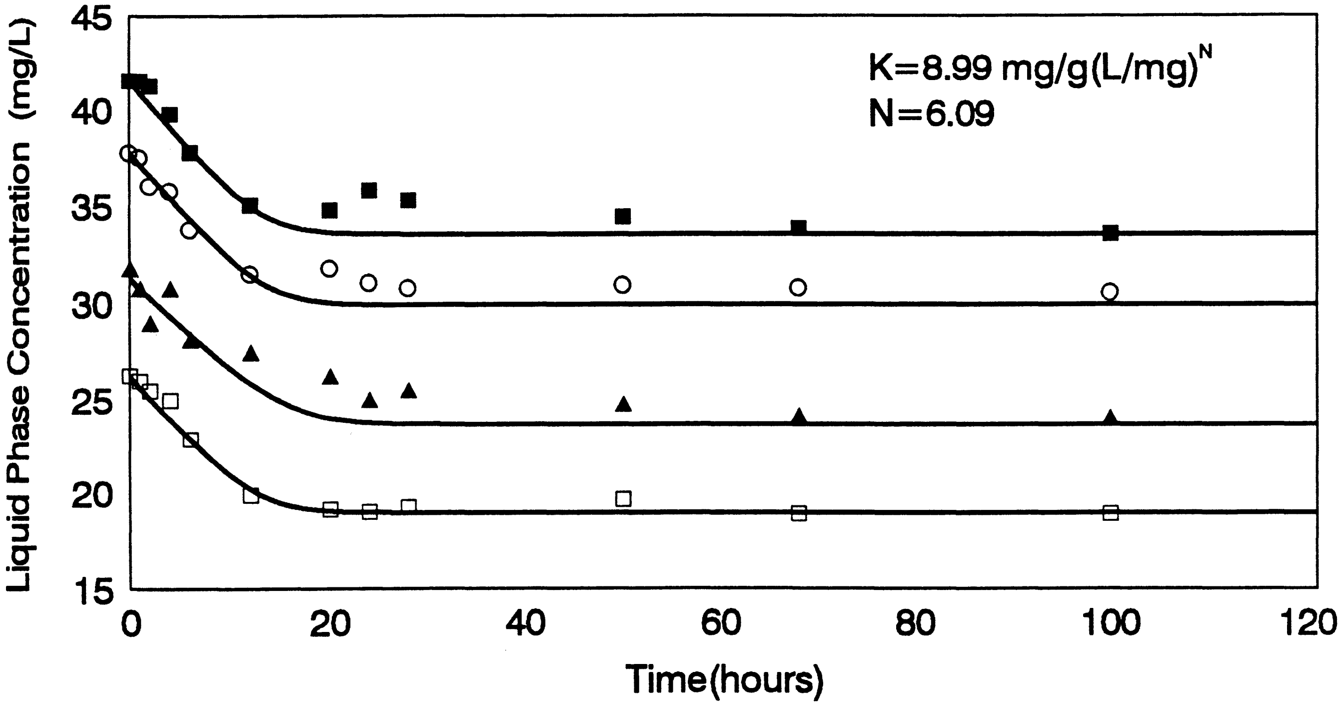


Figure 5.7B Observed and Predicted Kinetics of P Sorption in Dust in the Mixing System (C₀ =25,30,35 and 40 mg/L, β=0.1 g, V=200 mL, pH=5-6)

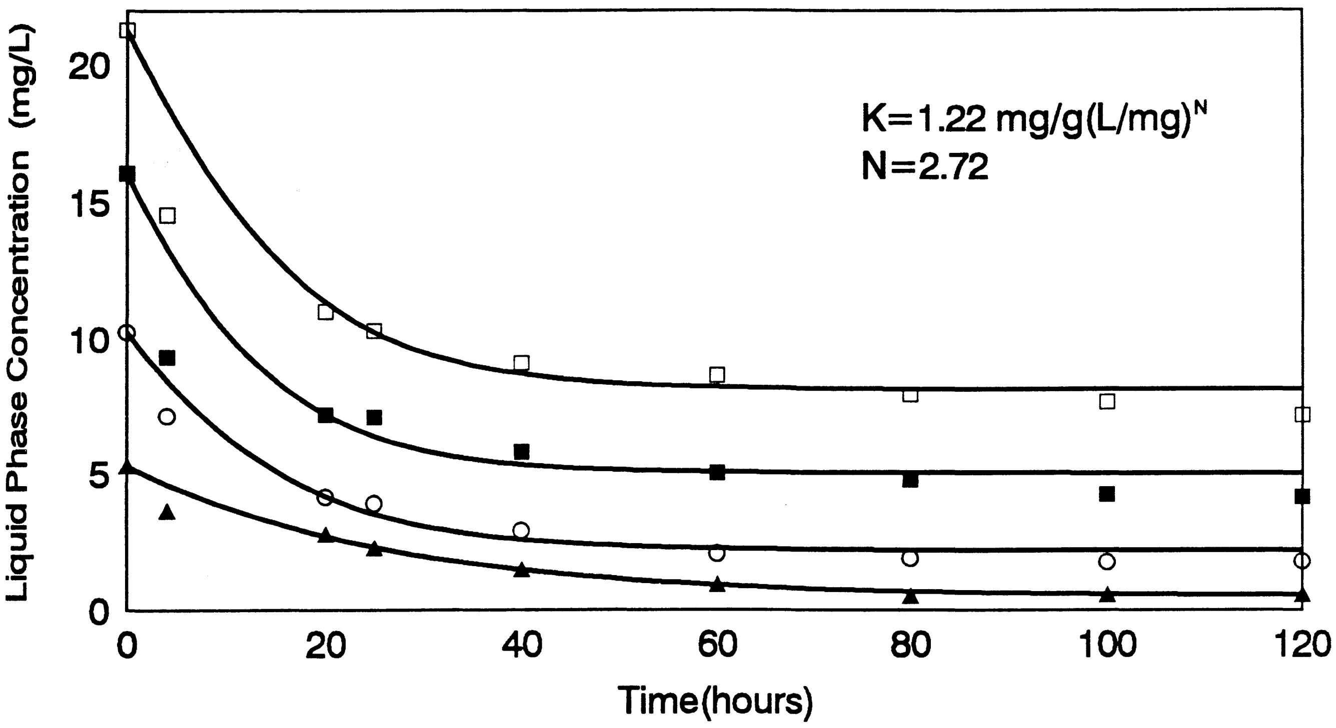


Figure 5.8A Observed and Predicted Kinetics of P Sorption in Cake in the Mixing System (C_o = 5,10,15 and 20 mg/L, β=1.0 g, V=200 mL, pH=5-6)

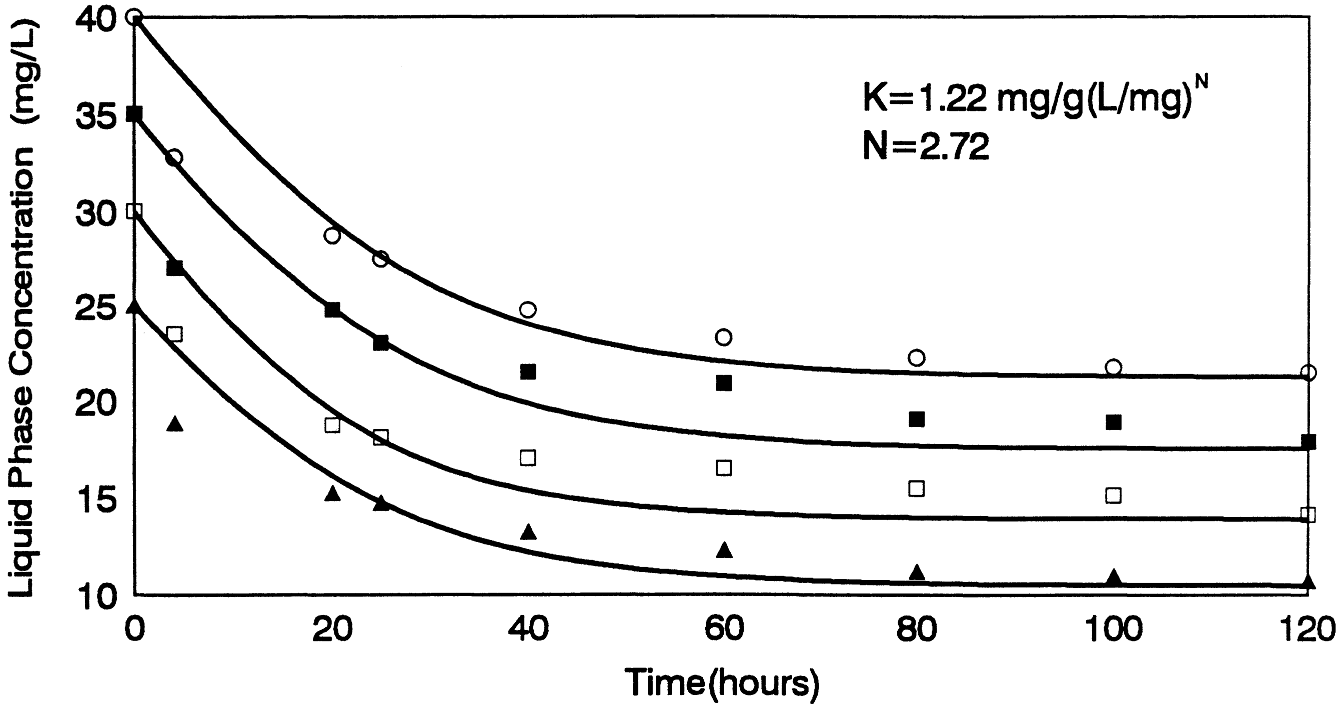


Figure 5.8B Observed and Predicted Kinetics of P Sorption in Cake in the Mixing System (C_o =25,30,35 and 40 mg/L, β=1.0 g, V=200 mL, pH=5-6)

The equilibrium concentration of P at different initial concentrations in the static system is tabulated in Table 5.8.

Table 5.8 Equilibrium Concentration of P in the Static System for Different Initial Concentrations (V=400 mL, pH=5-6)

	Soil (100.0 g)		Dust (0.4 g)		Cake (2.0 g)	
C_o (mg/L)	C_e (mg/L)	S_e (mg/g)	C_e (mg/L)	S_e (mg/g)	C_e (mg/L)	S_e (mg/g)
5	0.90	0.016	0.20	5.70	0.80	0.78
10	2.40	0.031	0.90	10.10	2.30	1.48
15	4.75	0.051	4.00	11.25	5.00	2.05
20	6.30	0.053	8.30	12.50	7.60	2.36
25	11.25	0.063	12.25	14.25	11.50	2.65
30	15.75	0.068	15.75	15.00	15.50	3.10

An interesting phenomenon was observed in these experiments when soil was used as an adsorbent. The solid phase concentration in the static system increased steadily with the increase of initial P concentration. Its maximum was observed at 0.068 mg/g. The solid phase concentration in the mixing system, on the other hand, increased rapidly and kept constant with the increase of initial P concentration. Its maximum was observed at 0.044 mg/g (Table 5.4). P sorption and its kinetics are significantly affected by diffusion gradients which were caused by the agitation of solution with the adsorbent (Samuel and Osman, 1987). Soil retained a lesser amount of P due to the agitation of the P solution. $FePO_4$, $AlPO_4$, $Fe_3(PO_4)_2$, and $Ca_{10}(PO_4)_6(OH)_2$ are easily released as they are dissolved under anaerobic or reducing conditions (Nriagu, 1972). Physical turbulence caused by the agitation of the P solution accelerated the release of intrinsic P retained on the soil (Table 5.3). The release of P from the soil caused a reduction of P adsorbed in the mixing system and affected the kinetics of P sorption significantly.

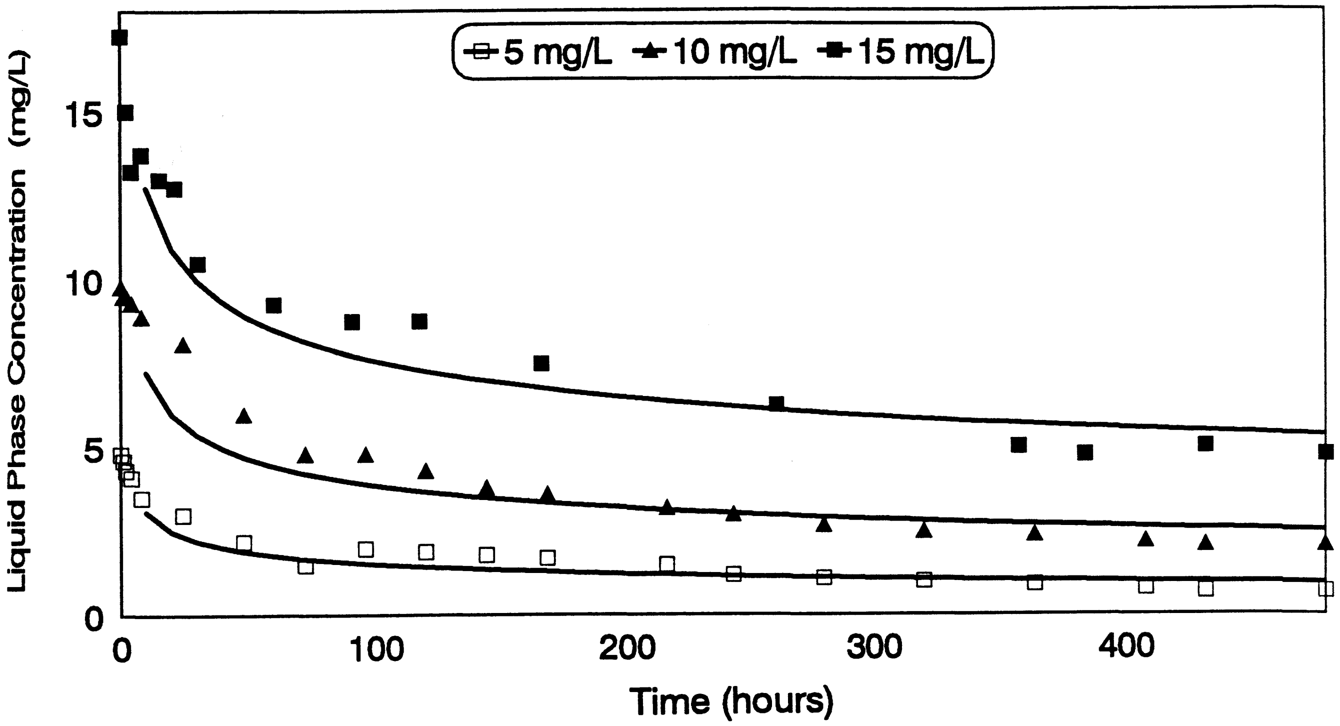


Figure 5.9A Kinetics of P Sorption in Soil in the Static System
(C_o = 5,10 and 15 mg/L, β=50.0 g, V=200 mL, pH=5-6)

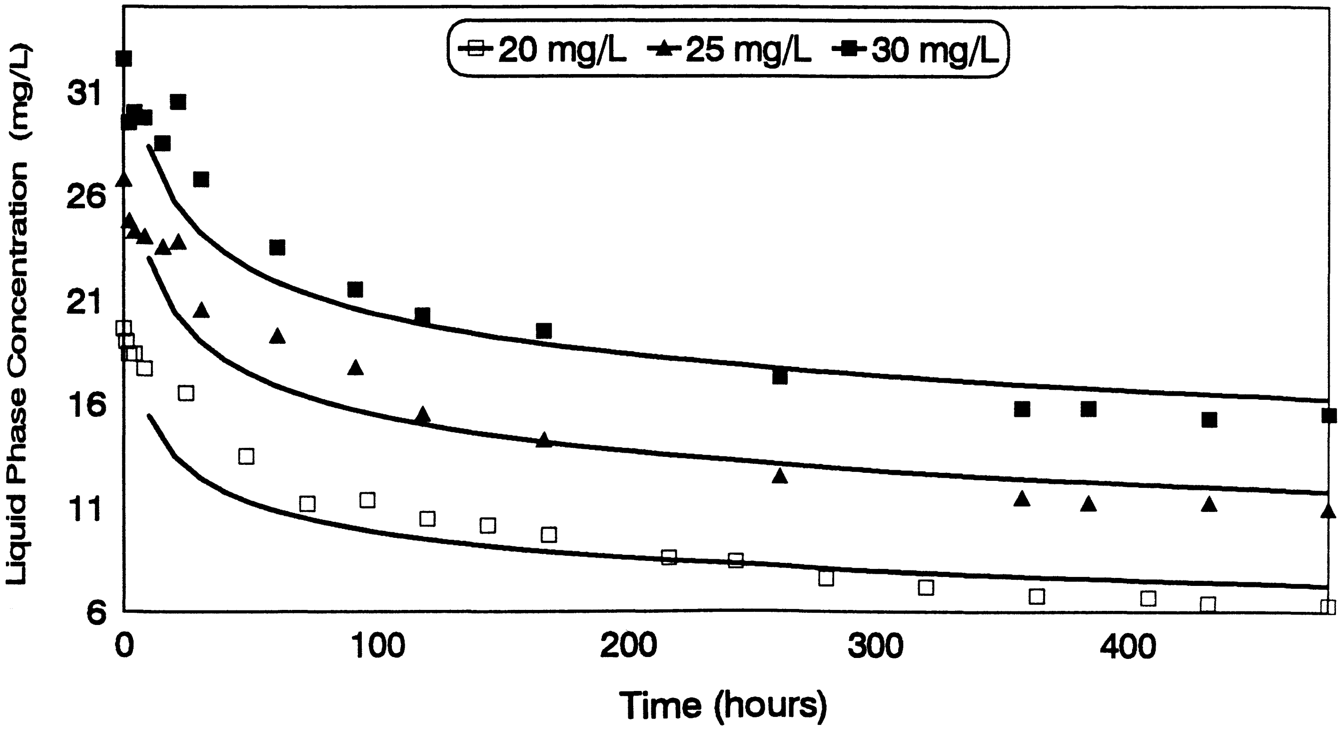


Figure 5.9B Kinetics of P Sorption in Soil in the Static System
(C_o = 20, 25 and 30 mg/L, β=50.0 g, V=200 mL, pH=5-6)

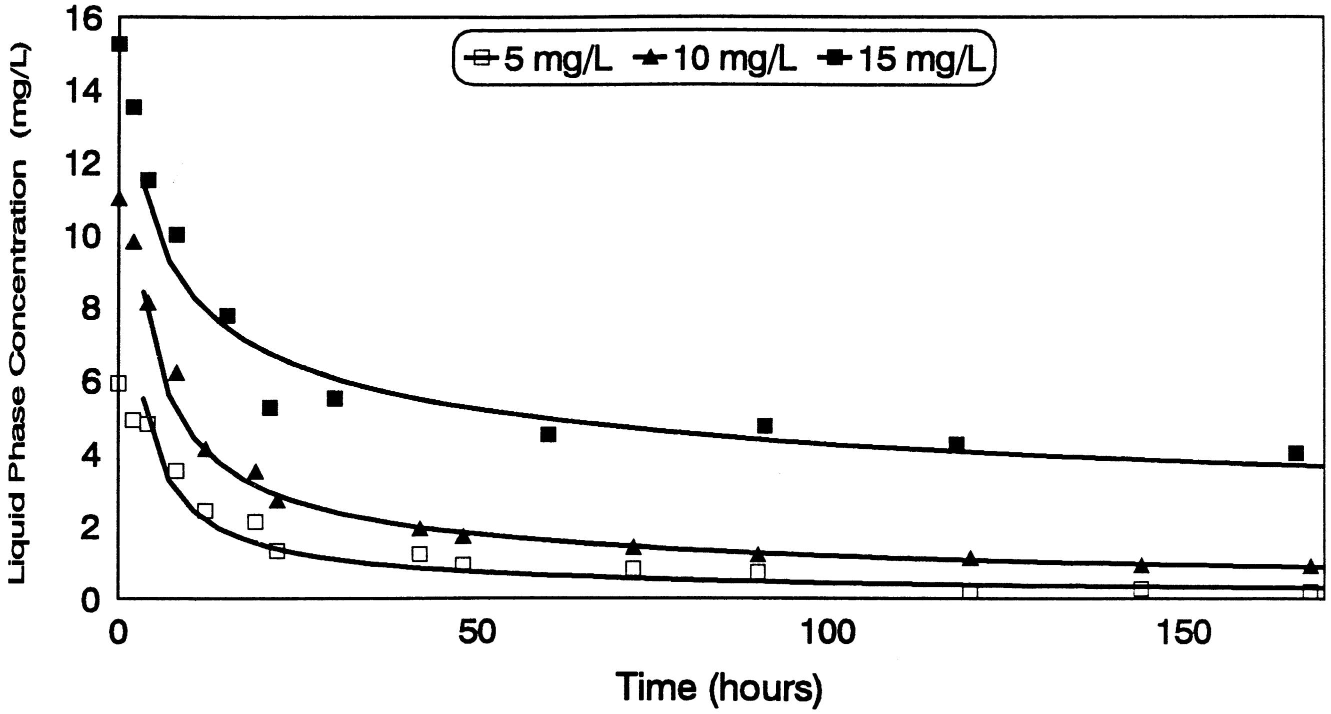


Figure 5.10A Kinetics of P Sorption in Dust in the Static System
(C_o = 5, 10 and 15 mg/L, β=0.1 g, V=200 mL, pH=5-6)

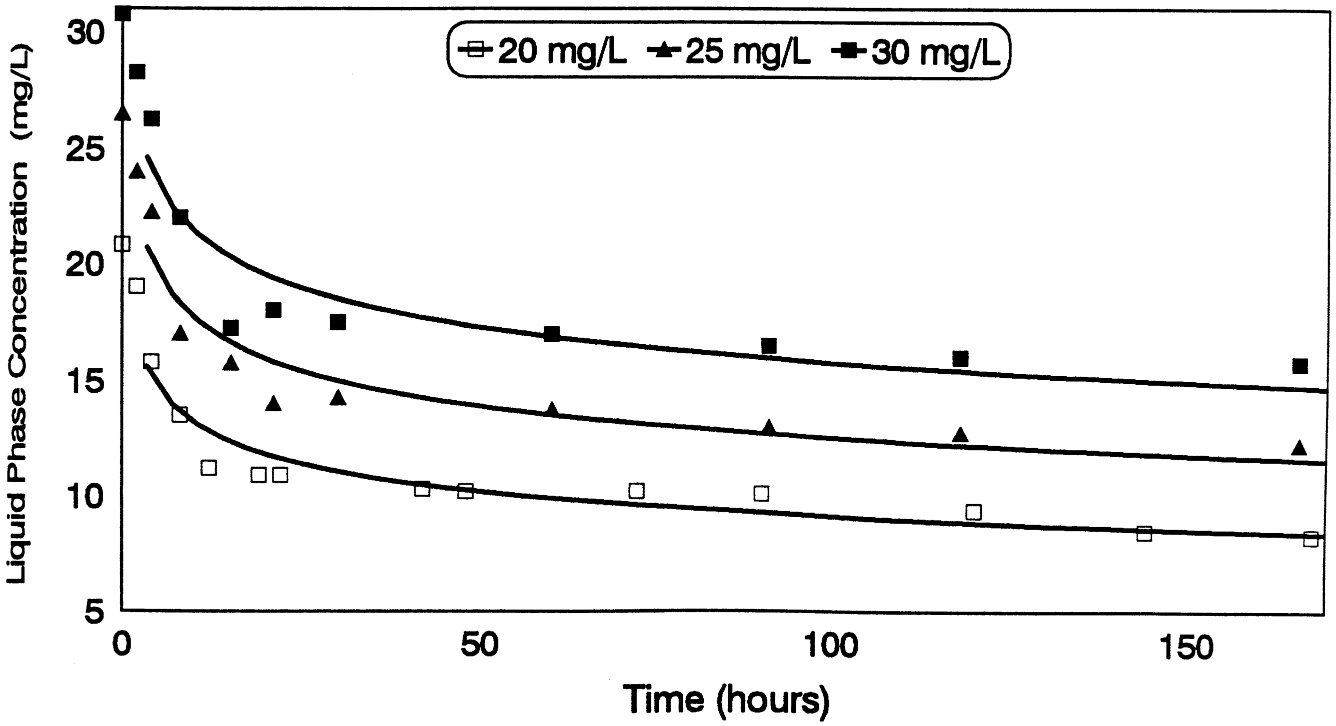


Figure 5.10B Kinetics of P Sorption in Dust in the Static System
(C_o = 20, 25 and 30 mg/L, β=0.1 g, V=200 mL, pH=5-6)

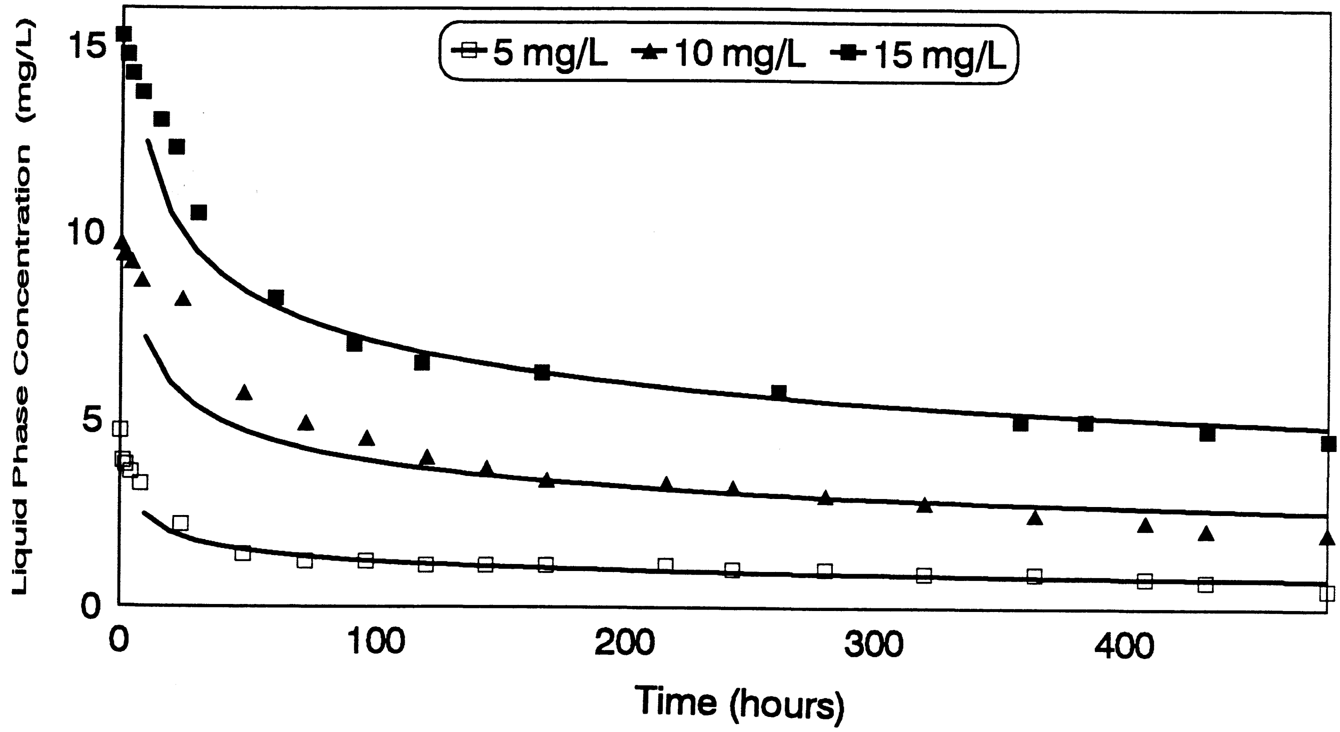


Figure 5.11A Kinetics of P Sorption in Cake in the Static System
(C_o = 5,10 and 15 mg/L, β=1.0 g, V=200 mL, pH=5-6)

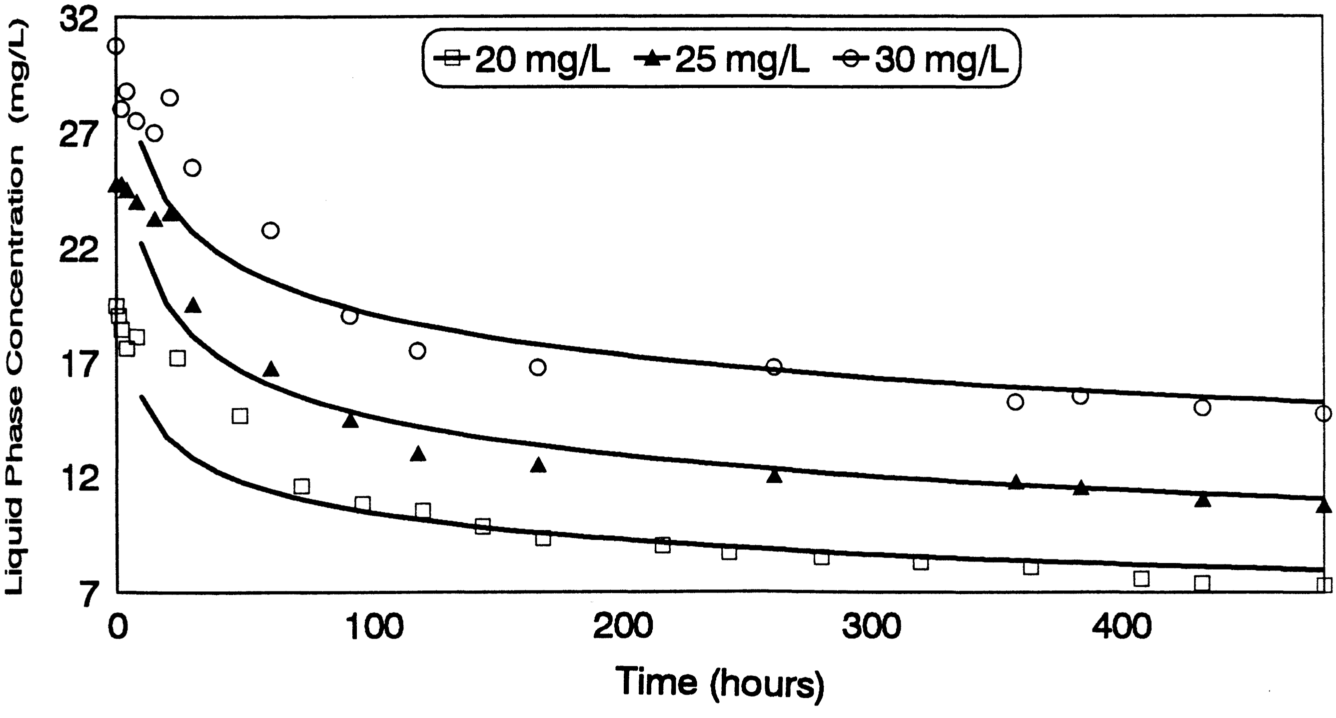


Figure 5.11B Kinetics of P Sorption in Cake in the Static System
(C_o = 20, 25 and 30 mg/L, β=0.1 g, V=200 mL, pH=5-6)

When dust and cake were used as the adsorbents, the solid phase concentration in the static system was observed to be less than that in the mixing system corresponding to the initial P concentration. Here the agitation supports the P removal due to the increase of diffusion and contact opportunity between the P solute and the adsorbents. This was quantified using empirical Freundlich and Langmuir isotherm constants. It was observed that the Freundlich isotherm K which represents the extensive property (sorptivity) of the adsorbents in the static system was similar to the one in the mixing system, whereas the reciprocal exponent (N) which represents the intensive property (affinity) decreased in the static system for all the adsorbents. The adsorbents showed similar sorption capacities for both systems. Although the amounts of P adsorbed corresponding to the initial P concentration in the mixing system were higher than those in the static system, the growth rate of P removal with the increase of initial P concentration was less due to the agitation. This leads to the decrease of the Freundlich isotherm constant N in the static system. It is apparent from Tables 5.9A and 5.9B that the Langmuir isotherm gave better correlations for P sorption than the Freundlich isotherm under the conditions tested.

Table 5.9A Freundlich Isotherm Constants (K, N) for Different Adsorbents in the Static System

Adsorbing Media	Soil	Dust	Cake
K [mg/g(L/mg)^N]	0.02	8.99	1.16
N	2.14	4.15	2.61
R^2 (Correlation coefficient)	0.96	0.92	0.99

Table 5.9B Langmuir Isotherm Constants (a, b) for Different Adsorbents in the Static System

Adsorbing Media	Soil	Dust	Cake
a (mg/g)	0.75	12.49	2.91
b (L/mg)	0.39	4.22	0.82
R^2 (Correlation coefficient)	1.00	0.98	0.99

5.2.4 Kinetics of P Sorption in the Static System

A series of batch experiments under static conditions was conducted to observe how the equilibrium stage reached for P in this static system. It was observed that P sorption in the static condition is a relatively slow process, usually taking a few days to adsorb 90% of the total amount of P adsorbed. The observed kinetic data of P sorption on soil, dust and cake were used to check the validity of the proposed model (SPNSM). The simulated results are presented along with the observed data in Figures 5.12A to 5.14B for different initial P concentrations. In the figures, the captions are the observed experimental values and the corresponding lines are the predicted ones. The film transfer constant (α) is approximated from the kinetic data itself. The values of the film transfer constants computed at various initial concentrations for soil, dust and cake are shown in Table 5.10. Slightly high fluctuations of film transfer constants were observed for dust (α ranges from 1.66 to 0.82 day^{-1}) compared to soil (α ranges from 0.26 to 0.10 day^{-1}) and cake (α ranges from 0.50 to 0.12 day^{-1}). The film transfer constant decreased with the increase in the initial concentration of P. This is also due to the fact that equilibrium stage was reached slowly as the initial P concentration increased. The distribution of film transfer constants in the static system is more uniform than that in the mixing system.

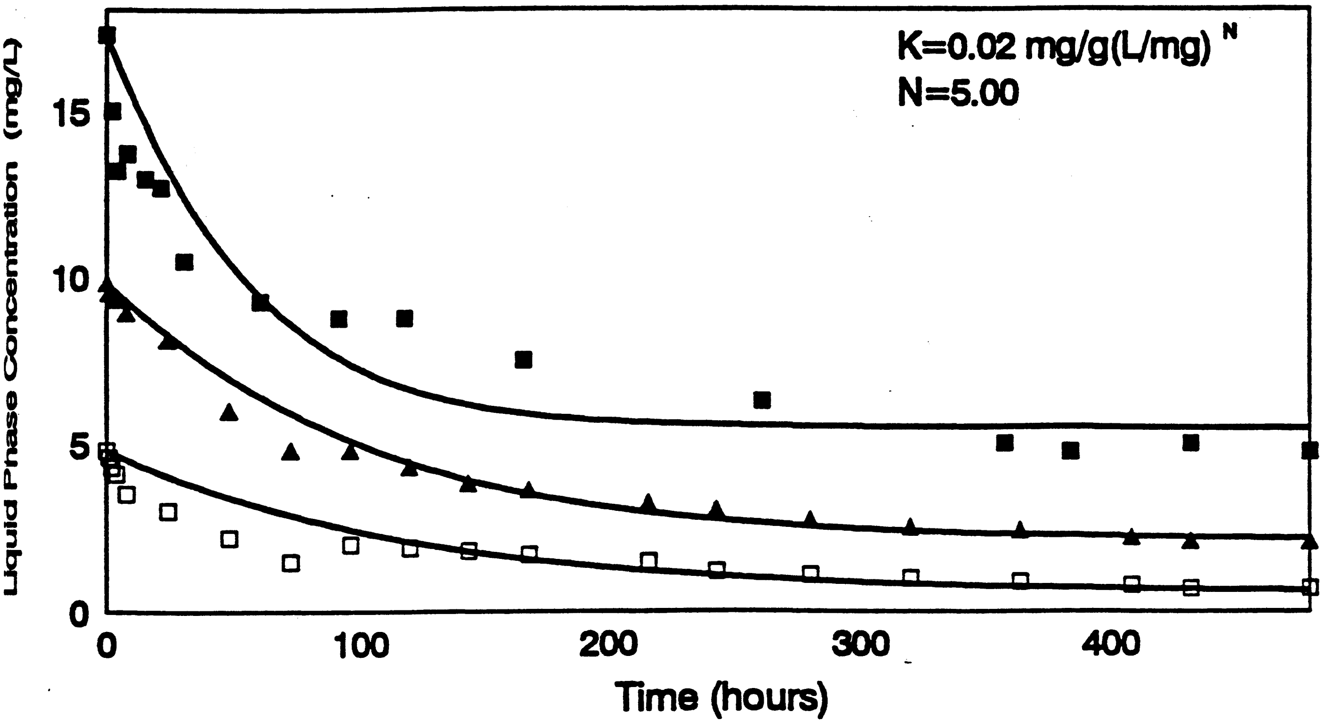


Figure 5.12A Observed and Predicted Kinetics of P Sorption in Soil in the Static System (C_o = 5,10 and 15 mg/L, β=50.0 g, V=200 mL, pH=5-6)

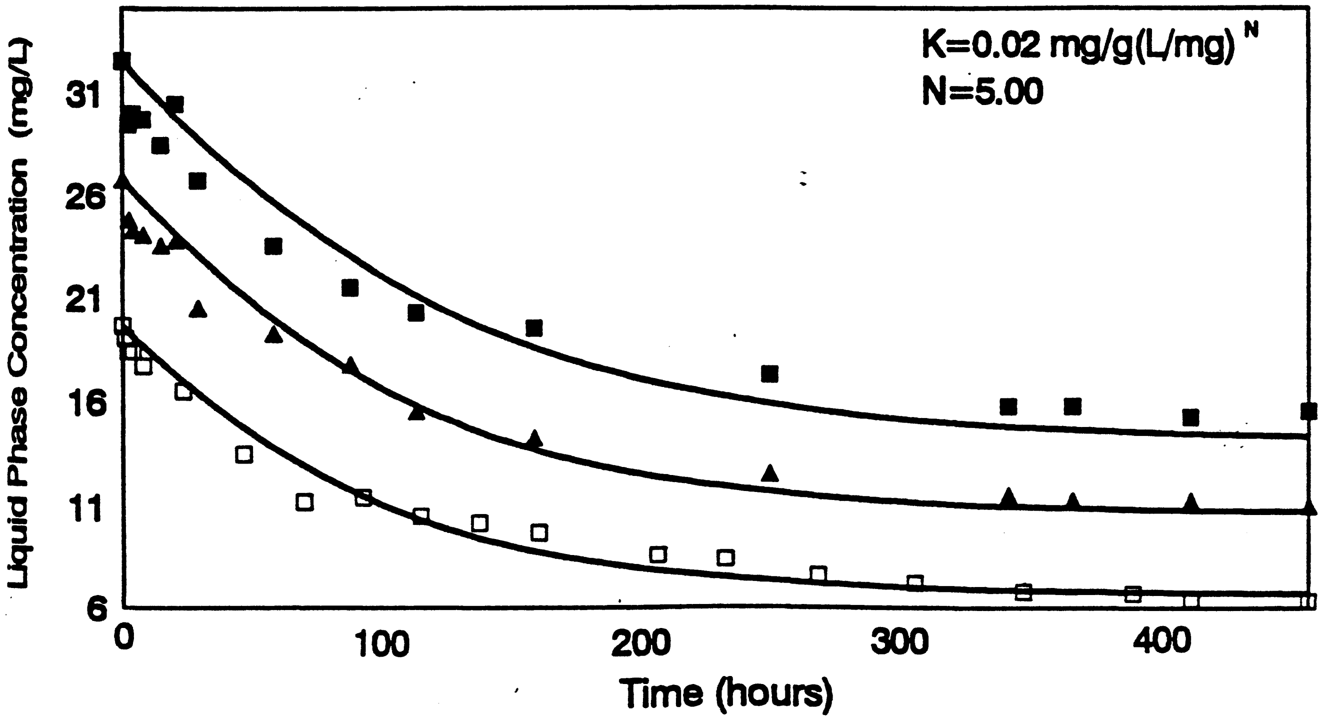


Figure 5.12B Observed and Predicted Kinetics of P Sorption in Soil in the Static System (C_o =20,25 and 30 mg/L, β=50.0 g, V=200 mL, pH=5-6)

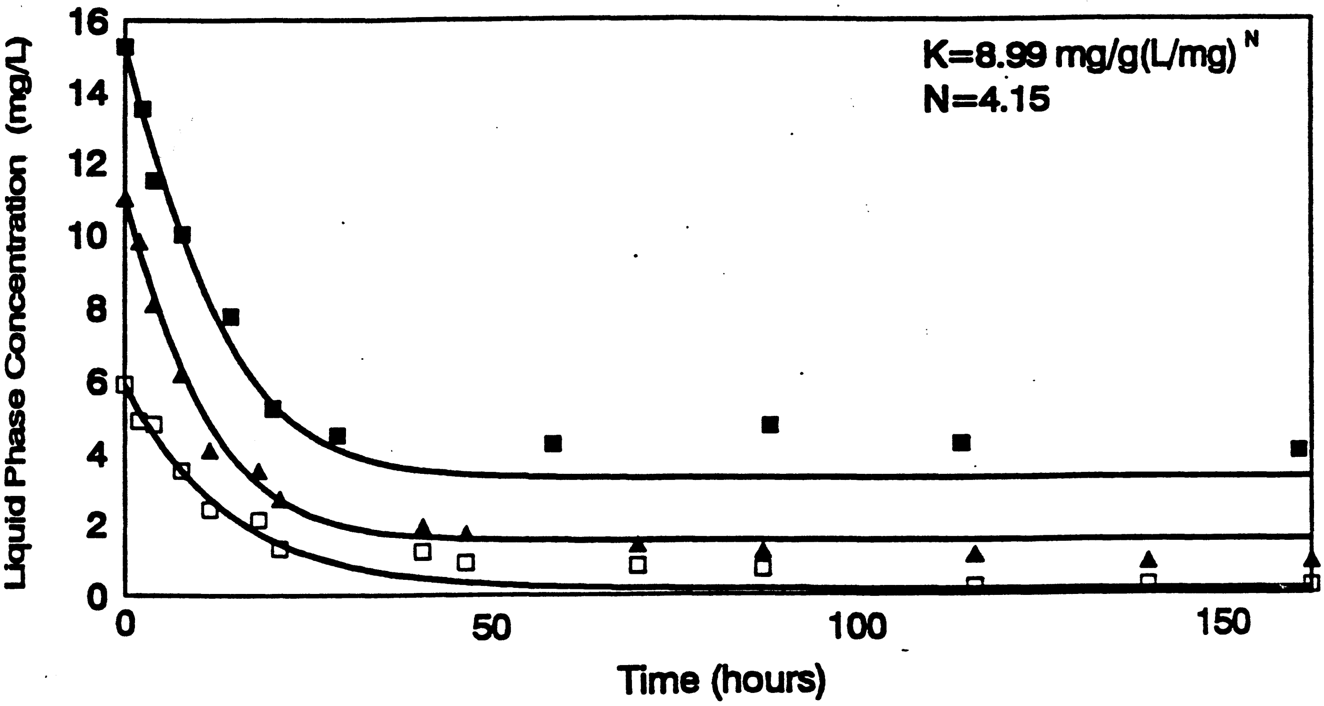


Figure 5.13A Observed and Predicted Kinetics of P Sorption in Dust in the Static System (C_o = 5,10 and 15 mg/L, β=0.1 g, V=200 mL, pH=5-6)

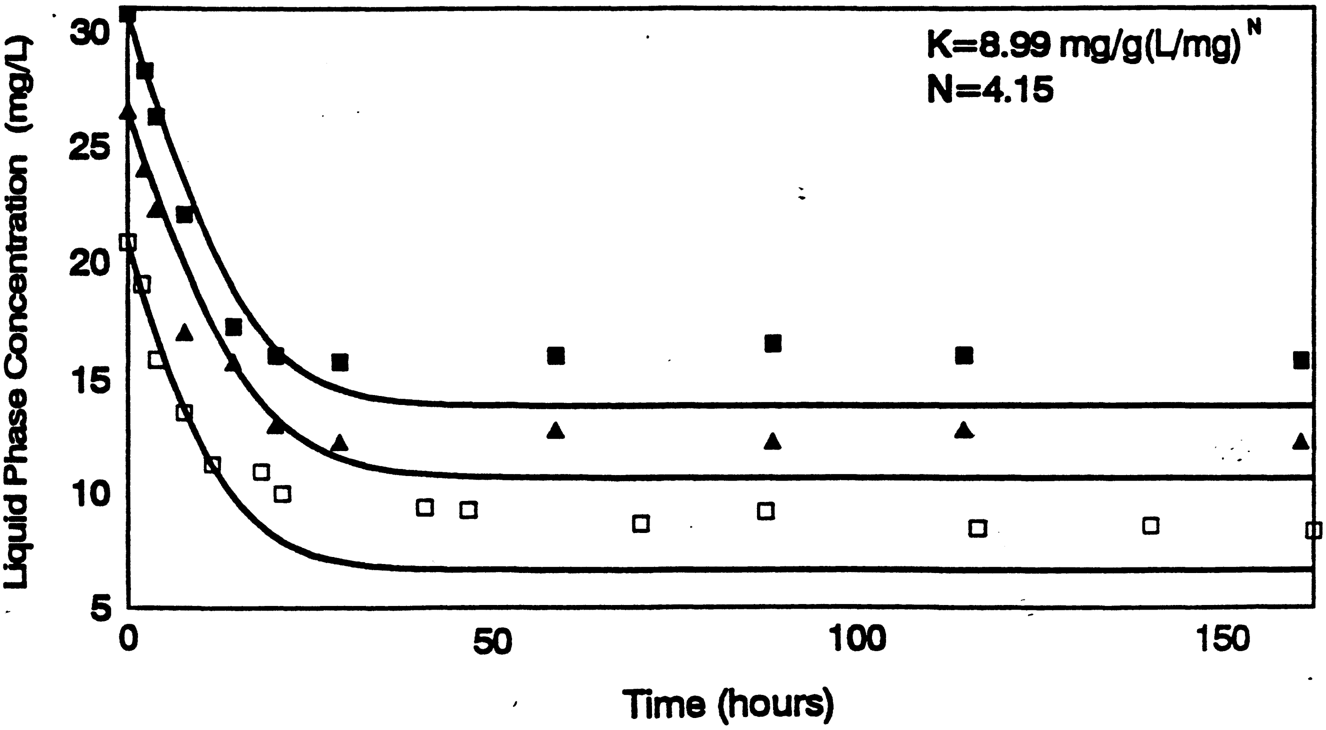


Figure 5.13B Observed and Predicted Kinetics of P Sorption in Dust in the Static System (C_o=20,25 and 30 mg/L, β=0.1 g, V=200 mL, pH=5-6)

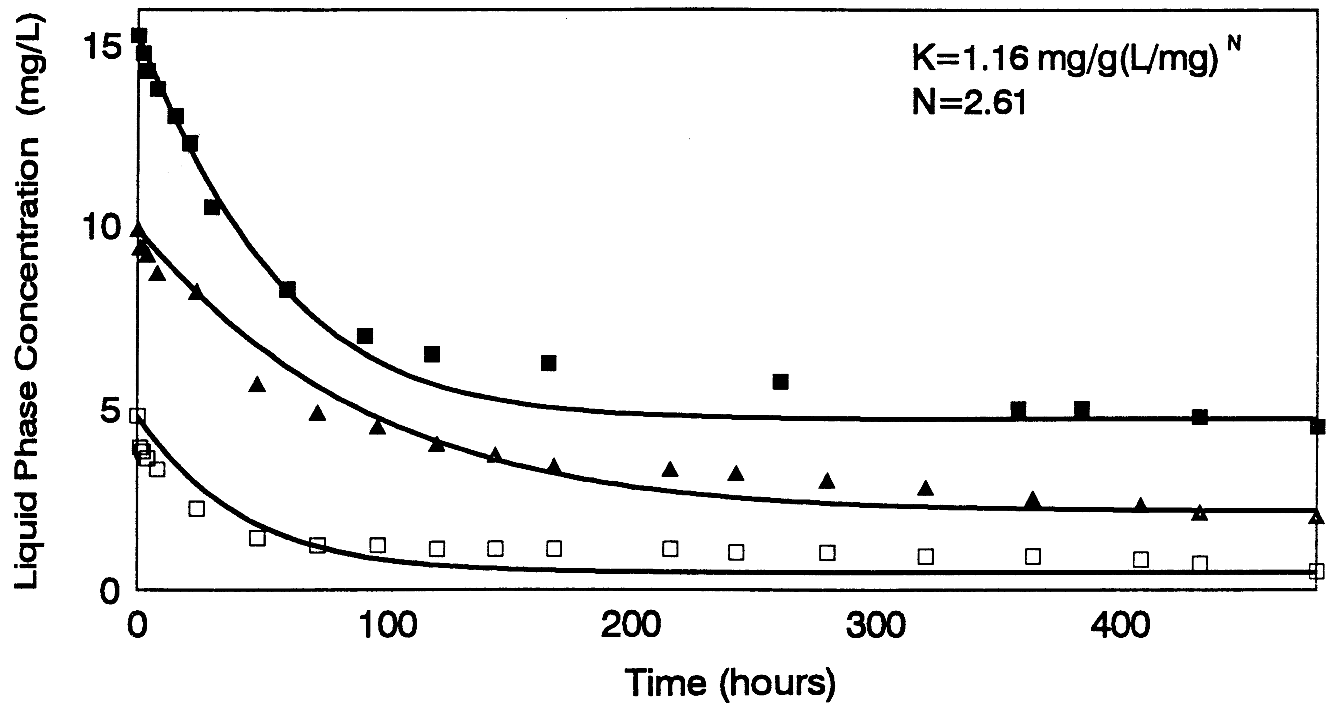


Figure 5.14A Observed and Predicted Kinetics of P Sorption in Cake in the Static System (C_o = 5,10 and 15 mg/L, β=1.0 g, V=200 mL, pH=5-6)

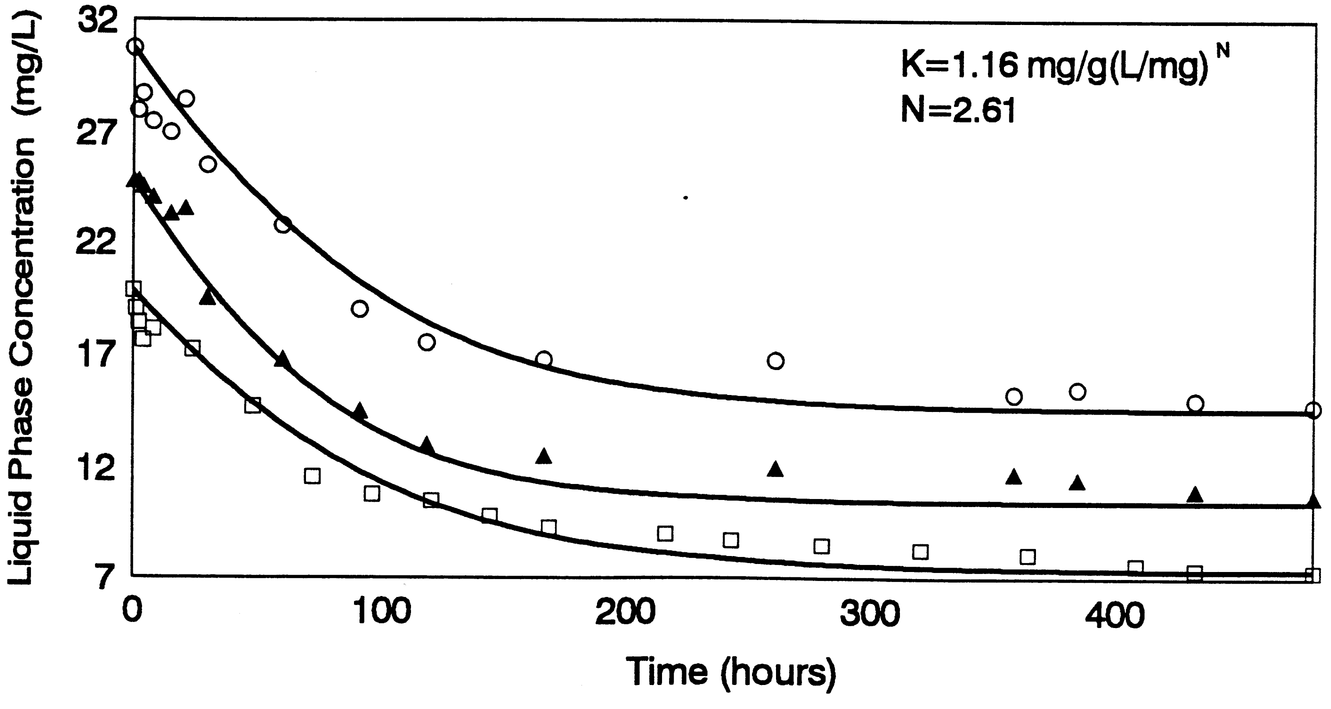


Figure 5.14B Observed and Predicted Kinetics of P Sorption in Cake in the Static System (C_o =20,25 and 30 mg/L, β=1.0 g, V=200 mL, pH=5-6)

Table 5.10 The Film Transfer Constant (α) of the Different Adsorbents for Various Initial Concentrations in the Static System

C_o (mg/L)	Soil (day^{-1})	Dust (day^{-1})	Cake (day^{-1})
5	0.17	1.56	0.50
10	0.17	1.66	0.19
15	0.14	1.27	0.26
20	0.26	1.27	0.14
25	0.12	0.86	0.17
30	0.10	0.82	0.12

5.2.5 pH Changes in the Static System

The pH of P solution in the static system was found to change with the sorption time. The pH of the P solution was only adjusted at the beginning stage of the experiment and no adjustments were made as sorption proceeded. The change in pH of the soil solution with time was measured and it was found to increase after a slight decrease at the initial stage (Figure 5.15A). This is in accordance with the observations of James et al. (1992). On the other hand, the pHs of the dust and cake solutions constantly decreased after a slight increase at the initial stage (Figures 5.15B to 5.15C). The initial change in pH occurred to balance the pH of the adsorbent and solution. According to Bucksteeg et al. (1985), the dissolved P compounds, chiefly orthophosphates, are mainly immobilised in the adsorbent matrix as a result of physio-chemical reactions, giving rise to metaphosphate complexes. The immobilisation is more intensive and long lasting for adsorbents which have high aluminium or iron contents. Finer particle size results in weak acid conditions.

The intrinsic pH of soil, dust and cake was observed to be 7.5, 11.8 and 9.0, respectively (Table 5.3). As physical sorption and chemical precipitation take place in soil in the presence of P solution, the hydrogen ions (H^+) remaining in the solution decreased the pH initially. As the soil particles concentration, however, is much higher than the P concentration in the solution, the final pH of the solution reverted to the intrinsic pH of the soil. In the cases of dust and cake, the high alkalinity of the adsorbents caused a sharp initial increase in the pH of the P solution. The pH of the solutions decreased gradually as the P sorption proceeded because of the hydrogen ions (H^+) remaining in the solution (Manivasakan, 1988 ; Vigneswaran and Manivasakan, 1989).

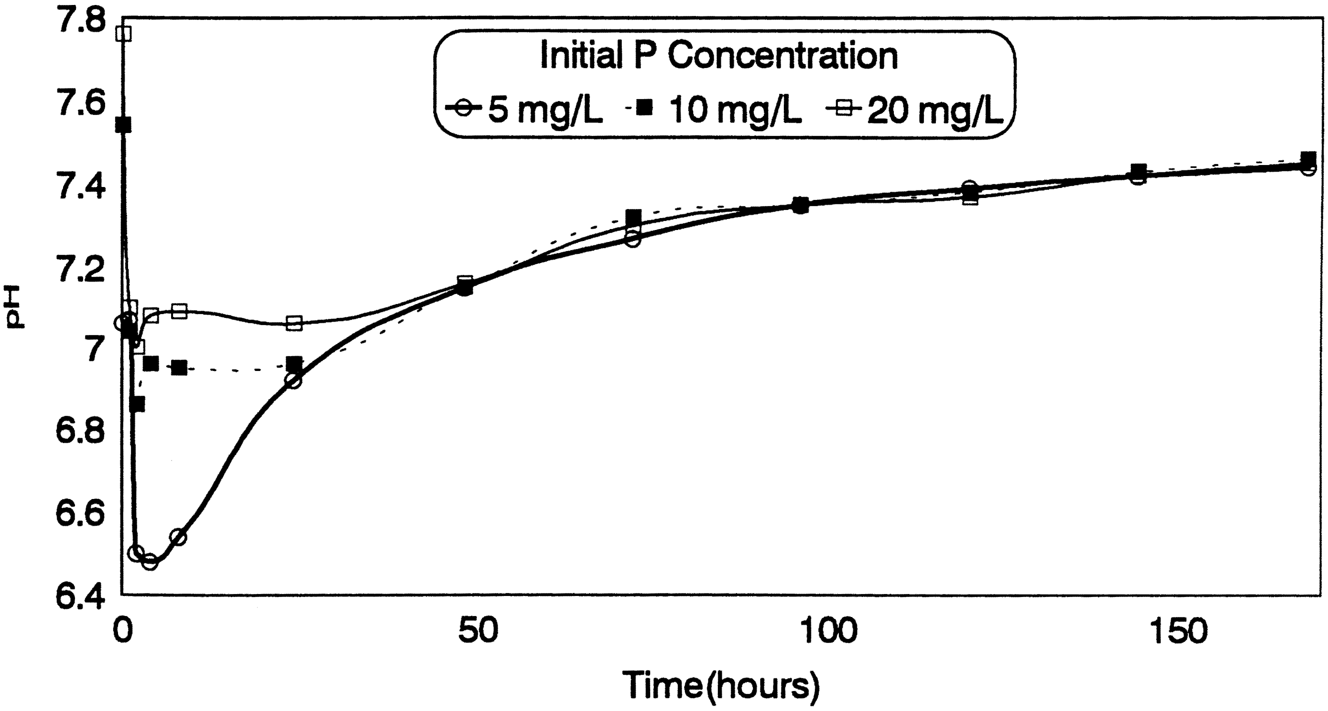


Figure 5.15A pH changes in the Static System for Soil Solution
(C_o=5, 10 and 15 mg/L, β=100.0 g, V=400 mL)

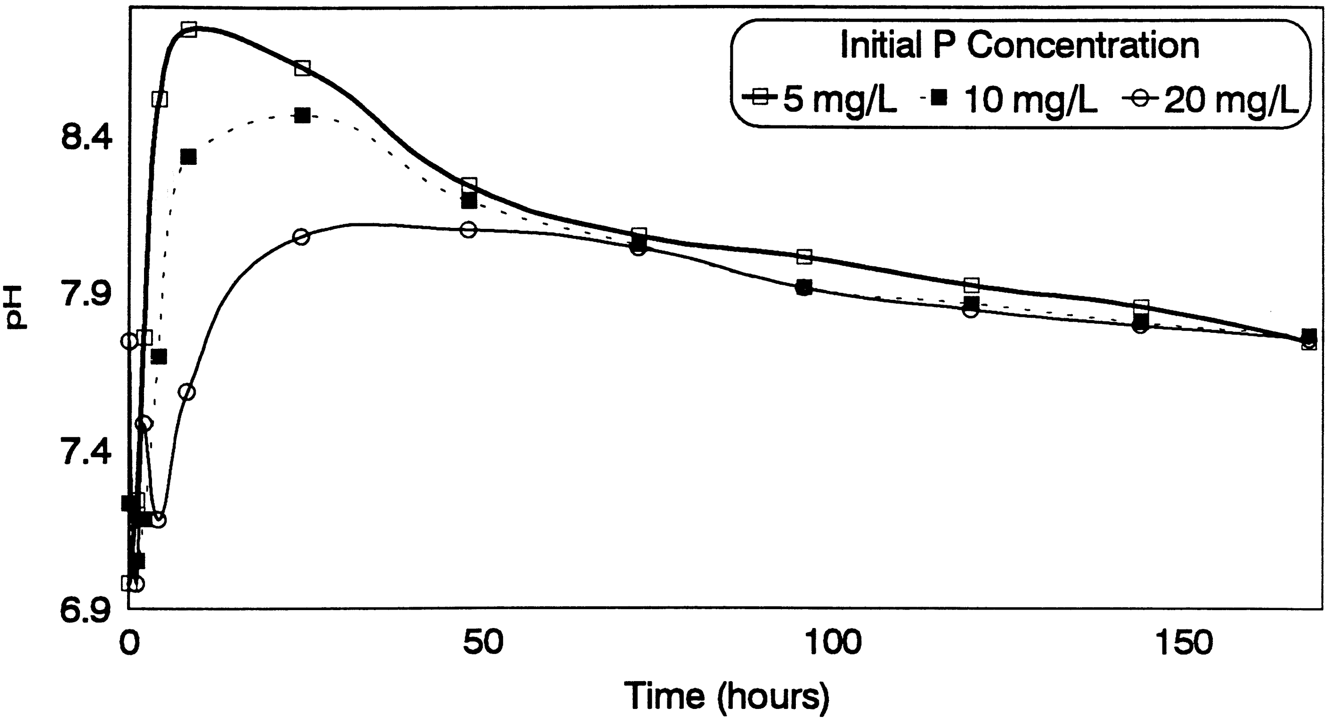


Figure 5.15B pH changes in the Static System for Dust Solution
(C_o=5, 10 and 15 mg/L, β=0.4 g, V=400 mL)

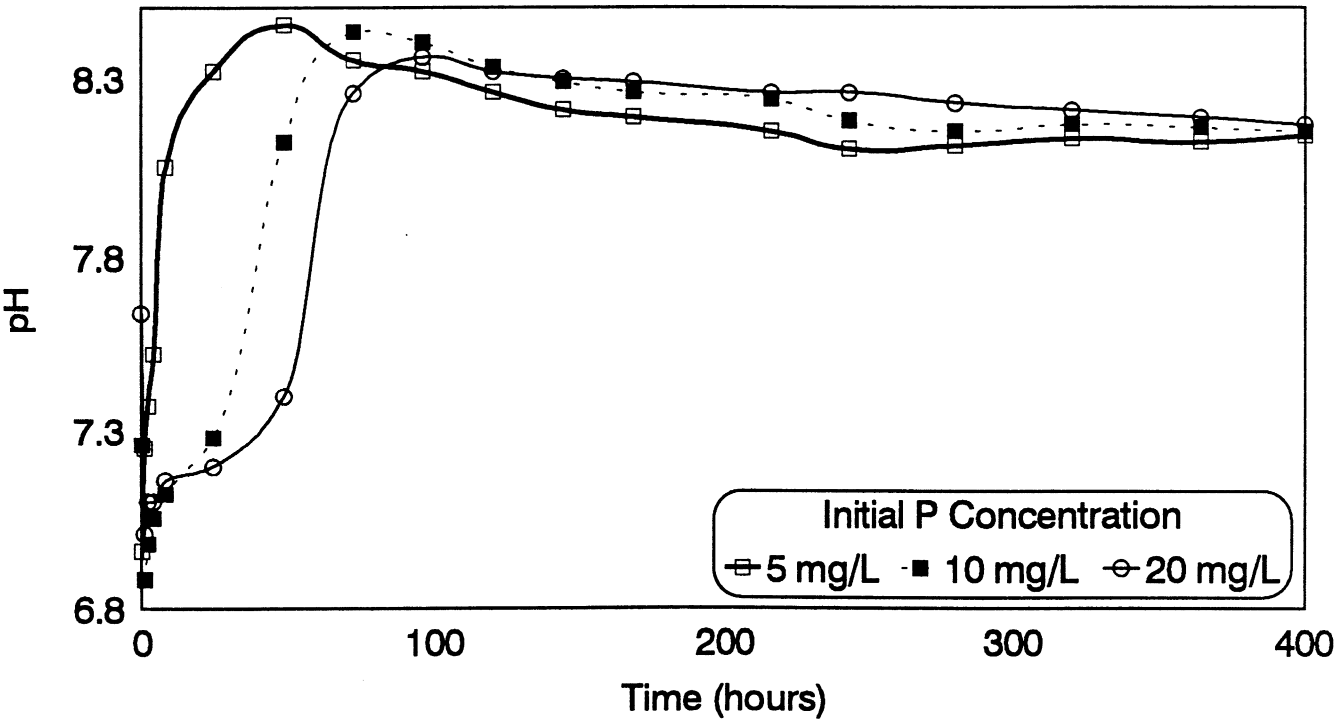


Figure 5.15C pH changes in the Static System for Cake Solution
(C_o=5, 10 and 15 mg/L, β=2.0 g, V=400 mL)

5.2.6 Effect of pH on P Removal

The pH of the P solution was observed to play a critical role in the rate of removal and the removal mechanism of P. The batch experiments in the mixing system conducted with the soil in the pH range of 2 to 12 indicated that P removal was at a minimum at pH 2. Then P removal increased up to a pH of 6 (Figure 5.16). P removal again decreased up to pH 8, after which it increased up to pH 12 (0.038 mg/g to 0.058 mg/g). Similar batch experiments conducted with dust in the same pH range showed that the P removal was at a minimum at pH 2. P removal was high in the pH range of 4 to 10 (Figure 5.17). Table 5.11 shows the amount of P adsorbed in the soil and dust at different pH levels.

Table 5.11 The Amount of P Adsorbed at Different pH levels
in the Mixing System (V=200 mL)

pH		2	4	6	8	10	12
S_e (mg/g)	Soil (50 g)	0.038	0.043	0.050	0.039	0.043	0.058
	Dust (0.1 g)	1.41	12.75	13.31	13.30	13.30	9.41

Yamada et al. (1986) observed that the P ion is adsorbed on slag in P solutions at pH 7-8, and the sorption decreased rapidly below pH 6 and above pH 8. They observed that the P in slag was dissolved in the buffer solution below pH 5.9 and was not dissolved in buffer solutions of pH 7-9. Christensen (1984) reported from his Cd sorption experimental results that pH is the most critical factor governing the distribution of Cd between soil and solute. The sorption capacities of the soils were found to increase approximately three times for each unit increase in pH in the pH interval of 4 to 7.

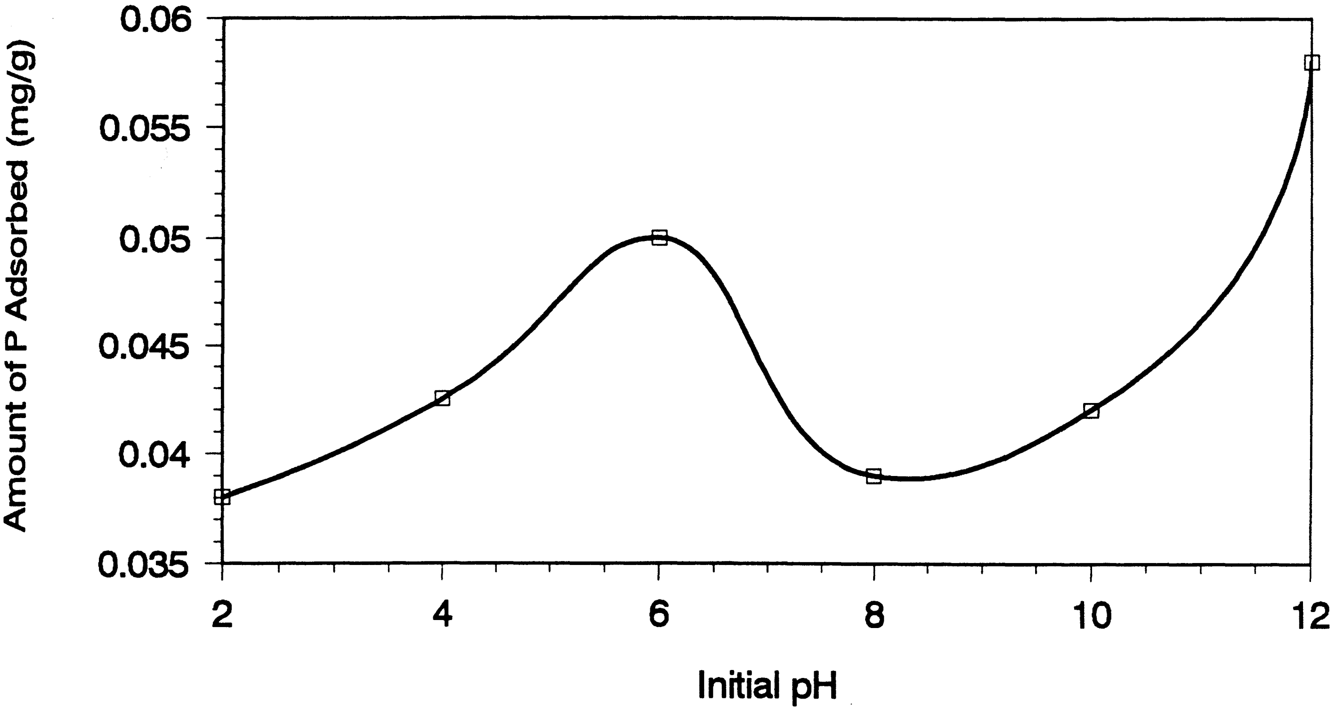


Figure 5.16 Effect of pH on P Removal in the Mixing System for Soil Solution
(C_o=20 mg/L, β=50.0 g, V=200 mL, Sorption Time=120 hours)

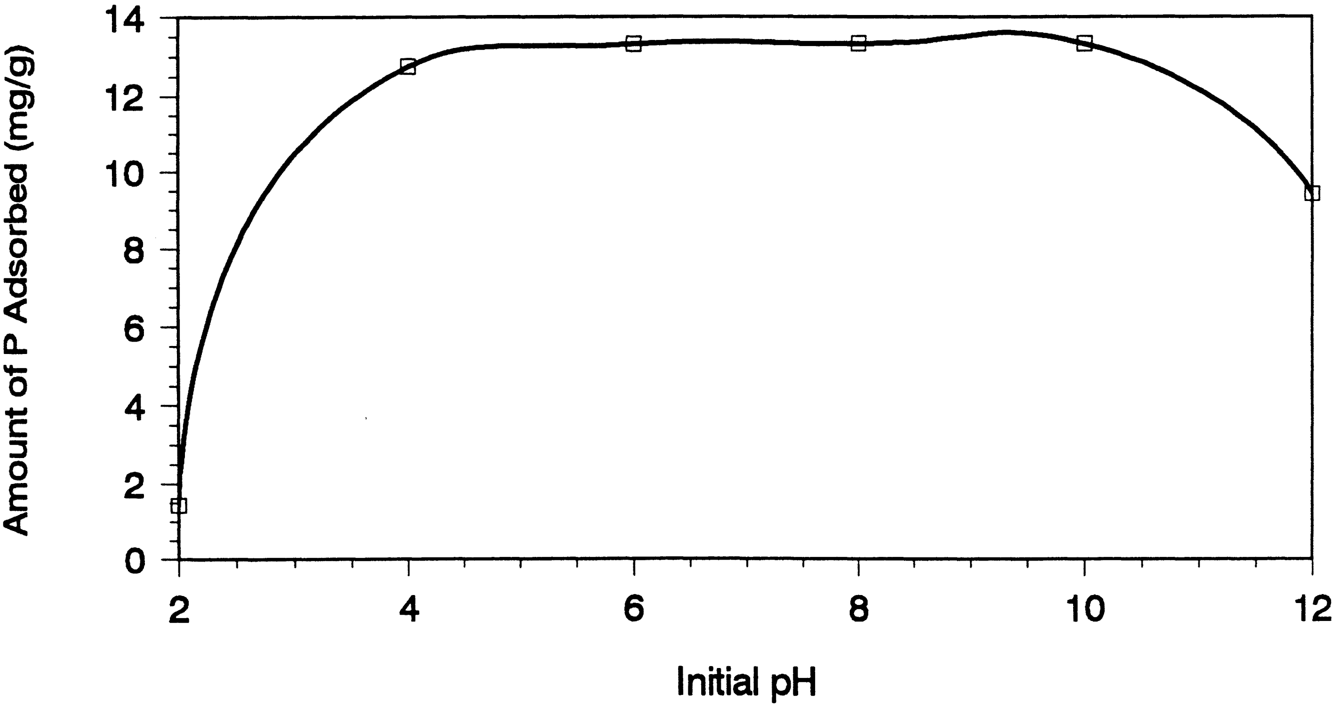


Figure 5.17 Effect of pH on P Removal in the Mixing System for Dust Solution
(C_o=20 mg/L, β=0.3 g, V=200 mL, Sorption Time=120 hours)

An important phenomenon of pH changes in soil was observed in batch experiments. The final pH of the P solution increased for the initial pH in the range 2 to 7. For the initial pH in the range 7 to 12, the final pH decreased with respect to initial pH. Similar batch experiments conducted with dust in the same pH range showed that the final pH of the P solution increased for the initial pH maintained at pH 2-9 and decreased for pH values greater than 9. The increase and decrease in pH is graphically represented in Figure 5.18. A similar phenomenon was observed in the sorption of heavy metals by Vigneswaran and Manivasakan (1989).

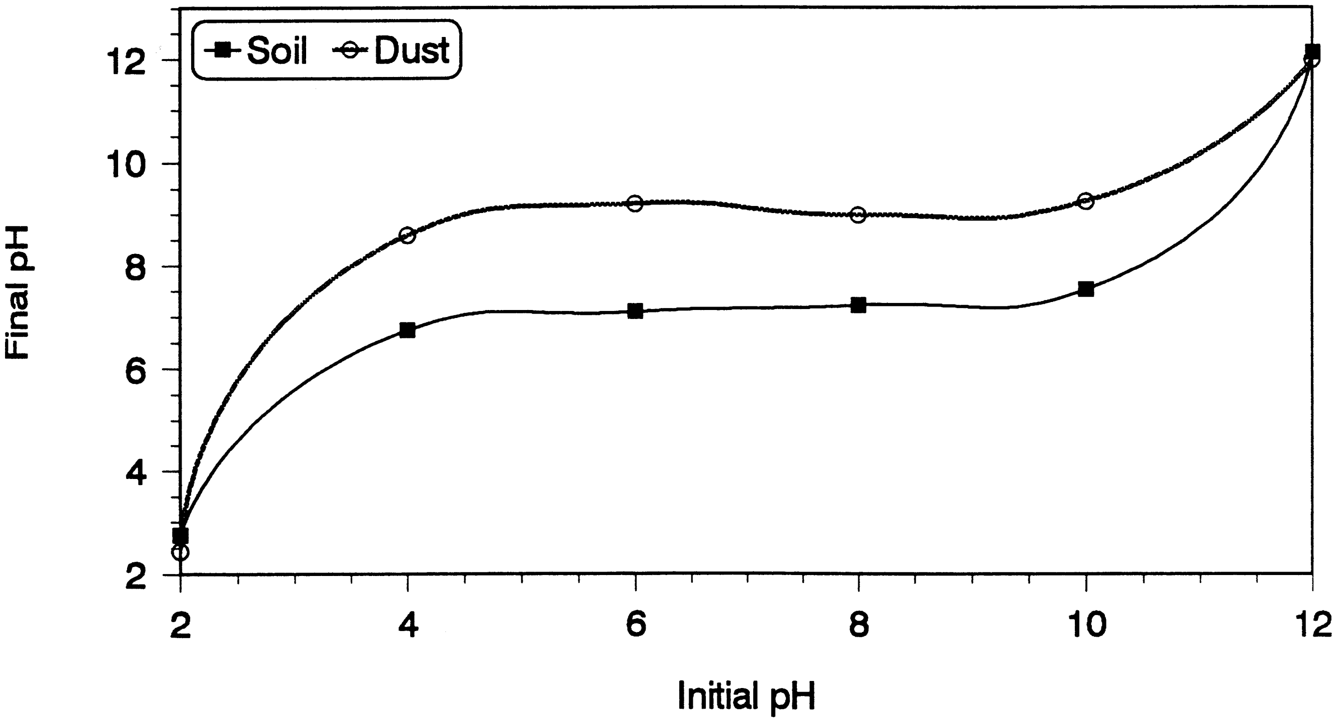


Figure 5.18 Influence of Removal Mechanism on Final pH in the Mixing System (Amount of Soil=50 g, Amount of Dust=0.3 g, C_o=20 mg/L, V=200 mL, Sorption Time=120 hours)

The change in pH can be explained in the following way. When precipitation of P takes place in alkaline solution, ionic P is adsorbed onto the adsorbents, leaving hydrogen ions (H^+) in the solution. This causes a decrease in final pH of the solution. However, when sorption predominates in acidic solutions, the hydrogen ions are reduced, thus causing an increase in the final pH of the solution (Vigneswaran et al., 1989). With these explanations and from Figures 5.19 and 5.20, it can be stated that at pH < 7, the final pH increases due to the decrease of hydrogen ions and at pH >7, the final pH decreases due to the precipitation of P ions. In dust, the final pH was kept constant at around 9.5 for initial pH in the range of 4 to 10. The high intrinsic pH and sorption capacity of dust caused an increase of the final pH. Mortimer (1971) observed that orthophosphate ions react with species of Al^{3+} and Fe^{3+} in relatively acidic soils whereas they react with $CaCO_3$ to form relatively insoluble hydroxy apatite in alkaline soils. The effect of pH on P removal may vary depending on the specific adsorbents and the P concentration.

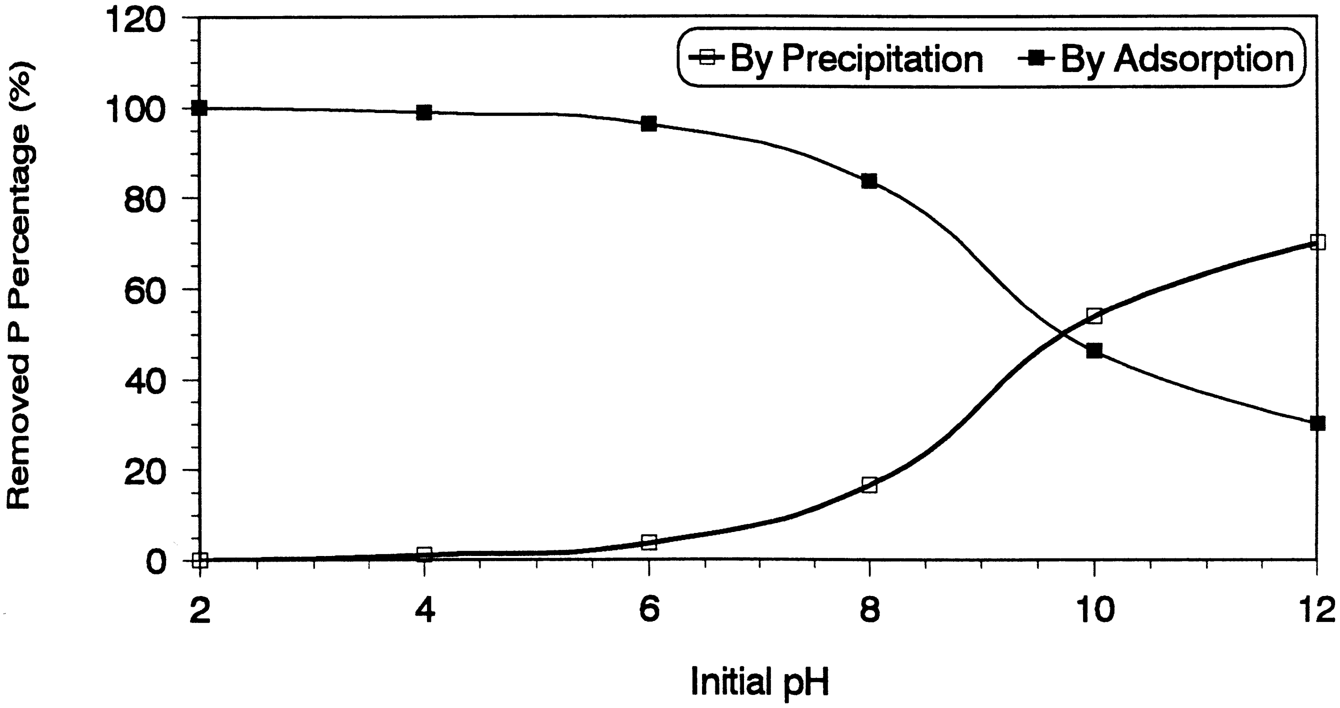


Figure 5.19 Effect of pH on P Removal Mechanism (Mixing System; Soil as Adsorbent, C_o=20 mg/L, β=50 g, V=200 mL, Sorption Time=120 hours)

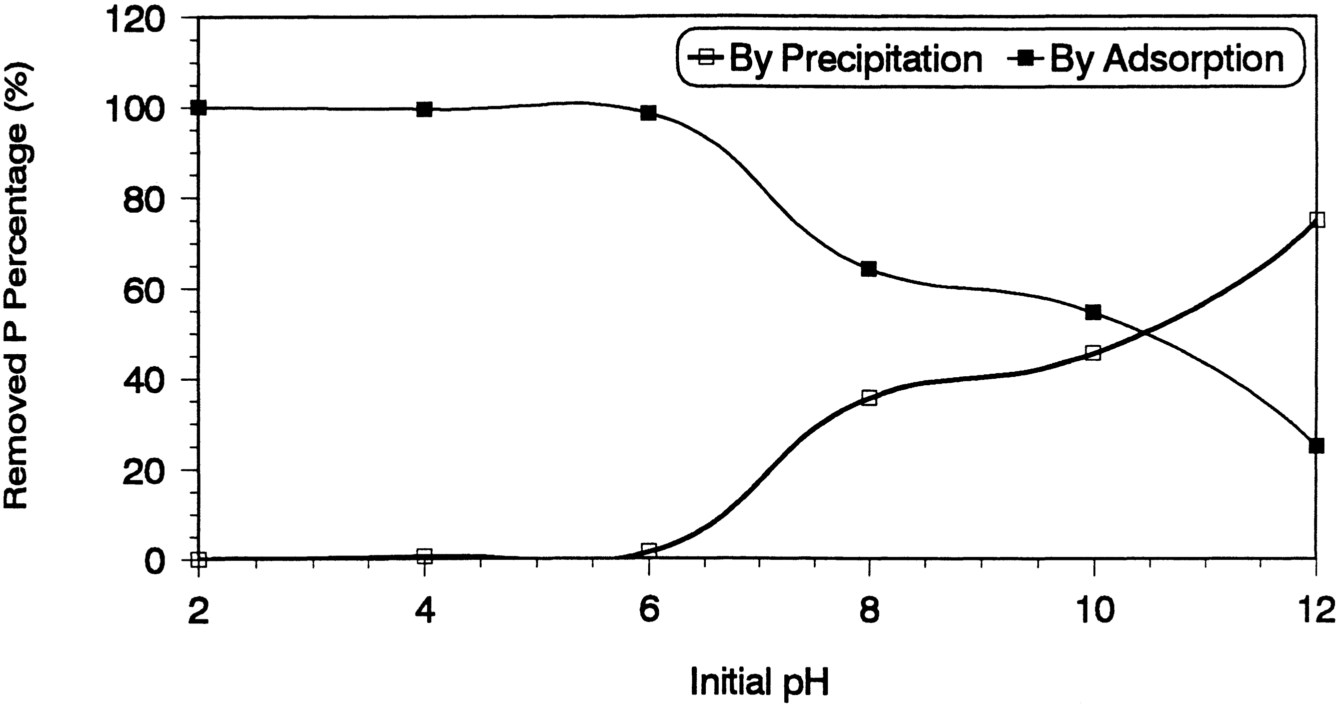


Figure 5.20 Effect of pH on P Removal Mechanism (Mixing System; Dust as Adsorbent, C_o=20 mg/L, β=0.3 g, V=200 mL, Sorption Time=120 hours)

5.2.7 Effect of Precipitation on P Removal

Chemical precipitation experiments were conducted to study the relative importance of sorption and precipitation under different conditions. The amount of P removed by precipitation alone was calculated at various pH levels and was compared with that occurring by sorption alone (Figures 5.19 and 5.20). The results obtained from the batch precipitation experiments indicated that a considerable precipitation of P was observed at a pH greater than 8. Further, this reduction increased with the increase of pH. Figures 5.19 and 5.20 show that the dominant removal mechanism of P at pH>10 is precipitation and at pH<10 is sorption. Jenkins et al. (1970) observed that the predominant species at high pH (pH=12) are PO_4^{3-}, HPO_4^{2-}, $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$, whereas at low pH (pH=2), H_2PO^{4-}, $H_2P_3O_{10}^{3-}$ and $H_2P_2O_7^{2-}$ are the main species. Past studies which dealt with the precipitation of heavy metals revealed that chemical precipitation is the predominant mechanism at high pH (Bhuvendralingam and Vigneswaran, 1987; Christensen, 1984). Manivasakan (1988) observed that the precipitation of heavy metals depends mainly on pH, mixing rate and settling time.

Figure 5.21 graphically shows the effect of precipitation on P removal at various pH levels. The reduction of P concentration by precipitation was found to be insignificant for a pH range of 2 to 6, both for soil and dust. Thus the dominant removal mechanism of P at pH<6 is physical sorption, and the effect of chemical precipitation can be neglected over this pH range. A significant reduction of P, however, was observed over a pH range of 6 to 12. The reduction of the P concentration was greater for dust than for soil. This may be due to the presence of high amounts of calcium ions (Ca^{2+}) in dust compared to soil. The calcium ions (Ca^{2+}) retained in dust (67.96 cmol (+)/kg) assist in P complexation. $CaCO_3$ may encourage P removal by raising the pH and shifting the chemical equilibrium toward precipitation of calcium phosphate (Effer and Driscoll, 1985). $CaCO_3$ was observed to enhance P removal by coprecipitation and sorption of P by replacement of water, hydroxyl ions or bicarbonate ions at the coordinate positions (Aulenbach and Meisheng, 1988). These results reinforce past studies on precipitation of heavy metals. Aulenbach and Meisheng (1988) suggested that sorption may be responsible for initial P removal, but it was not the mechanism for continuous P removal. They also concluded that calcium present in the wastewater enhanced precipitation of P. Crystallisation of hydroxy apatite (HAP), $Ca_5(PO_4)_3OH$, in aqueous solution is described by the following equation:

$$3PO_4^{3-} + 5Ca^{2+} + OH^- \rightarrow Ca_5(PO_4)_3OH \qquad \ldots (5.1)$$

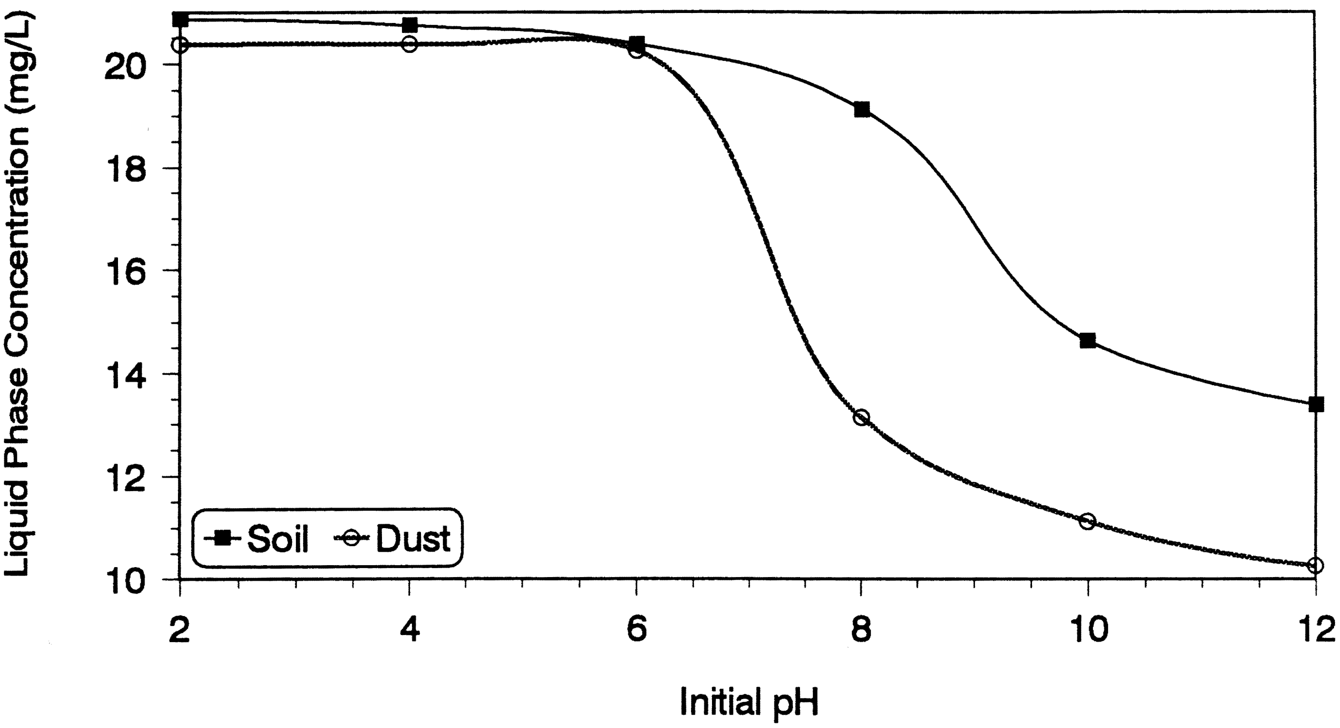


Figure 5.21 Effect of pH on P Removal by Precipitation in the Mixing System (C_o=20.9 mg/L for Soil, C_o=20.4 mg/L for Dust, V=200 mL, Precipitation Time=120 hours)

The final pH of the P solution in batch precipitation experiments was similar to the initial pH of the P solution for pH values less than 7 (both in the case of soil and dust). Beyond pH 8, it was found to decrease compared to the initial pH. Since precipitation of P predominates at pH levels greater than 8, the concentration of hydrogen ions increases in the solution. This causes a reduction in the final pH of the P solution. However, the pH reduction was less sharp than that in the sorption experiments (Figure 5.22). Table 5.12 shows the amount of ionic P removed by precipitation at different pH values.

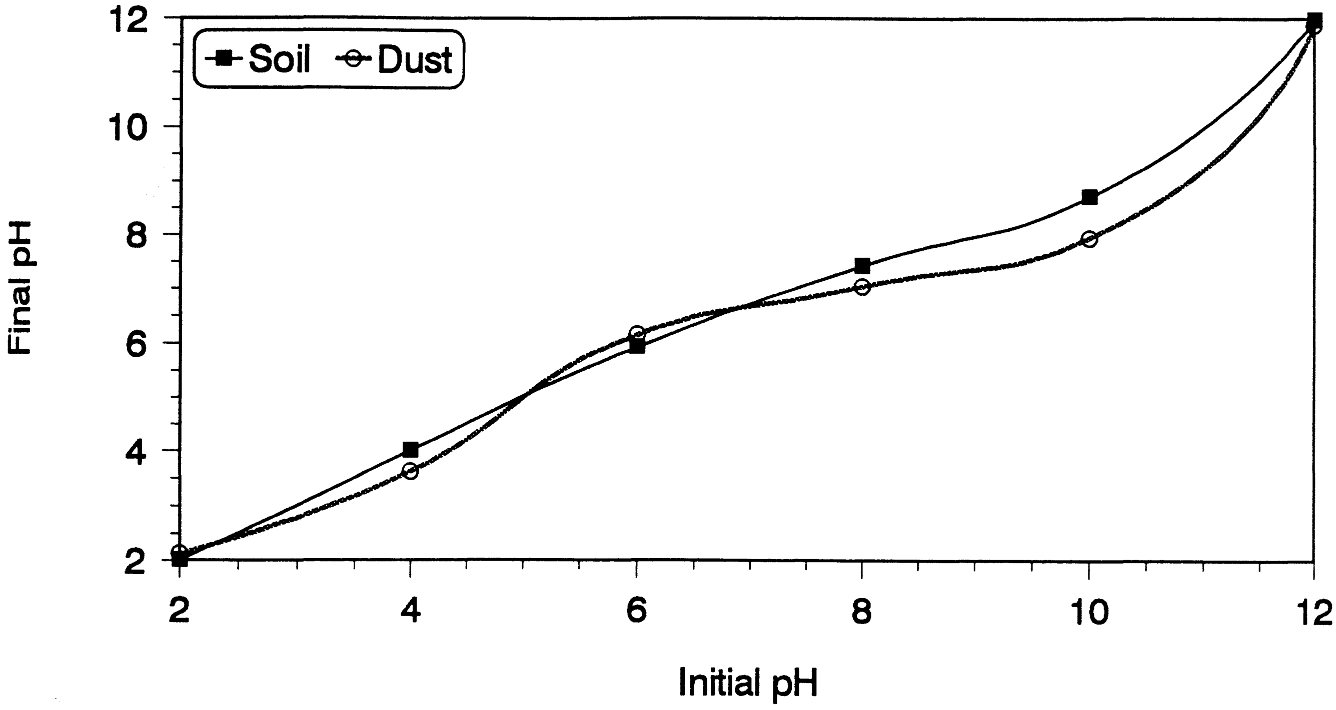


Figure 5.22 Effect of Precipitation on Final pH in the Mixing System
(C_o=20.9 mg/L for Soil, C_o=20.4 mg/L for Dust, V=200 mL,
Precipitation Time=120 hours)

Table 5.12 Amount of Ionic P Removed by Precipitation at Different pH
(C_o for Soil=20.9 mg/L, C_o for Dust=20.4 mg/L, V=200 mL)

pH		2	4	6	8	10	12
P Removed by Precipitation (mg/L)	Soil (50 g)	0	0.13	0.50	1.75	6.25	10.75
	Dust (0.3 g)	0	0	0.10	7.25	9.25	10.88

5.3 Batch Flocculation Experiments

Flocculation is the process by which small particles agglomerate to form larger aggregates. In order for flocculation to occur the particles need to collide, and hence there must be a relative movement between the particles. There are two types of flocculation - perikinetic and orthokinetic flocculation. During perikinetic flocculation, very small particles collide and join together as they move under Brownian motion. The frequency of collisions is proportional to the concentration of particles. When an aggregate grows large, flocculation is no longer significantly affected by Brownian motion. For large particles or aggregates (>1 μm), orthokinetic flocculation predominates. The rate of orthokinetic flocculation is proportional to the velocity gradient and the square of the numerical concentration of particles (Barnes et al., 1986).

Since the removal mechanisms differ in alkaline solutions of P from those in acidic solutions, a series of batch flocculation experiments was conducted to investigate the effect of flocculation on P removal. From the batch precipitation experiments, precipitation was observed to be the dominant mechanism in the removal of P in alkaline solution. The possibility of using dust as an adsorbent was investigated in the batch flocculation experiments. From the flocculation study the extent of P removal was found to depend on: (i) Flocculant (adsorbent) dose, (ii) Flocculation (contact) time (T_f), (iii) Mixing rate and (iv) pH.

5.3.1 Effect of Flocculant (Adsorbent) Dose

Batch flocculation (in-line adsorbent addition) experiments were conducted with jar test equipment. Experimental details are given in Chapter IV (Section 4.2.3). Figure 5.23A shows the effect of flocculant dose for initial P concentrations of 10, 20 and 30 mg/L. Mixing velocity and flocculation time were fixed at 60 rpm and 30 minutes respectively. As the flocculant dose (amount of adsorbent) increased, the removal efficiency increased gradually. This effect was found to be higher for lower initial P concentrations. Figure 5.23B shows the effect of flocculant dose at various flocculation times. The ionic P reduction in the solution was observed to increase with flocculation time.

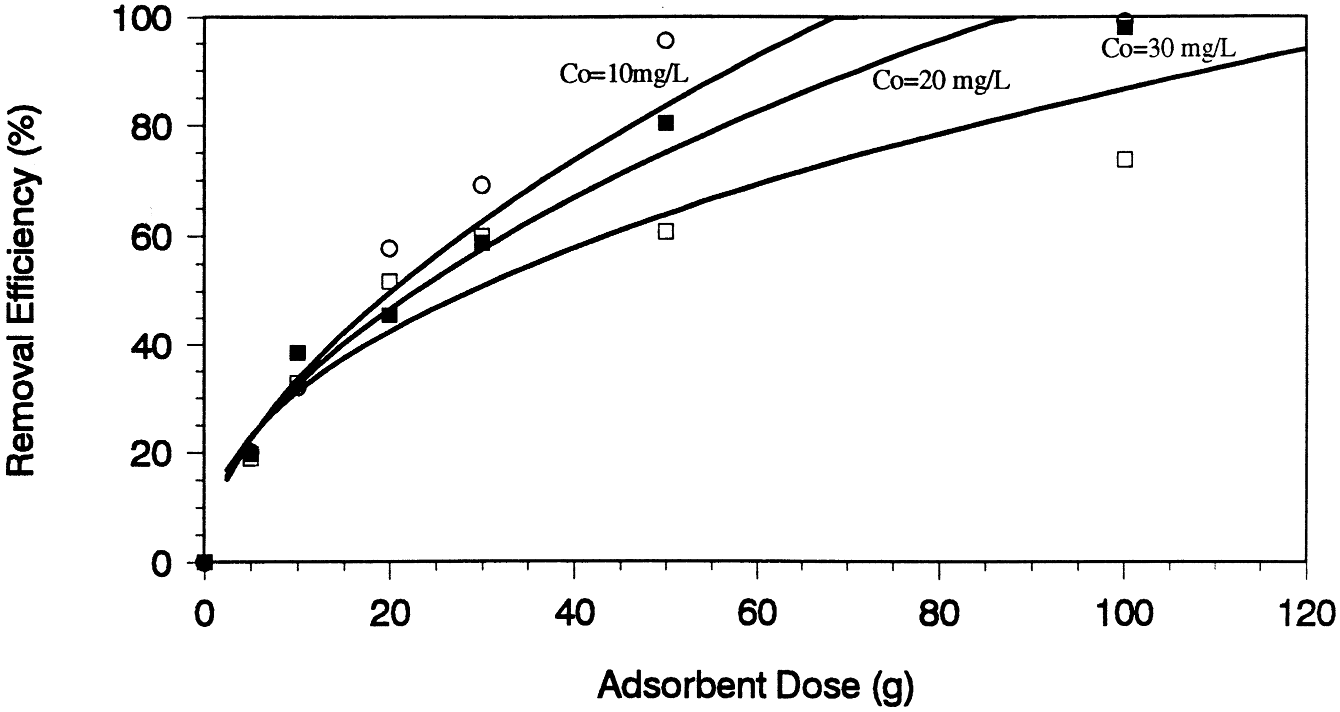


Figure 5.23A Effect of Flocculant (Dust) Dose and Initial P Concentration on P Removal Efficiency (T_f=30 min., Mixing velocity = 60 rpm, C_o=10, 20, 30 mg/L, pH=5-6)

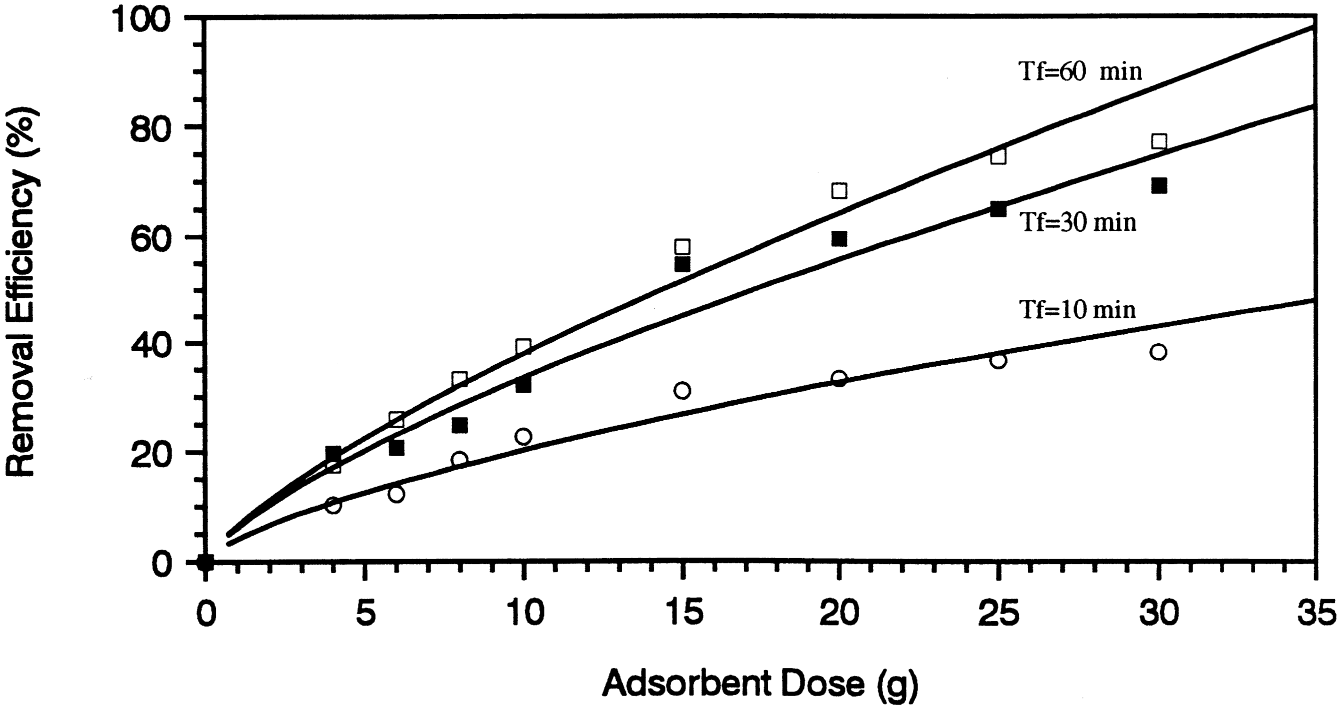


Figure 5.23B Effect of Flocculant (Dust) Dose and Flocculation Time on P Removal Efficiency (Mixing Velocity = 60 rpm, C_o= 20 mg/L, pH=5-6)

5.3.2 Effect of Flocculation (Contact) Time

Flocculation time was found to play an important role in the reduction of ionic P concentrations in solution. The removal efficiency of P was observed to increase with flocculation time both for very high (30,000 mg/L) and comparatively low (2,000 mg/L) flocculant doses (Figures 5.24A and 5.24B). P complexation with Al, Ca, Fe and other chemicals present in dust is expected to be high with the increase in flocculant dose and flocculation time. In the presence of dust (as adsorbent), P in the solution undergoes chemical precipitation followed by physical sorption on the surface of dust particles. This process was enhanced by the provision of mixing gradient and flocculation time (Figures 5.24A and 5.24B).

Flocculation involves changes in the physical properties of solids whereas precipitation involves changes in the chemical properties of P. The process of P precipitation involves a chemical reaction in which P ions combine chemically to form insoluble compounds which are easily adsorbed to the surface of the adsorbent (dust).

Precipitation followed by flocculation involves a chemical reaction between ions that are dissolved in the P solution, and the reaction product is a solid (suspended in the solution or adsorbed on the surface of dust). Precipitation will occur if the product of concentration of ions (as measured by the solubility product) is greater than the solubility product constant (K_{sp}). The precipitation reaction can be written as follows:

$$mA^{n+} + nB^{m-} \Leftrightarrow A_mB_n \qquad \text{... (5.2)}$$

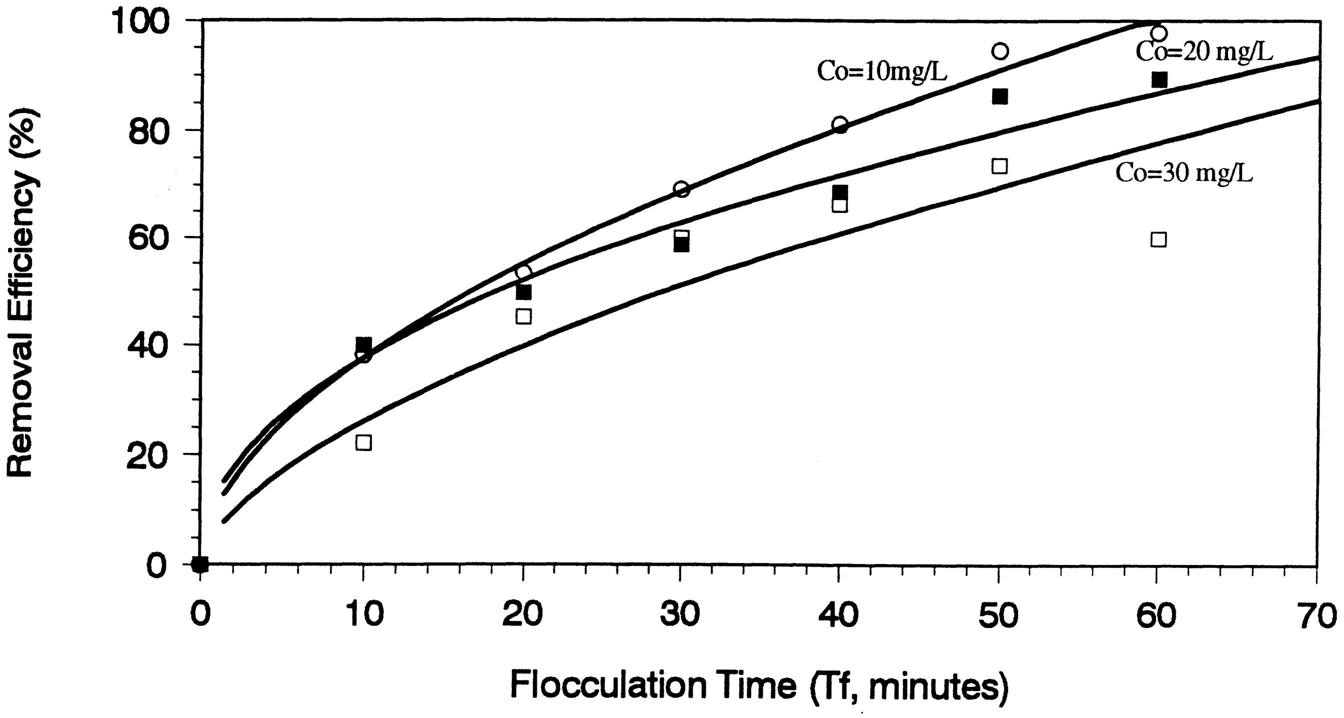


Figure 5.24A Effect of Flocculation Time at High Flocculant (Dust) Dose (Mixing velocity = 60 rpm, Dust Dose = 30 g, C_o=10, 20, 30 mg/L, pH=5-6)

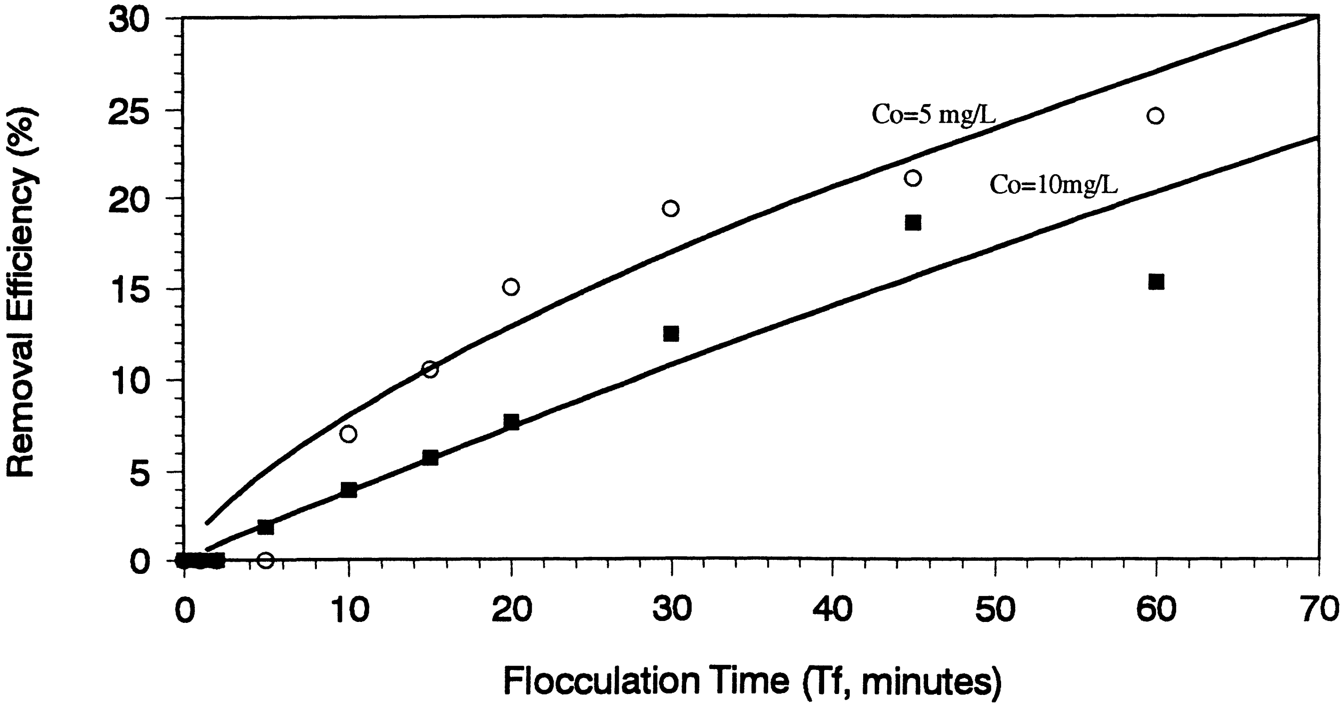


Figure 5.24B Effect of Flocculation Time at Low Flocculant (Dust) Dose (Mixing velocity = 60 rpm, Dust Dose = 2 g, C_o=5 and 10 mg/L, pH=5-6)

The product of the ion concentrations ($[A^{n+}][B^{m-}]^n$) can be compared with the constant K_{sp}, and precipitation occurs if:

$$[A^{n+}][B^{m-}]^n > K_{sp} \qquad \text{... (5.3)}$$

Various kinds of cations will react with P as flocculation time increases and hence a number of different precipitates may form simultaneously. Each precipitation reaction has its own particular value of K_{sp}. Therefore the amount of each precipitate formed will vary. Table 5.13 shows the major cations present in the adsorbent (dust) and the possible insoluble compounds that they may form in the solution.

Table 5.13 Major Cations Found in Dust and the Possible Insoluble Compounds Formed in the Solution.

Major Cations	Precipitate Formed
Fe^{2+} or Fe^{3+}	$Fe(OH)_2$ $Fe(OH)_3$ $FePO_4$
Ca^{2+}	$CaCO_3$ $Ca_3(PO_4)_2$ $Ca_5(PO_4)_3OH$
Mg^{2+}	$Mg(OH)_2$ $Mg_3(PO_4)_2$ $MgNH_4PO_4$
Al^{3+}	$Al(OH)_3$ $AlPO_4$

5.3.3 Effect of Mixing

The mixing rate (or intensity) also played an important role in the reduction of ionic P concentration in solution. When wastewater percolates through a soil or slag, depending on the percolation velocity and pore size, the mixing intensity (velocity gradient; G) will vary. In other words, mixing intensity is a function of soil or slag pore size and percolation velocity. High P removal was observed with the increase in the mixing velocity (Figure 5.25).

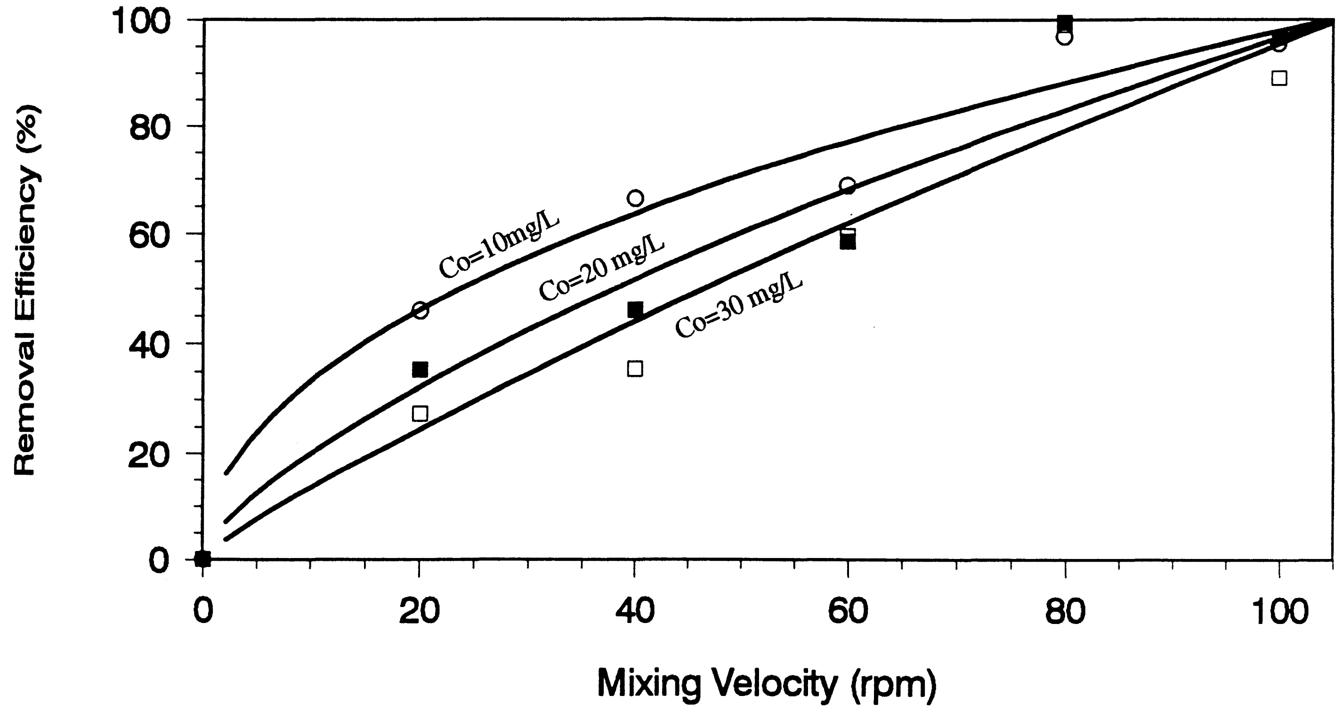


Figure 5.25 Effect of Mixing Velocity on P Removal
(T_f = 30 minutes, Dust Dose = 30 g, C_o=10, 20, 30 mg/L, pH=5-6)

5.3.4 pH Changes at Batch Flocculation Experiments

The pH change in the supernatant of the P solution was obvious with the removal of P. The pH of the solution was adjusted only before the start of flocculation experiments and no adjustments were made as flocculation proceeded. The pH of the P solution was found to increase with the adsorbent dose (Figure 5.26). The intrinsic pH of the adsorbent is 11.8 and it is the main factor which causes the increase in the pH of the P solution.

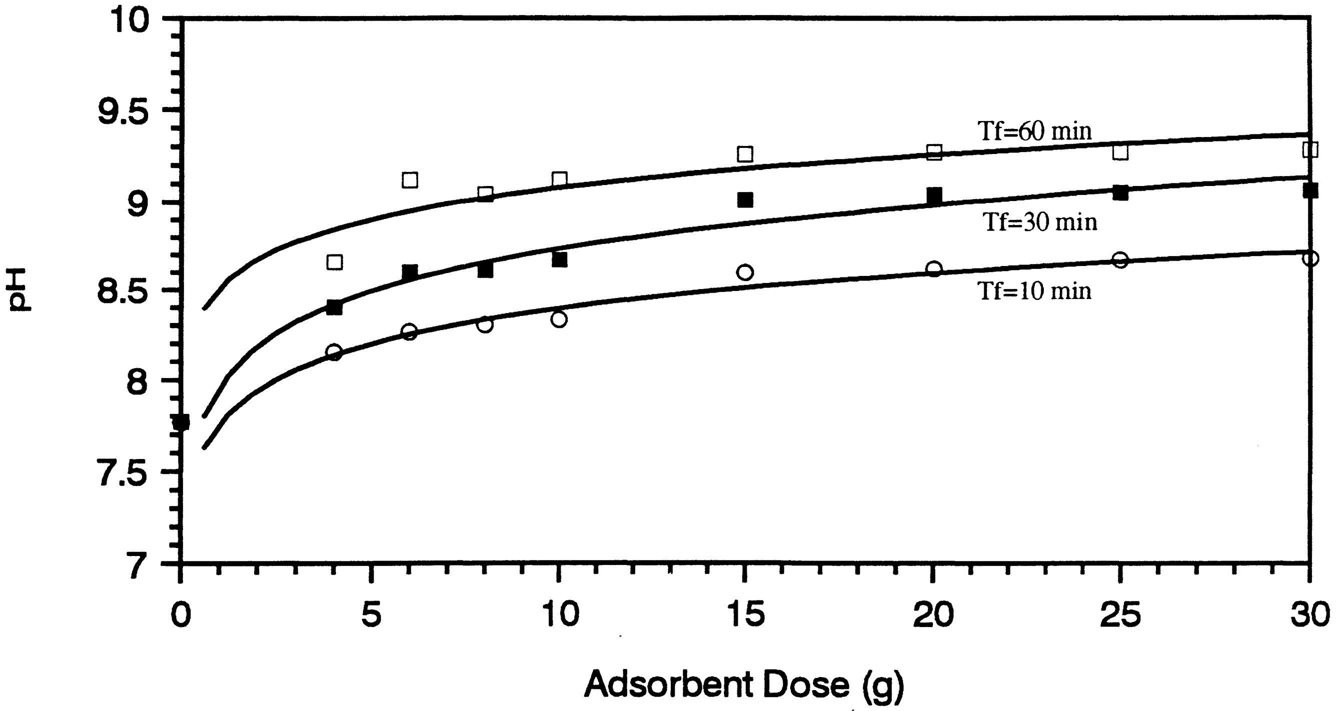


Figure 5.26 pH Changes at Different Flocculation (Mixing) Times (Mixing Velocity = 60 rpm, C_o= 20 mg/L, pH=5-6)

5.4 P Sorption in the Presence of Foreign Material

Ammonia nitrogen is generally found together with P in wastewater. Consequently, a series of batch experiments were conducted to study P sorption in the presence of NH_4 as a foreign material. Dust and cake were used as the adsorbents.

5.4.1 Effect of NH_4 on P Sorption in Dust

The standard P solution, the standard NH_4 solution and the adsorbent (dust) were thoroughly mixed before allowing the P removal to take place. The initial concentration of NH_4 was maintained at 40 mg/L while initial P concentrations were varied. A known amount of dust (0.1 g) was thoroughly shaken with the standard P and NH_4 solutions. The amount of P adsorbed by dust in the presence of NH_4 is shown in Table 5.14. Also presented is the percentage reduction of P compared to the corresponding P removal without NH_4 in the solution (ie. the single solute experiment). The amount of P adsorbed by dust in the presence of NH_4 was less than that in the single solute system (Table 5.14). This effect may be a combination of reduced activities (due to increased ionic strength and complex formation) and competition by NH_4 for dust sorption sites.

Table 5.14 Solid Phase Concentration of P and the Percentage of P Reduction in the Presence of NH_4 for Dust (NH_4=40 mg/L, V=200 mL, β=0.1 g, pH=5-6)

C_e (mg/L)	5	10	15	20	25	30	35	40
S_e (mg/g)	5.5	5.5	6.0	6.5	7.5	7.8	8.0	8.0
Percentage Reduction (%)	33.4	56.0	57.1	55.2	49.1	47.7	44.8	48.4

The percentage of P reduction in the presence of NH_4 ranged from 33 to 57% depending on the initial P concentration. The effect of foreign material has been studied with different solutions. For example, an investigation of the effect of Ca on Cd sorption in soils indicated that the presence of Ca in soil solutions effectively competed with Cd for sorption sites (Christensen, 1984). An increase in Ca concentration from 10^{-3} to 10^{-2} M reduced the Cd sorption capacity of the sandy loam soil to approximately one third. Christensen (1987) observed the effective reduction of Cd sorption in Danish soils by the mixture of Ni, Co, and Zn, and of Cr, Cu, and Pb. He concluded that Zn, which was present in larger concentrations, accounted for most of the observed competition with Cd. Manivasakan (1988) found a decrease of Cd sorption with increasing Ca concentration. Kaneko and Nakajima (1988) conducted continuous packed column experiments to study the effect of ammonium on the effluent P concentrations. Magnesia clinker was used as a packing medium. Their results revealed that the presence of ammonium ions tended to decrease the sorption capacity of P. Table 5.15 shows the Freundlich and Langmuir isotherm constants of dust in the presence of NH_4. The Freundlich isotherm constant K decreased from 8.99 mg/g(L/mg)^N (in single solute system) to 4.40 mg/g (L/mg)^N (in the presence of NH_4), demonstrating that the sorption capacity and affinity of P were reduced in the presence of NH_4.

Table 5.15 Freundlich and Langmuir Isotherm Constants of P in the Presence of NH_4 for Dust (NH_4=40 mg/L, V=200 mL, β=0.1 g, pH=5-6)

Freundlich Isotherm Constants		Langmuir Isotherm Constants	
K[mg/g(L/mg)^N] N	4.40 6.66	a(mg/g) b(L/mg)	7.37 1.07
R^2	0.83	R^2	0.55

5.4.2 Effect of NH_4 on P Sorption in Cake

Another series of batch experiments conducted with cake as adsorbent showed that the solid phase concentration of P in the presence of NH_4 was also less than the single solute system. The amount of P adsorbed on cake is shown in Table 5.16. Also presented is the percentage of P reduction for comparison. The average reduction of P sorption compared to the single solute experiment was 10%. Table 5.17 shows the static Freundlich and Langmuir isotherm constants for cake.

5.4.3 P Sorption in the Synthetic Wastewater

Batch sorption experiments were also conducted to observe P sorption behaviour in the presence of synthetic wastewater. The characteristics of the wastewater are shown in Table 4.2. The solid phase concentration of P in the multi-solute system is presented in Table 5.18. Due to the competition for sorption sites in soil, sorption of P is expected to decrease. But blooming of bacteria in synthetic wastewater caused high uptake of P onto the adsorbent, and the solid phase concentration of P increased both for soil and dust compared to the single solute system.

Table 5.16 Solid Phase Concentration of P and the Percentage of P Reduction in the Presence of NH_4 for Cake (NH_4=40 mg/L, V=200 mL, β=0.1 g, pH=5-6)

C_e (mg/L)	5	10	15	20	25	30	35	40
S_e (mg/g)	0.9	1.2	1.9	2.3	2.3	3.2	3.4	3.5
Percentage Reduction (%)	1.1	27.3	11.9	11.2	19.3	1.6	1.2	5.7

Table 5.17 Freundlich and Langmuir Isotherm Constants of P in the Presence of NH_4 for Cake (NH_4=40 mg/L, V=200 mL, β=1.0g, pH=5-6)

Freundlich Isotherm Constants		Langmuir Isotherm Constants	
K[mg/g(L/mg)^N]	1.01	a(mg/g)	2.51
N	2.66	b(L/mg)	1.06
R^2	0.88	R^2	0.45

Table 5.18 Solid Phase P Concentration in the Presence of Synthetic Wastewater for Soil and Dust

Initial P Concentration C_o (mg/L)	S_e (mg/g) in Soil	S_e(mg/g) in Dust
10	0.044	15.50
20	0.078	21.00
30	0.094	17.50
40	0.109	11.25

5.5 P Removal in Column Experiments

The field conditions were simulated in the laboratory by packing the columns with the same soil, dust and cake used in batch experiments. The results from column (dynamic) experiments at various influent concentrations, pore water velocities and adsorbent depths are described systematically below. The column experiments were carried out mainly; (i) to compare the P sorption under the batch (mixing and static system) and column experiments, (ii) to find the breakthrough pattern of P under various conditions and (iii) to validate the mathematical model used. The pH of the P solution in the influent was maintained in the range of 6 to 7.

5.5.1 P Removal in the Soil Column

P sorption rates into soil at different influent concentrations, pore water velocities, soil depths and water levels above the soil medium in the soil column, are presented below.

5.5.1.1 Effect of Influent P Concentration

(a) Column Sorption Isotherm of P in Soil

Column sorption experiments were performed in a column packed with 5 cm deep soil for different influent concentrations of P (5, 10, 20, 30, 40 and 50 mg/L). Other experimental details are given in Chapter IV (Section 4.3.1). The velocity could not be kept constant for different influent concentrations of P and it varied from 1.53 to 5.14 cm/day. The equilibrium liquid phase concentration and the corresponding solid phase P concentration determined experimentally are presented in Table 5.19. The solid phase concentrations from batch experiments are calculated from the equilibrium isotherm constants determined by the mixing and static systems to compare these with those from column experiments. The amount of P initially dissolved or retained in soil was deducted.

Table 5.19 Amount of P Adsorbed in Soil in the Batch and Column Experiments

C_o (mg/L)		5	10	20	30	40	50
S_e (mg/g)	From Column Experiment (Dynamic System)	0.019	0.036	0.068	0.097	0.126	0.154
	From Batch Experiment (Mixing System)	0.028	0.032	0.036	0.039	0.042	0.044
	From Batch Experiment (Static System)	0.042	0.059	0.081	0.098	0.112	0.124

The solid phase concentrations calculated using batch experimental isotherm constants in the mixing system are substantially lower than those computed from dynamic column experiments except for the initial concentration of 5 mg/L. On the other hand, the solid phase concentrations computed from batch experimental isotherm constants in the static system were higher than those determined from column experiments at low influent P concentrations (<30 mg/L). The parameters K, N and a, b for Freundlich and Langmuir isotherms respectively were evaluated from the amounts of P adsorbed in the soil column. The isotherm constants determined from column experiments are presented in Table 5.20. The sorption phenomena in the dynamic system was described better by the Freundlich isotherm than by the Langmuir isotherm. This observation agrees with those made by researchers on the sorption of heavy metals (Christensen, 1984; Vigneswaran et al. ,1989; Bajracharya and Vigneswaran,1990).

Table 5.20 Freundlich and Langmuir Isotherm Constants for Soil in the Dynamic System

Freundlich Isotherm Constants		Langmuir Isotherm Constants	
$K[mg/g(L/mg)^N$ N	4.55×10^{-3} 1.11	a(mg/g) b(L/mg)	7.47×10^{-1} 5.09×10^{-3}
R^2	0.98	R^2	0.96

(b) Model Validation

The mathematical models presented in Chapter III were fitted to the column experimental breakthrough data for various influent concentrations of P. This was accomplished by making use of the fitting program, MCMFIT (Bajracharya and Barry, 1995). A brief description of MCMFIT is presented in Section 3.2.3. In the operation of MCMFIT to determine the best fitting parameters, the pulse time was set to a very large number (9999.0) so that a complete breakthrough is obtained. The S-curve isotherm parameters of α_1 and α_4 (Eqn. 3.18) were fixed at -1.0 and 1.0 respectively so that Eqn. 3.18 reduced to the Freundlich isotherm. The fraction of sites (α_6) was set at zero and held constant. The two site sorption model then reduced to a non-equilibrium process. The entrance boundary condition type one was used by selecting MODE=1. The Freundlich isotherm constants K and N were calculated as 4.55×10^{-3} $mg/g(L/mg)^N$ and 1.11 respectively from the analysis of column experiments. The dispersion coefficient (D_s) and kinetic mass transfer coefficient (α_5) were obtained by fitting procedures. Table 5.21 shows the optimal parameter values as determined by MCMFIT for different influent concentrations. The dispersion coefficient (D_s) was constant (0.58 cm^2/day) while the kinetic mass transfer coefficient (α_5) gradually decreased as the influent concentration of P was increased. This was coincident with the equilibrium stage being attained quickly as the influent P concentration was increased.

Table 5.21 The Optimal Parameter Values of MCMFIT for Different Influent Concentrations of P

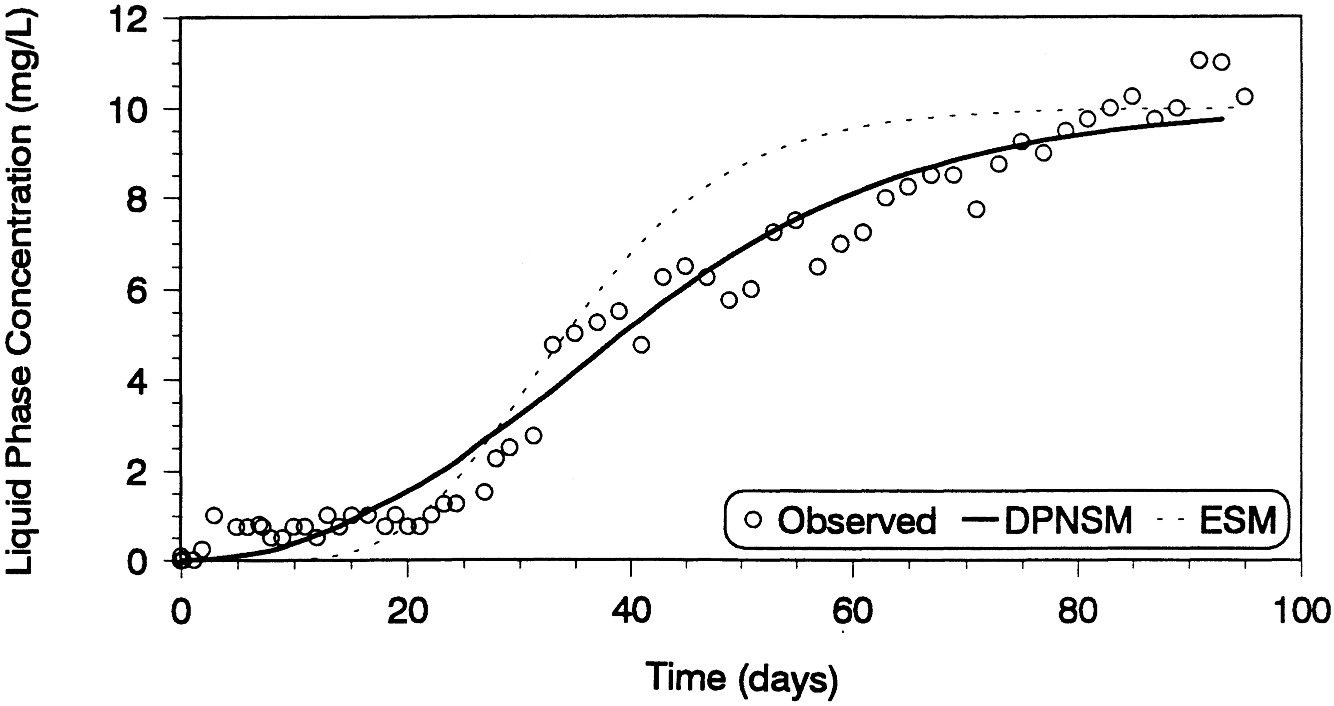
Parameter Values	C_o=10 mg/L	C_o=20 mg/L	C_o=30 mg/L	C_o=40 mg/L
D_s (cm^2/day)	0.58	0.58	0.58	0.58
α_5(day^{-1})	0.23	0.18	0.13	0.10

In the DPNSM, the equilibrium P concentrations in the soil column were represented by the Freundlich isotherm. For simulation purposes, the Freundlich isotherm constants K and N evaluated from the column experiment were used. The experimental breakthrough data and their simulated results are presented in Figures 5.27A to 5.27D. All the column results exhibited characteristic, nearly S-shaped, breakthrough curves, such that final effluent concentrations approximately corresponded to the influent P concentrations. The simulated results based on Freundlich isotherm constants K and N determined from column experiments fitted satisfactorily the corresponding experimental breakthrough data. The small variation in the experimental data may be due to the flow fluctuation which is unavoidable.

The predictions by the Equilibrium Sorption Model (ESM) are shown in the same figures (Figures 5.27A to 5.27D). The DPNSM reduces to the ESM when the kinetic mass transfer coefficient (α_5) and the fraction of site (α_6) take values of zero and 1.0 respectively. The rest of the parameters were the same as before. The ESM did not predict the spreading of the breakthrough curve of P, especially for high influent concentrations of 30 and 40 mg/L.

It is apparent from the experimental data that the P solute reaches early breakthrough when high influent P concentrations (>30 mg/L) were used. This means the partitioning coefficient 'k' is higher for lower concentrations.

(A) C_o=10 mg/L



(B) C_o=20 mg/L

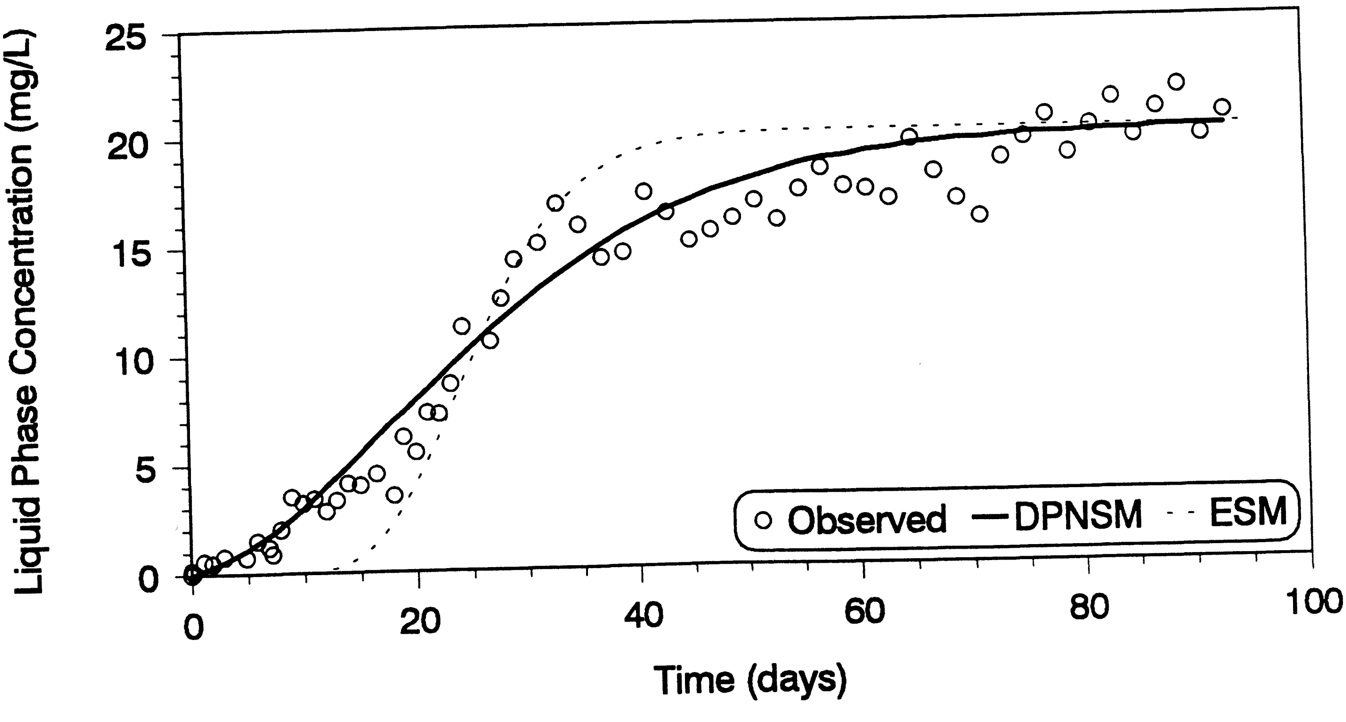
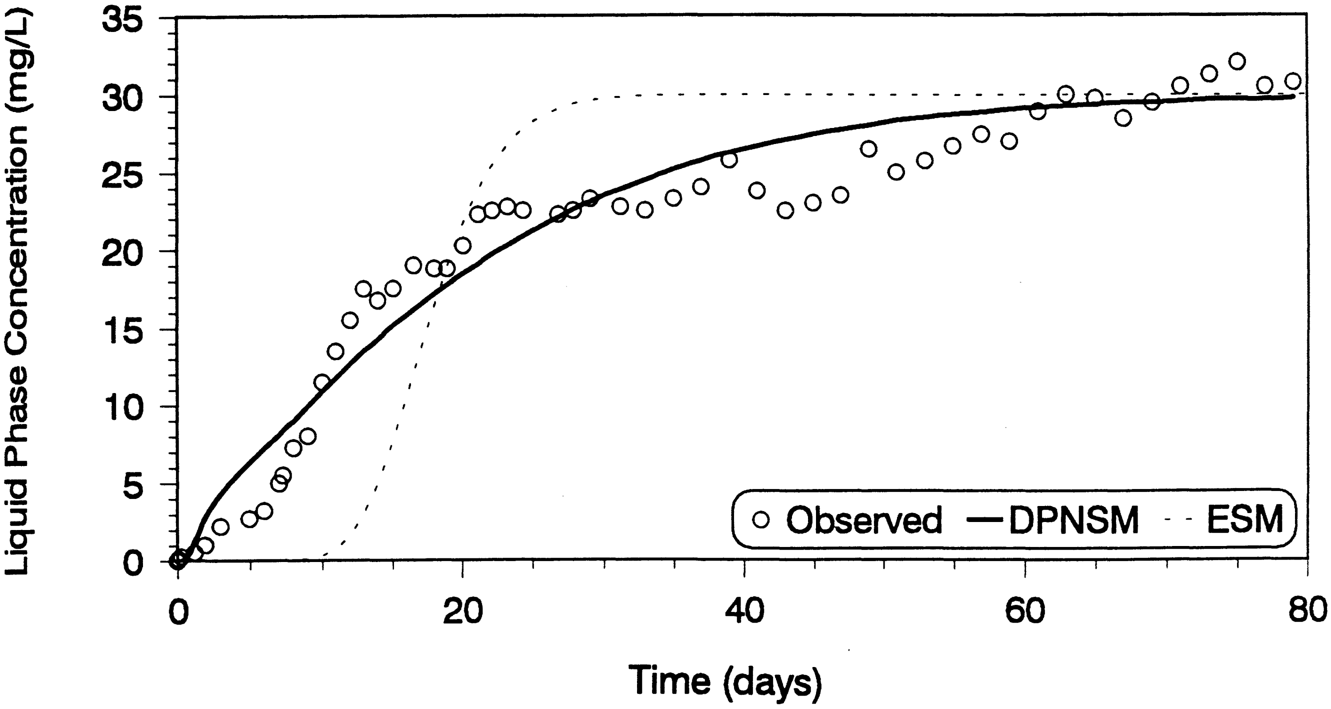


Figure 5.27: Phosphorus Concentration History Curves in Soil (w=1.53 cm/day, D_s=0.58 cm^2/day, α_5 =0.23 day^{-1} for C_o=10 mg/L, α_5 =0.18 day^{-1} for C_o=20 mg/L, K=4.55x10^{-3} mg/g$(L/mg)^N$, N=1.11, H=5 cm, pH=6-7)

(C) C_o=30 mg/L



(D) C_o=40 mg/L

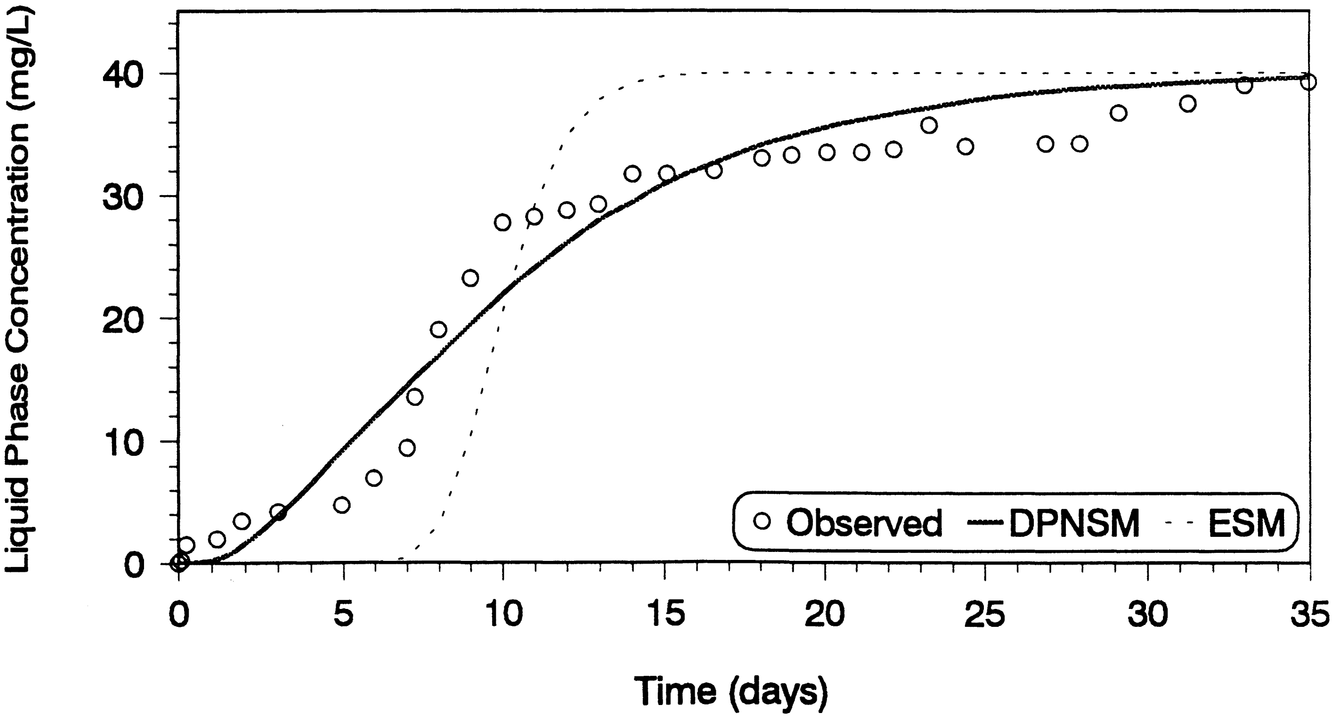


Figure 5.27(Cont'd): Phosphorus Concentration History Curves in Soil (w=1.53 cm/day, D_s=0.58 cm^2/day, α_5 =0.13 day^{-1} for C_o=30 mg/L, α_5 =0.10 day^{-1} for C_o=40 mg/L, K=4.55x10^{-3} mg/g(L/mg)^N, N=1.11, H=5 cm, pH=6-7)

Thus the spreading of the breakthrough curve should decrease with the increase of influent concentration (Tiwaree, 1989). However, it is difficult to make such a conclusion from the experimental breakthrough data and simulated results, as they are influenced by pore water velocity. Table 5.22 shows the observed and predicted relative Darcy velocities for a P concentration corresponding to 50% of the influent P concentration. The observed relative Darcy velocity (w_s/w) was calculated directly from the experimental data (for example, for C_o=10 mg/L, w_s is 2.5cm / 40 day for 50% of P removal; thus the observed Darcy velocity (w_s/w) is 4.08×10^{-2} for w=1.53 cm/day). At influent P concentrations of 10 to 40 mg/L, P migrated 25 to 16 times slower than water.

Table 5.22 Observed and Predicted Relative Darcy Velocities of P

C_o (mg/L)	Observed Relative Darcy Velocity from Experimental Data	Predicted Relative Darcy Velocity from Soil Analysis	Retardation Factor (R_d)
10	4.08×10^{-2}	9.21×10^{-2}	10.9
20	4.72×10^{-2}	9.80×10^{-2}	10.2
30	7.16×10^{-2}	1.02×10^{-1}	9.8
40	6.08×10^{-2}	1.04×10^{-1}	9.6

The predicted relative Darcy velocities for P were obtained from Eqn. 3.12 of Chapter III and they were found to be higher than those of the actually observed values for P. The retardation factor (R_d) decreased with the increase of influent P concentration. The retardation factor as explained in Chapter III can be calculated from $R_d=1+\rho K_d/\Theta$ for a linear isotherm and $R_d=1+(\rho/\varepsilon)K\Theta C^{(\Theta-1)}$ for the Freundlich isotherm. Here the value of R_d presented is based on the Freundlich isotherm.

The laboratory soil column experiments of low Cd concentrations monitored in terms of solute breakthrough for up to 600 days revealed that the observed relative Cd Darcy velocities were in good agreement with predictions by relative solute velocity equations (Christensen, 1984). All the columns exhibited a characteristic S-shaped breakthrough curve showing the final effluent Cd concentrations approximately corresponded to influent Cd concentrations. In Christensen's (1984) experiments, Cd at low concentrations migrated 500 to 770 times slower than water in slightly acidic pH conditions. This indicated a very restricted mobility of Cd in unpolluted soils. The mobility of P observed in the present study is also restricted in the soil but not to the extent of Cd.

5.5.1.2 Effect of Pore Water Velocity

Soil column experiments were conducted with an influent P concentration of 30 mg/L at three different pore water velocities. The soil was packed up to 5 cm deep in the column. The other experimental conditions are given in Chapter IV (Section 4.3.1). The observed breakthrough results (Figure 5.28A) were initially fitted by MCMFIT to estimate the kinetic mass transfer coefficient (α_5). Freundlich isotherm constants K and N and dispersion coefficient (D_s) were fixed at the values obtained from the previous experimental fitting results. The range of the kinetic mass transfer coefficient (α_5) used was 0.12 to 0.25 days^{-1}. Table 5.23 presents the model parameters of DPNSM. The kinetic mass transfer coefficient (α_5) decreased as the pore water velocity increased. The immobile film layer surrounding soil particles becomes thinner and thinner as the pore water velocity increases. This is due to the equilibrium stage being reached faster with the increase in pore water velocity. The prediction by DPNSM was quite satisfactory (Figure 5.28A). The curves are nearly S-shaped with more spreading and long breakthrough times as the pore water velocity decreases. The slope of the breakthrough curves becomes more steep with less spreading as pore water velocity increases. One possible reason for this is the variation of the mass transfer rate which is considerably greater at low pore water velocities than at higher velocities (Keinath and Weber, 1968).

Table 5.23 The Model Parameters of DPNSM at Various Pore Water Velocities

Parameters	w=1.00 (cm/day)	w=1.55 (cm/day)	w=2.30 (cm/day)
D_s(cm^2/day)	0.58	0.58	0.58
α_5(day^{-1})	0.25	0.19	0.12
K[mg/g(L/mg]^N	4.55×10^{-3}	4.55×10^{-3}	4.55×10^{-3}
N	1.11	1.11	1.11
R^2	0.98	0.96	0.96

MCMFIT was also used to estimate all the model parameters of DPNSM which result in the best fit. The optimal parameters estimated were the Freundlich isotherm constants K and N, the pore water velocity (w), dispersion coefficient (D_s) and kinetic mass transfer coefficient (α_5). Table 5.24 presents these optimal parameter values giving the best fit for different pore water velocities. The parameter values shown in Table 5.24 were different from the values obtained directly from the column experiments. Since MCMFIT was designed to estimate the optimal parameter values by matching improved mixing cell model predictions with measured experimental data, there can be a number of sets of model parameters which fit the observed breakthrough data. This is the limitation of all fitting procedures. The observed and fitted curves are shown in Figure 5.28B. They were similar to the fitted results by DPNSM in Figure 5.28A even though the model parameters are different, as shown in Tables 5.23 and 5.24. To observe the effect of pore water velocity on P sorption, the breakthrough data obtained from soil column experiments at different pore water velocities were compared.

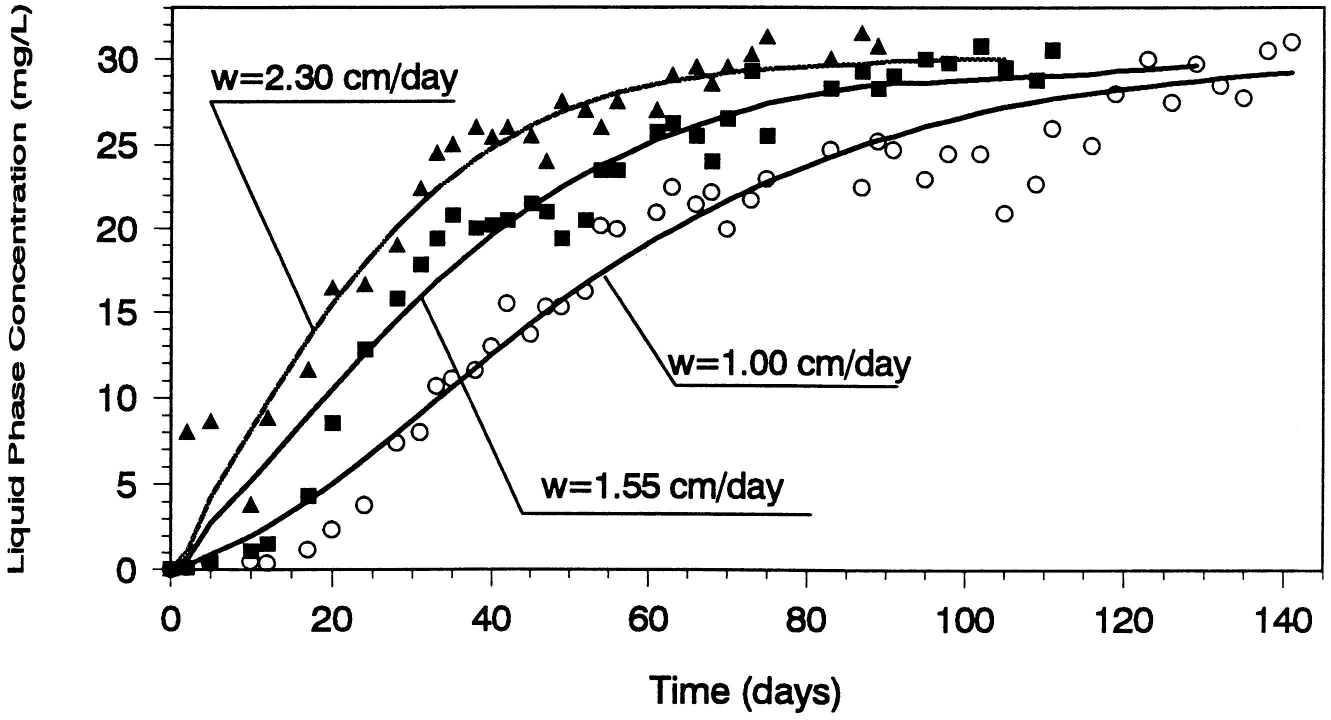


Figure 5.28A Observed and DPNSM Predicted Concentration History Curves of P for Different Pore Water Velocities in Soil (C_o=30 mg/L, D_s=0.58 cm^2/day, α_5 = 0.25 day^{-1}, K=4.55x10^{-3} mg/g(L/mg)^N, N=1.11, H=5 cm, pH=6-7)

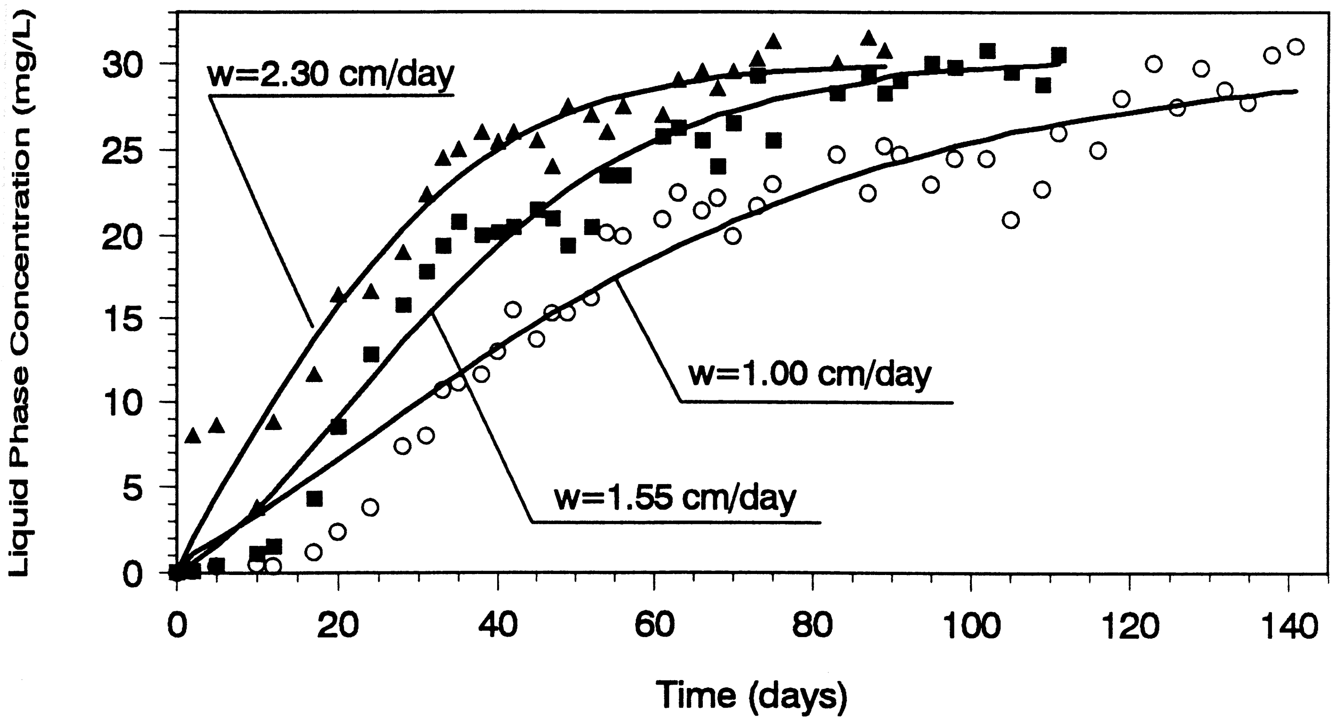


Figure 5.28B Observed and MCMFIT fitted Concentration History Curves of P for Different Pore Water Velocities in Soil (C_o=30 mg/L, D_s=1.19 cm^2/day, H=5 cm, pH=6-7)

Table 5.24 The Best Curve Fitting Parameter Values of MCMFIT at Various Pore Water Velocities

Parameters	w=1.00 (cm/day)	w=1.55 (cm/day)	w=2.30 (cm/day)
w(cm/day)	1.18	1.91	2.89
D_s(cm^2/day)	1.19	1.19	1.19
α_5(day^{-1})	1.59	0.23	0.16
K[mg/g(L/mg)^N]	4.14×10^{-3}	4.18×10^{-3}	4.40×10^{-3}
N	1.01	1.00	1.12
R^2	0.98	0.98	0.96

Table 5.25 shows the soil column parameters at three different pore water velocities. Breakthrough times at 50% and 100% influent P concentrations decreased as the pore water velocity increased. As the pore water velocity increased, the contact time between P solute and the soil particles became less and less. Thus the amount of P solute retained in the soil decreased as the pore water velocity increased.

Table 5.25 Comparison of Soil Column Parameters at Different Pore Water Velocities.

Parameters	w = 1.00 cm/day	w = 1.55 cm/day	w = 2.30 cm/day
T_{50} (days)	41.5	27.0	18.5
T (days)	123.0	95.0	66.0
S_e (mg/g)	1.07×10^{-1}	9.85×10^{-2}	9.26×10^{-2}
w_s/w	7.53×10^{-2}	7.72×10^{-2}	8.85×10^{-2}

where,

T_{50} (days) = Breakthrough time at 50 % influent concentration
T (days) = Breakthrough time
S_e (mg/g) = Solid Phase Concentration
w_s/w = Relative Darcy Velocity at 50 % concentration

The relative Darcy velocity at 50% concentration increased with the increase in the pore water velocity. As the pore water velocity increased, the residence time of P solute reduced resulting in a lesser sorption of P. On the other hand, the high pore water velocity supplies larger amount of P solute within the same period of time. The driving force to propel the P solute on the soil surface is greater with the increase of pore water velocity due to the increase of bulk solution concentration of P solute per unit time. This also leads to early breakthroughs at high pore water velocities. A similar trend was observed in an earlier study with Cd through soil (Tiwaree, 1989).

5.5.1.3 Effect of Adsorbent Depth

The effect of adsorbent depth in the mobility of P was also studied. The experimental and simulated P breakthrough curves by DPNSM for soil depths of 2 to 5 cm are shown in Figures 5. 29A and 5.29B. As expected, the soil column with the greater depth gave a later breakthrough than that with a shallower depth. As soil depth increases, P sorption increases in soil particles due to the increase of surface area mass loading which leads to a delayed breakthrough.

The breakthrough times to achieve 50% and 100% influent concentrations increased significantly with the increase of soil depth (Table 5.26). As the soil depth increases, the contact time between P solute and soil medium increases, thus increasing the amount of P solute retained in soil medium. The relative Darcy velocity at different depths was observed to be in the range of 1.04×10^{-1} to 1.97×10^{-1}.

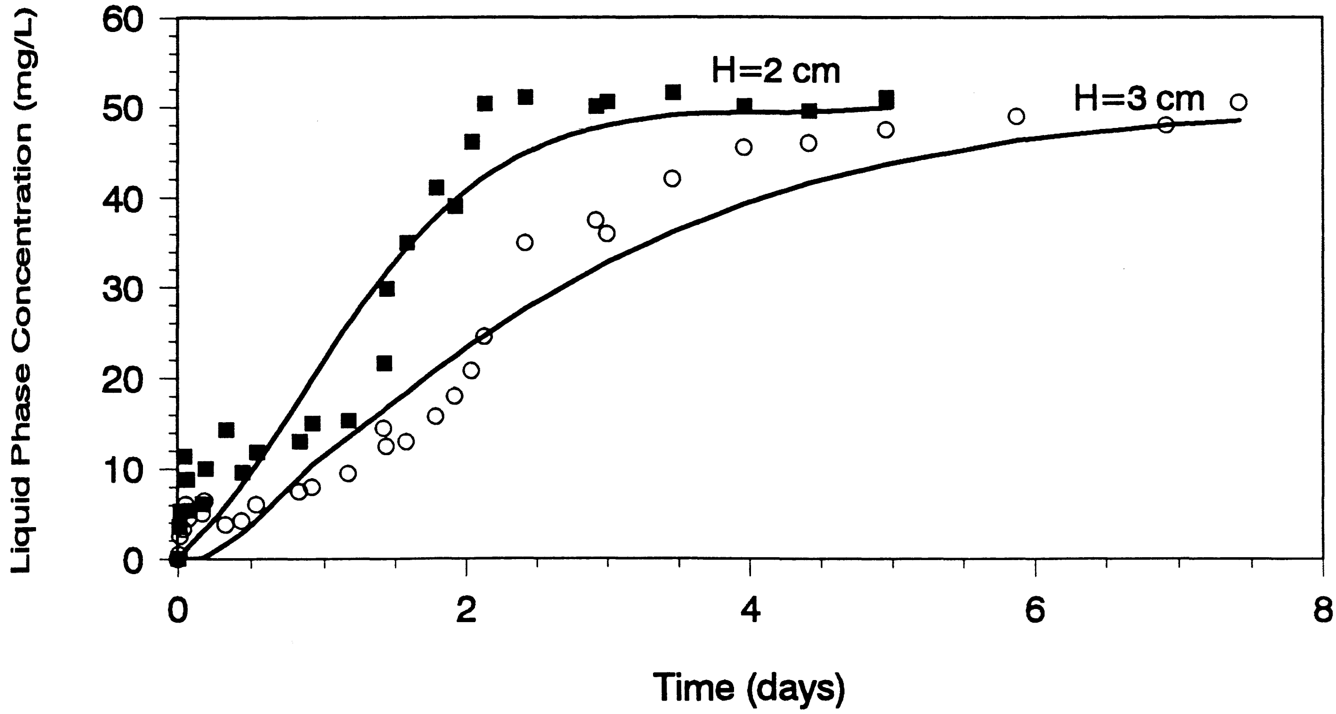


Figure 5.29A Phosphorus Concentration History Curves at Different Soil Depths (C_o=50 mg/L, H=2 and 3 cm, w=38.0 for 2 cm, w=11.8 cm/day for 3 cm, D_s=0.58 cm^2/day, α_5=0.33 day^{-1} for 2 cm, α_5=0.65 day^{-1} for 3 cm, K=4.55x10^{-3} mg/g(L/mg)^N, N=1.11, pH=6-7)

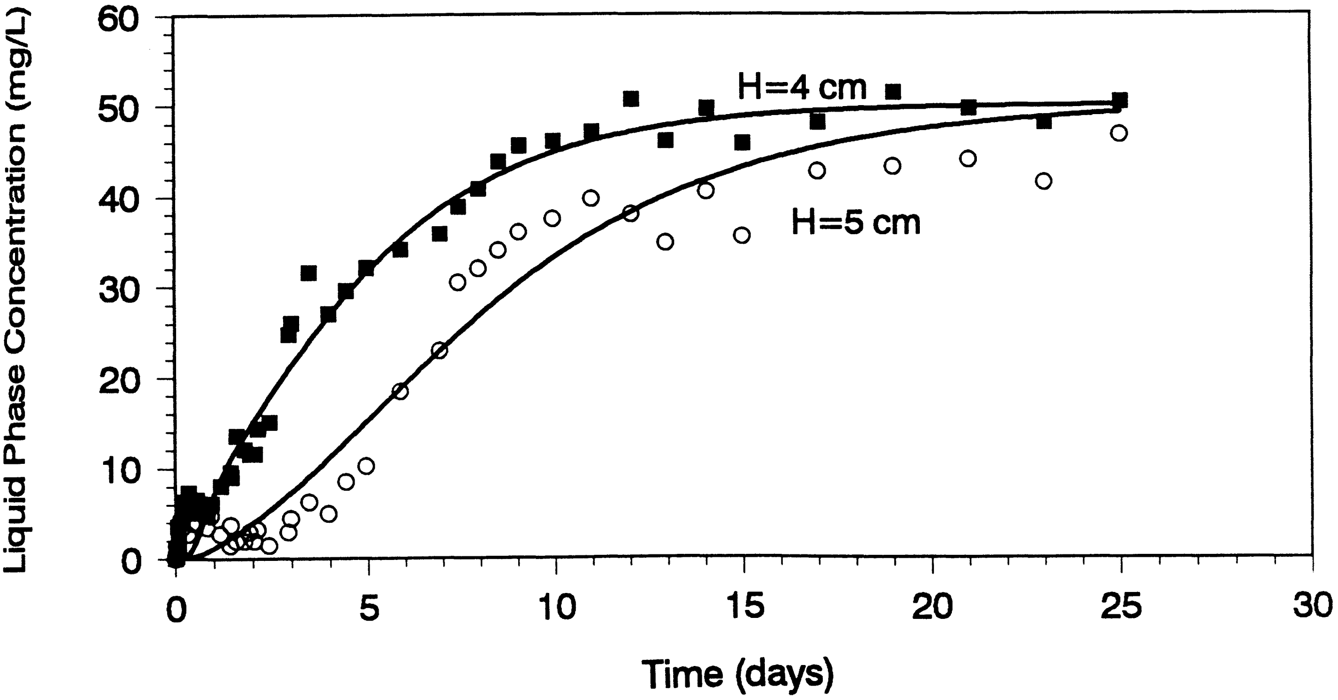


Figure 5.29B Phosphorus Concentration History Curves at Different Soil Depths (C_o=50 mg/L, H=4 and 5 cm, w=9.21cm/day for 4 cm, w=4.95 cm/day for 5 cm, D_s=0.58 cm^2/day, α_5=0.98 day^{-1} for 4 cm, α_5=1.49 day^{-1} for 5 cm, K=4.55x10^{-3} mg/g(L/mg)^N, N=1.11, pH=6-7)

Table 5.26 Soil Column Parameters at Different Adsorbent Depths

Parameters	Soil Depth 2 cm	Soil Depth 3 cm	Soil Depth 4 cm	Soil Depth 5 cm
T_{50} (days)	1.40	2.35	2.96	7.20
T (days)	2.13	7.42	19.00	36.00
S_e (mg/g)	5.23×10^{-2}	6.89×10^{-2}	8.52×10^{-2}	9.20×10^{-2}
w_s/w	1.04×10^{-1}	1.24×10^{-1}	1.97×10^{-1}	1.24×10^{-1}

MCMFIT was used to estimate the optimal value of the kinetic mass transfer coefficient (α_5) from the experimental breakthrough data. The Freundlich isotherm constants K and N, the pore water velocity (w) and dispersion coefficient (D_s) were fixed at the values obtained from the previous experimental and fitting results. The range of the kinetic mass transfer coefficient (α_5) was observed to be 0.33 to 1.49 day^{-1}. The prediction by DPNSM was quite satisfactory (Figures 5.29A and 5.29B).

5.5.1.4 Effect of Water Level

The effect of water level above the soil medium was also studied in terms of mobility of P. The experimental and simulated P breakthrough curves (using DPNSM) for water levels (heads) of 5, 15 and 25 cm are shown in Figure 5.30. As expected, the soil columns with lower water levels resulted in smaller pore water velocity, thus leading to a delayed breakthrough compared to the soil column with a higher water level. This delayed breakthrough is due to the longer contact time, which also caused more P retention in the soil. The observed breakthrough data was first fitted using MCMFIT to estimate the kinetic mass transfer coefficient (α_5). The Freundlich isotherm constants K and N, the pore water velocity (w) and dispersion coefficient (D_s) were fixed at the values obtained from the previous experiments and fitting results. The range used for kinetic mass transfer coefficient (α_5) in MCMFIT was 0.28 to 0.43 day^{-1}. The prediction by DPNSM was not as good (R^2 ranges to 0.88 to 0.92) as in the previous simulations (Figure 5.30).

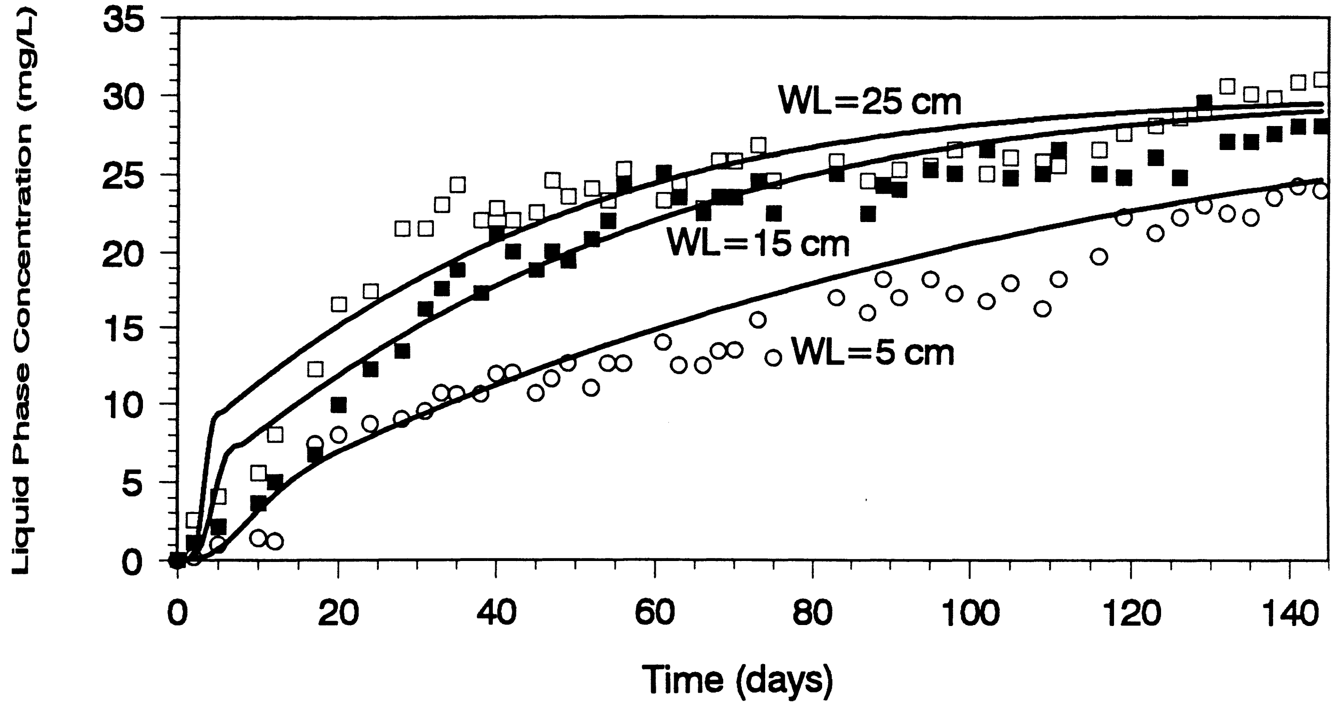


Figure 5.30 Phosphorus Concentration History Curves for Different Water Levels above Soil Column (C_0=30 mg/L; Water Level=5,15 and 25 cm; K=4.55×10^{-3} mg/g(L/mg)^N, N=1.11; D_s=0.58 cm^2/day; H=5 cm; pH=6-7; w=1.18 cm/day and α_5 =0.28 day^{-1} for 5 cm; w=1.91 cm/day and α_5=0.35 day^{-1} for 15 cm; w=2.89 cm/day and α_5 =0.43 day^{-1} for 25 cm)

5.5.1.5 Mechanisms of P removal in the Soil Column

As discussed in Chapter II, P removal in soil has been explained by several processes: sorption; precipitation involving transformation of applied soluble P to relatively insoluble calcium, aluminium, and iron phosphates; and biological immobilisation. In the present study, it has been observed that sorption is the governing P removal mechanism at pH < 8. Sorption alone, however, may not account for all the P removal over a long period of time, although DPNSM gave reasonably good predictions of the observed P breakthrough data.

From biotic and sterile column experiments, Aulenbach and Meisheng (1988) demonstrated that biological activity did not enhance total phosphorus removal. They found that physico-chemical reactions, not the biological activity, controlled the P removal process. Sorption may be responsible for initial P removal, but it is not the sole mechanism for continuous P removal. They also detected a large amount of $CaCO_3$, some $CaHPO_4$, a little $CaH_2P_2O_7$, and a small amount of $AlPO_4$ from their X-ray diffraction analysis in soil columns. The presence of the phosphate precipitates strongly supports the assumption that a slowly accumulated chemical precipitation process accomplishes the phosphorus removal. Some metal ions existing in the liquid phase, such as Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}, can precipitate phosphorus under favourable conditions (possibly at pH>7). Calcium is the most important ion, which results in $CaCO_3$ precipitation and fixation on the soil. This not only supplies the right alkaline pH condition to precipitate phosphorus, but also $CaCO_3$ itself can remove P (Effler and Driscoll, 1985). The intrinsic pH of the soil in the present study, however, is only 7.5 and the pH of the standard P solution ranged from 6 to 7. Therefore the effect of precipitation in P removal on the soil medium can be neglected although the sorption time was prolonged to up to 150 days.

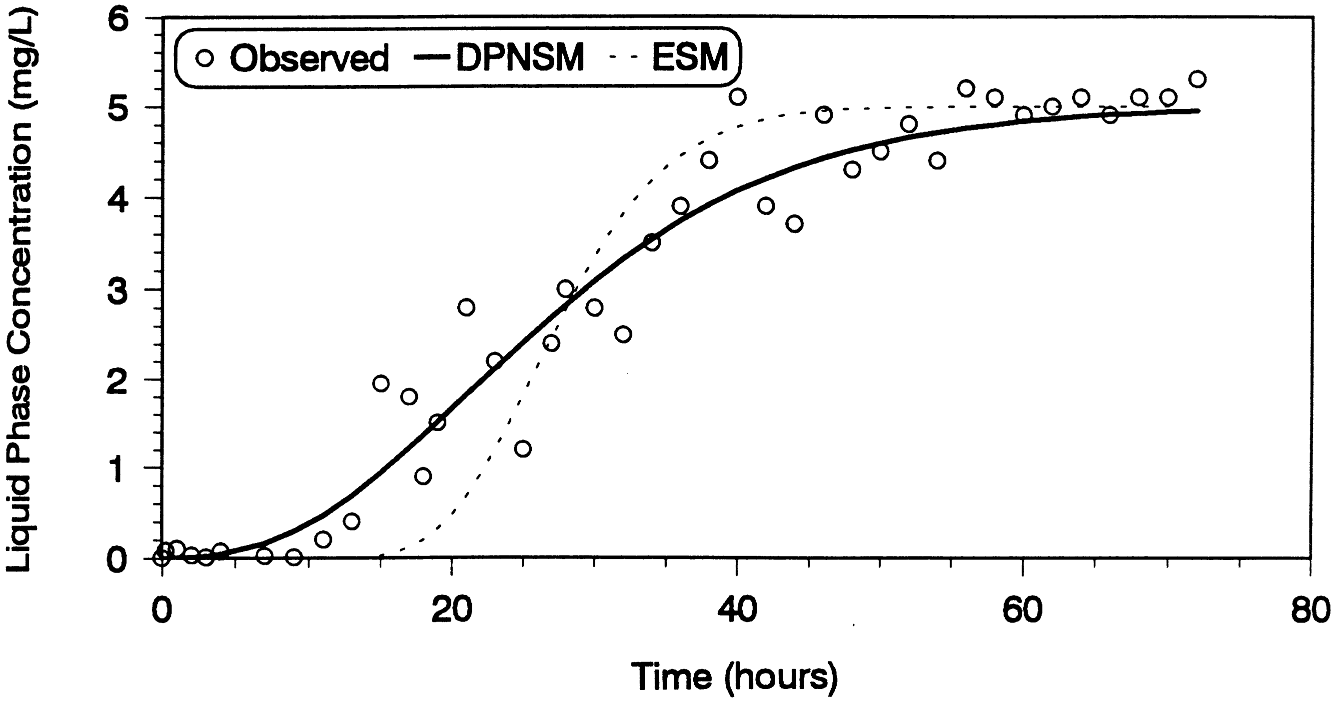
5.5.2 P Removal in the Dust Column

The results of P sorption experiments in the column packed with dust (the BHP steel industry waste product) are presented below. Also included is the verification of the mathematical models using the observed experimental data.

Column sorption experiments with different influent concentrations of P (5, 10, 20, 30, 40 and 50 mg/L) were performed in a column packed with 1 cm depth of dust. The pH was maintained at 6-7. Since the sorption capacity of dust was very high (15.5 mg/g for C_o=40 mg/L from the batch experiments) the entire cycle of sorption time taken to achieve breakthrough was long. The depth of the dust column was kept at 1 cm to shorten the breakthrough time and to reduce the possible effects of chemical precipitation. The possibility of P precipitation will increase as the contact time between P and dust particle increases. Experiments were conducted at a high pore water velocity (w=305 cm/day) with a view to reducing the breakthrough time (for the influent concentrations of 5, 10, 20 and 30 mg/L). Some experiments were conducted at low pore water velocities (w=37 and 43 cm/day respectively for the influent concentrations of 40 and 50 mg/L) to observe the concentration breakthrough pattern in detail. In the later experiments, the pore water velocity was kept low as it took only few hours to reach the breakthrough point for the influent concentrations of 40 and 50 mg/L at the high pore water velocity of 305 cm/day. The breakthrough curves were not very smooth and had minor crests and depressions. This is mainly due to the fluctuations of the pore water velocity with time which could not be controlled in the experiments. It was very difficult to maintain the velocities exactly equal in the dust columns. The pore water velocities reported are the average values for the entire run.

The breakthrough curves obtained with six different influent concentrations are shown in Figures 5.31A to 5.31F. Early breakthrough was observed with the increase of influent P concentration. The equilibrium liquid phase concentrations and the corresponding solid phase concentrations estimated experimentally are presented in Table 5.27. The experimental solid phase concentration was computed by extracting P from the dust in HNO_3 solution. This was done after the saturation of the dust medium was achieved. The amount initially dissolved in dust (1.30×10^{-4} mg/g) should be deducted from this value, which any case is negligible.

(A) C_o=5 mg/L



(B) C_o=10 mg/L

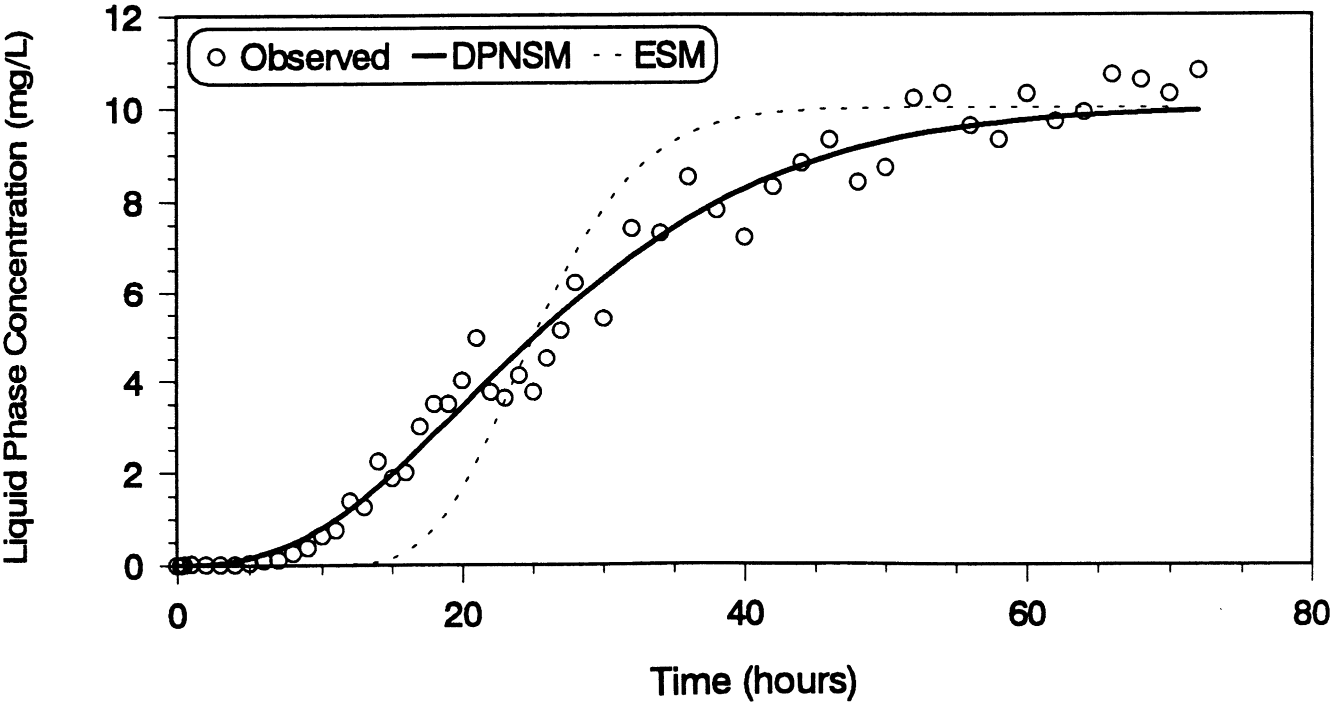
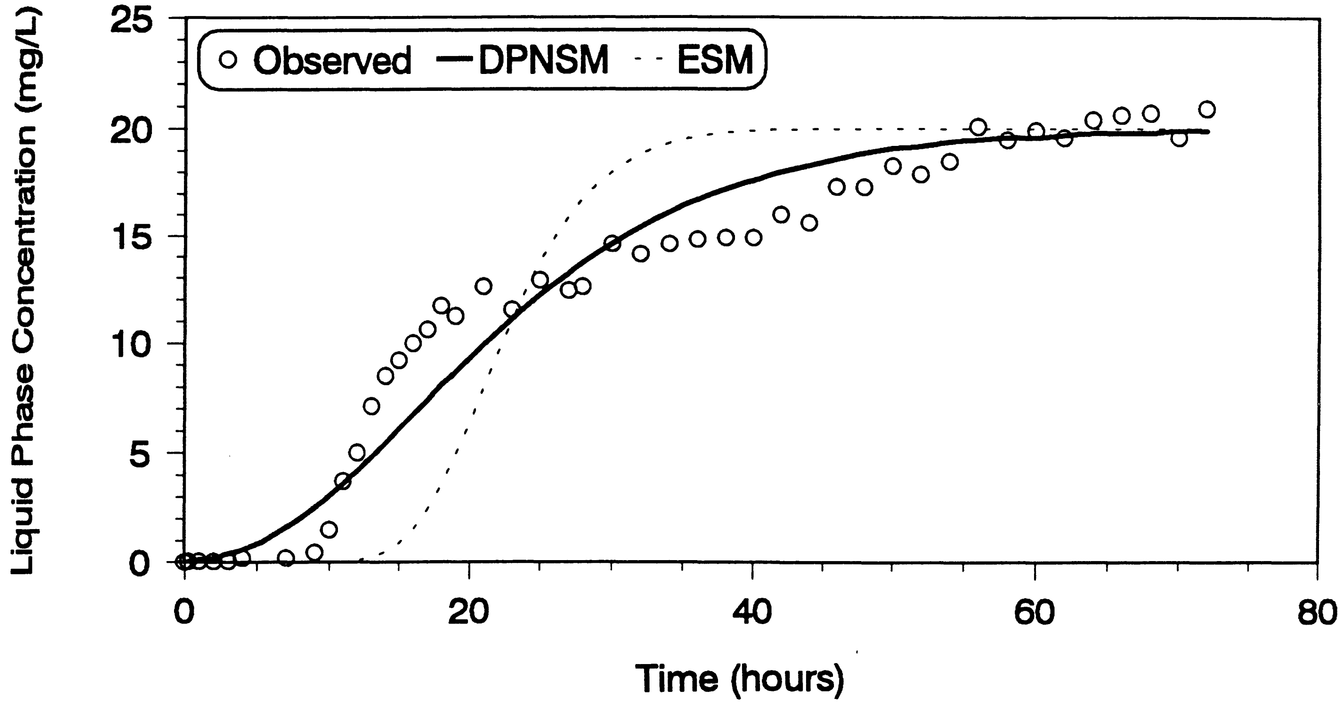


Figure 5.31 Phosphorus Concentration History Curves in Dust (w=305 cm/day, D_s=13.68 cm^2/day, K=2.61x10^{-1} mg/g$(L/mg)^N$, N=1.13, α_5=6.24 day^{-1} , H=1 cm, pH=6-7)

(C) C_o=20 mg/L



(D) C_o=30 mg/L

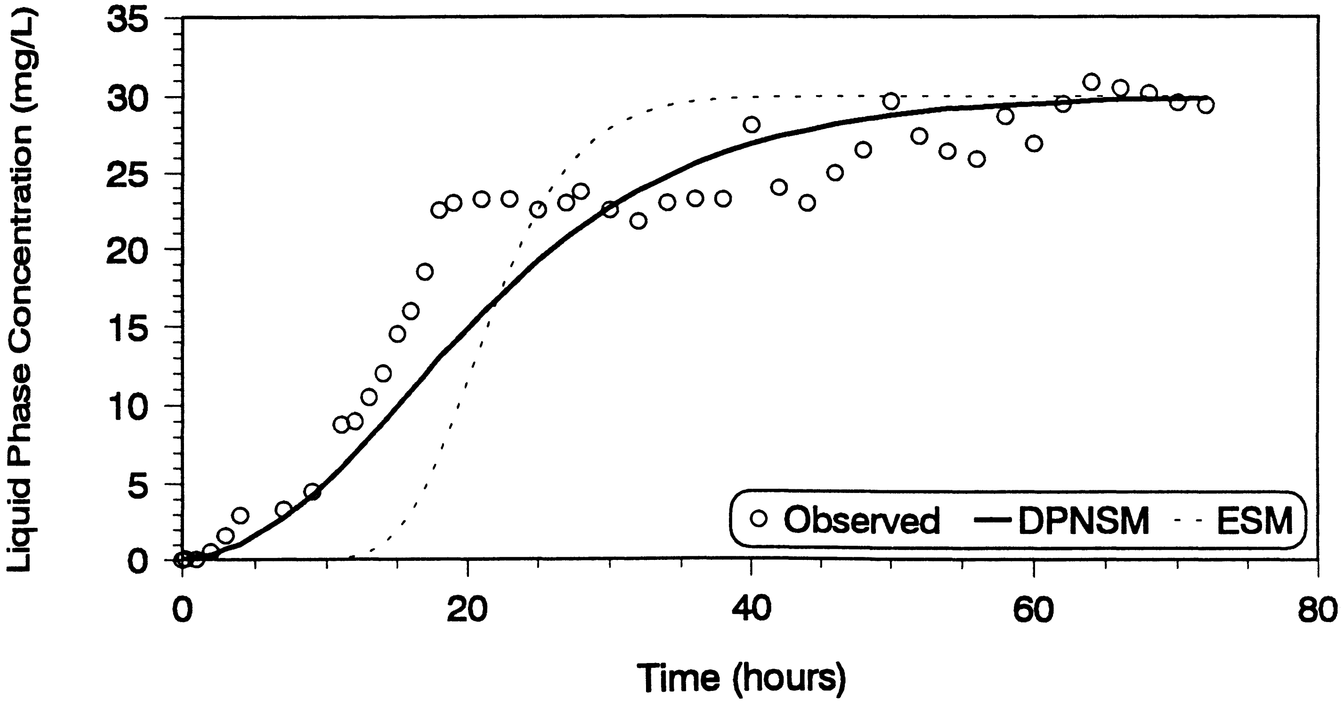
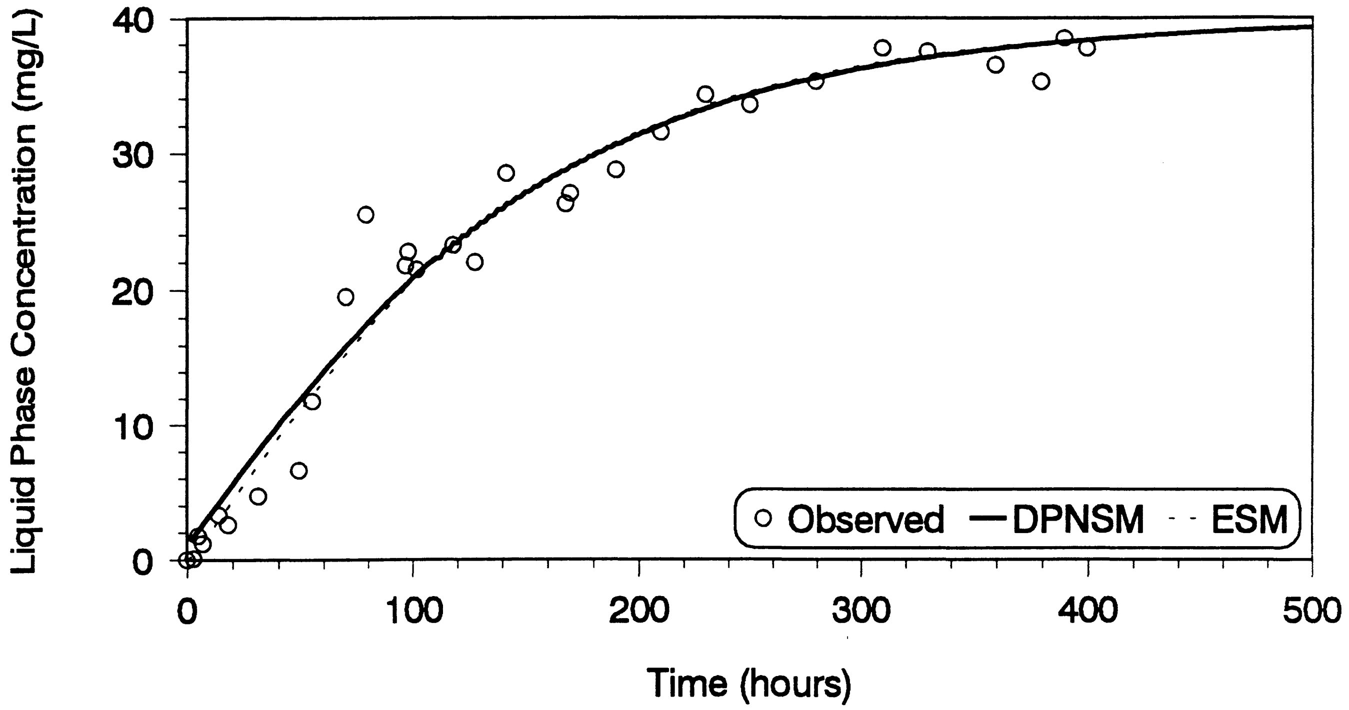


Figure 5.31(Cont'd) Phosphorus Concentration History Curves in Dust (w=305 cm/day, D_s=13.68 cm^2/day, K=2.61x10^{-1} mg/g$(L/mg)^N$, N=1.13, α_5=6.24 day^{-1}, H=1 cm, pH=6-7)

(E) C_o=40 mg/L



(F) C_o=50 mg/L

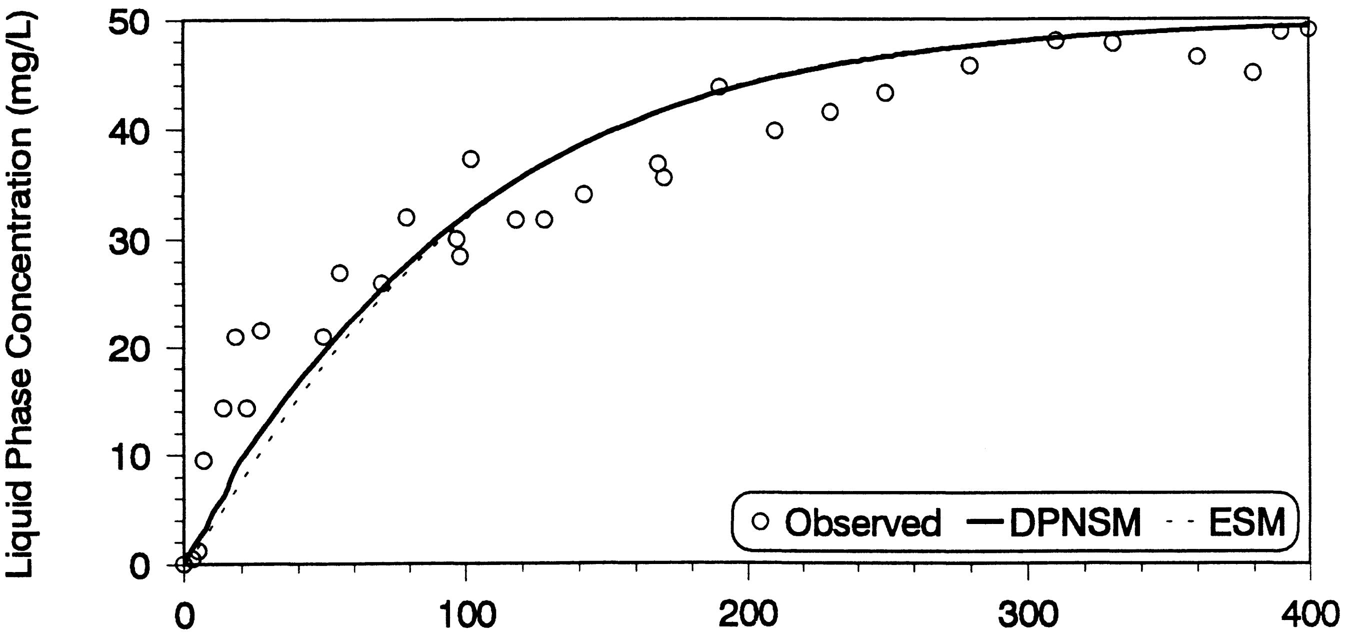


Figure 5.31(Cont'd) Phosphorus Concentration History Curves in Dust (w=37 cm/day for C_o=40 mg/L, w=43 cm/day for C_o=50 mg/L; D_s=13.68 cm^2/day, K=2.61x10^{-1} mg/g$(L/mg)^N$, N=1.13, α_5=6.24 day^{-1}, H=1 cm, pH=6-7)

Table 5.27 Amount of P Adsorbed in the Batch and Column Experiments for Dust

C_o (mg/L)		5	10	20	30	40	50
S_e (mg/g)	From Column Experiment (Dynamic System)	1.09	2.00	3.70	5.30	6.83	8.22
	From Batch Experiment (Mixing System)	11.71	13.12	14.70	15.71	16.47	17.09
	From Batch Experiment (Static System)	13.25	15.66	18.50	20.40	21.87	23.08

The estimate of the solid phase concentrations computed from dynamic column experiments are much lower than the ones calculated from batch experiment isotherm constants. They will be higher if the batch experiments were conducted under similar solid to liquid ratios as in the column experiments. In fact, the solid to liquid ratio in batch experiments has a significant effect on the estimation of isotherm constants. The isotherm constants increase with the decrease of solid to liquid ratio. The parameters K, N and a, b evaluated from the amounts of P adsorbed in dust columns are shown in Table 5.28. The sorption phenomena in this case was best described by the Freundlich isotherm rather than by the Langmuir isotherm.

Table 5.28 Freundlich and Langmuir Isotherm Constants for Dust

Freundlich Isotherm Constants		Langmuir Isotherm Constants	
K[mg/g(L/mg)^N] N	2.61×10^{-1} 1.13	a(mg/g) b(L/mg)	3.34×10 6.44×10^{-3}
R^2	0.99	R^2	0.88

The DPNSM predictions using dynamic Freundlich isotherms are shown in Figures 5.31A to 5.31F together with the experimental concentration profiles.

The dispersion coefficient (D_s) and kinetic mass transfer coefficient (α_5) used in the simulation were obtained by using MCMFIT. They are 13.68 cm²/day and 6.24 day^{-1} respectively. A simulation study with ESM was also made and the prediction was satisfactory only at high influent P concentrations (C_o=40 and 50 mg/L).

Table 5.29 shows the observed and predicted relative Darcy velocities for a P solution concentration corresponding to 50% of the influent concentration. The predicted relative Darcy velocities were found to be in good agreement with the actually observed values for P. This supports the validity of the model in predicting dust column experimental data.

Table 5.29 Observed and Predicted Relative Darcy Velocities in Dust

C_o (mg/L)	Observed Velocity from Experimental Data	Predicted Velocity from Dust Analysis	Retardation Factor (R_d)
5	1.46×10^{-3}	3.24×10^{-3}	309
10	1.86×10^{-3}	3.51×10^{-3}	285
20	2.45×10^{-3}	3.80×10^{-3}	263
30	2.64×10^{-3}	3.98×10^{-3}	251
40	3.38×10^{-3}	4.12×10^{-3}	243
50	3.98×10^{-3}	4.22×10^{-3}	234

For the influent concentrations of 5 to 50 mg/L, the P solute in dust was found to migrate 685 to 250 times slower than water. The mobility of P is highly restricted in the dust medium due to the high sorption capacity of P in dust.

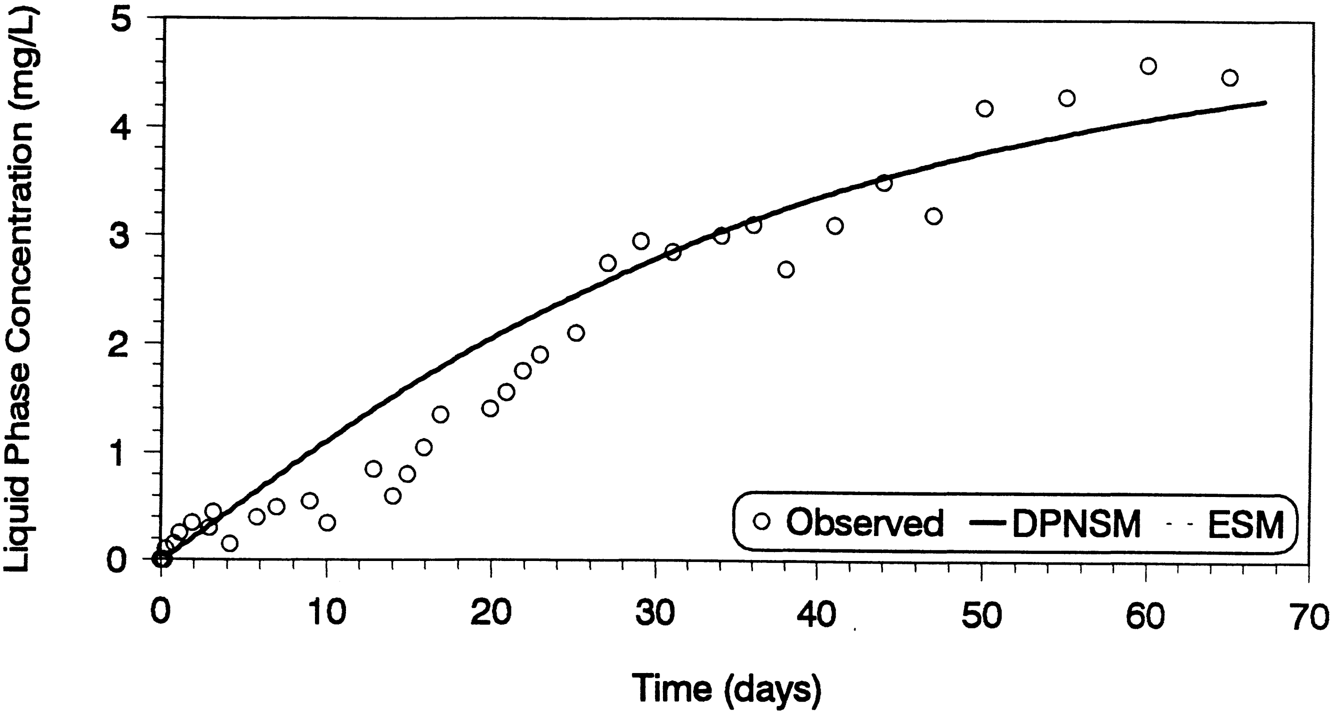
5.5.3 P Removal in the Cake Column

The P sorption in the cake column was investigated at various influent concentrations of P. The characteristics of cake are presented in Chapter IV (Tables 4.1, 4.2 and 4.3). The verification of the mathematical models are included in this section.

Column sorption experiments for various influent concentrations of P (5, 10, 20, 30, 40 and 50 mg/L) were performed with 3 cm deep cake columns with a view to calculating the isotherm constants under dynamic conditions. The pH varied from 6 to 7. Pore water velocities ranged from 10.2 to 60.0 cm/day. The breakthrough curves were not smooth and had minor crests and depressions because of velocity variations. It was difficult to maintain the pore water velocities exactly constant throughout the entire experiments.

The breakthrough curves obtained with six different influent concentrations are shown in Figures 5.32A to 5.32F. There was an earlier breakthrough at high influent concentrations. The equilibrium liquid phase concentrations and the corresponding solid phase concentrations estimated experimentally are presented in Table 5.30. The estimates of the solid phase concentrations corresponding to the liquid phase concentrations using batch experiment isotherm constants are substantially higher than those computed from dynamic column experiments. The amount of P initially dissolved in cake was deducted. This amount (3.50×10^{-4} mg/g) was negligible.

(A) C_o=5 mg/L



(B) C_o=10 mg/L

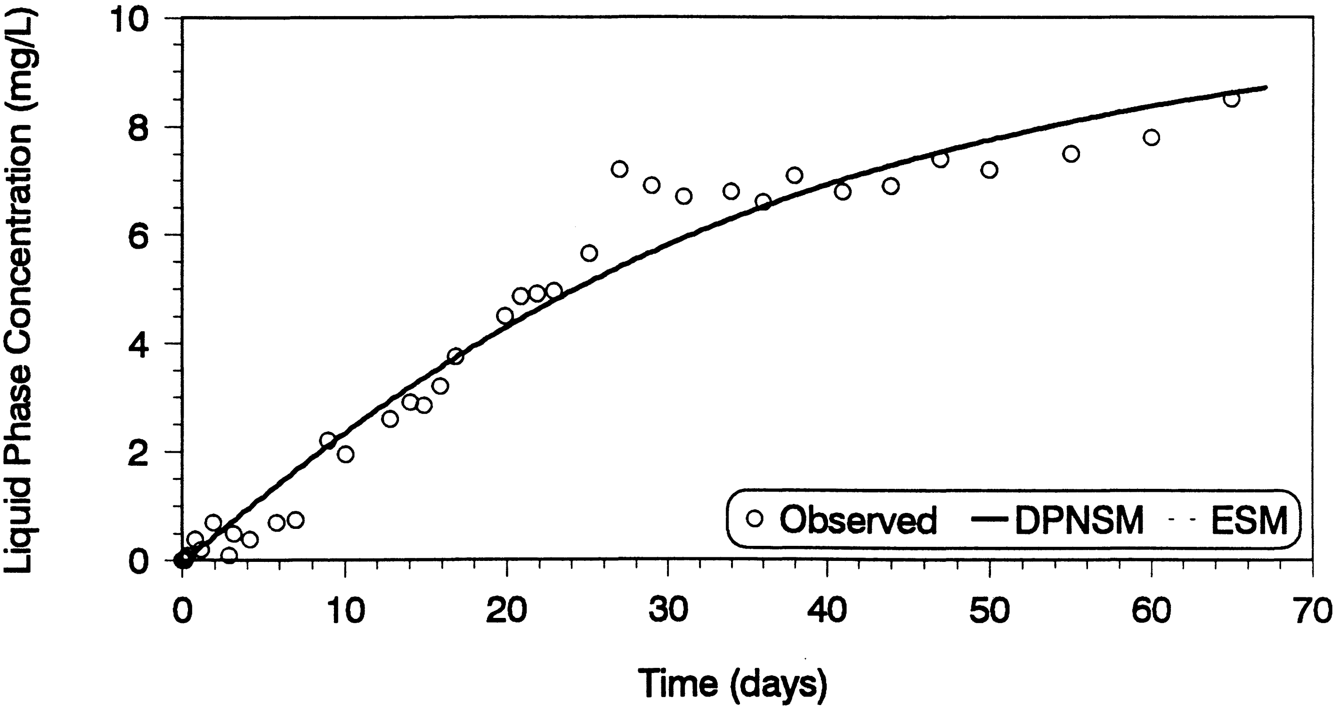
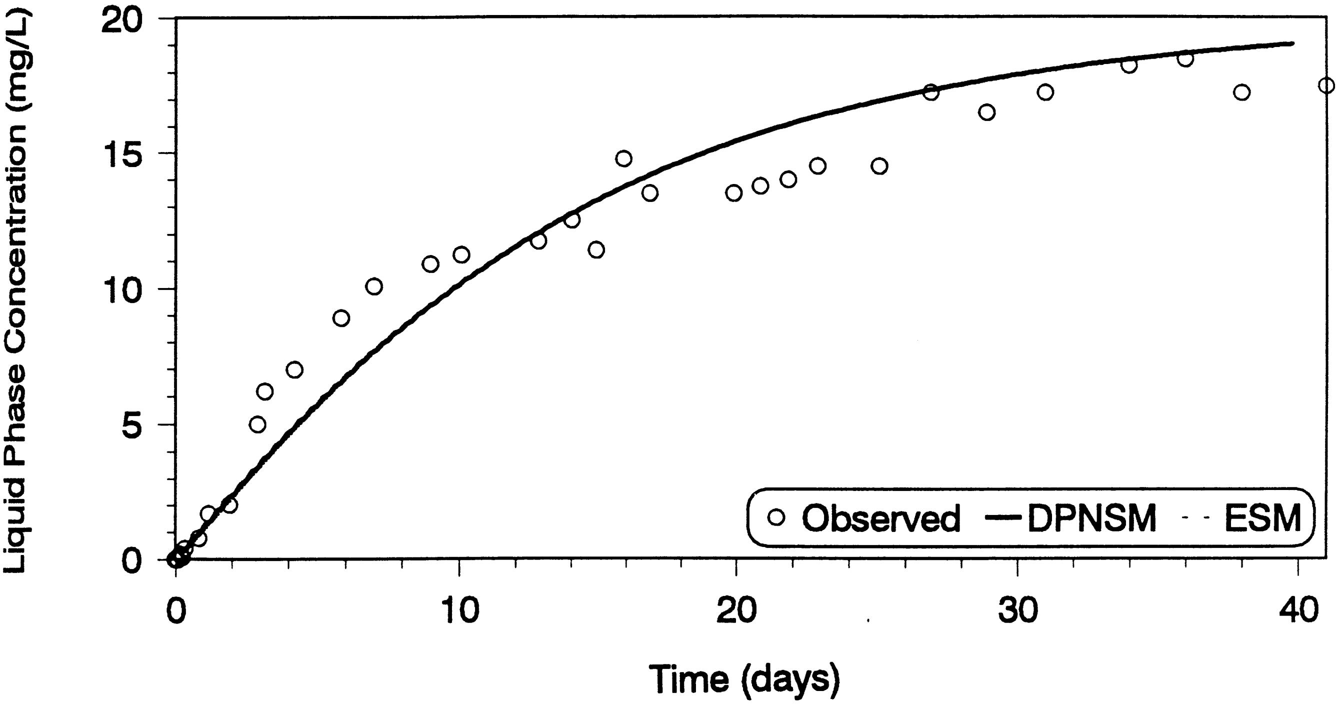


Figure 5.32 Phosphorus Concentration History Curves in Cake (w=10.2 cm/day, D_s=1.42 cm^2/day, K=8.17x10^{-2} mg/g(L/mg)^N, N=1.09, α_5=0.37 day^{-1}, H=3 cm, pH=6-7)

(C) C_o=20 mg/L



(D) C_o=30 mg/L

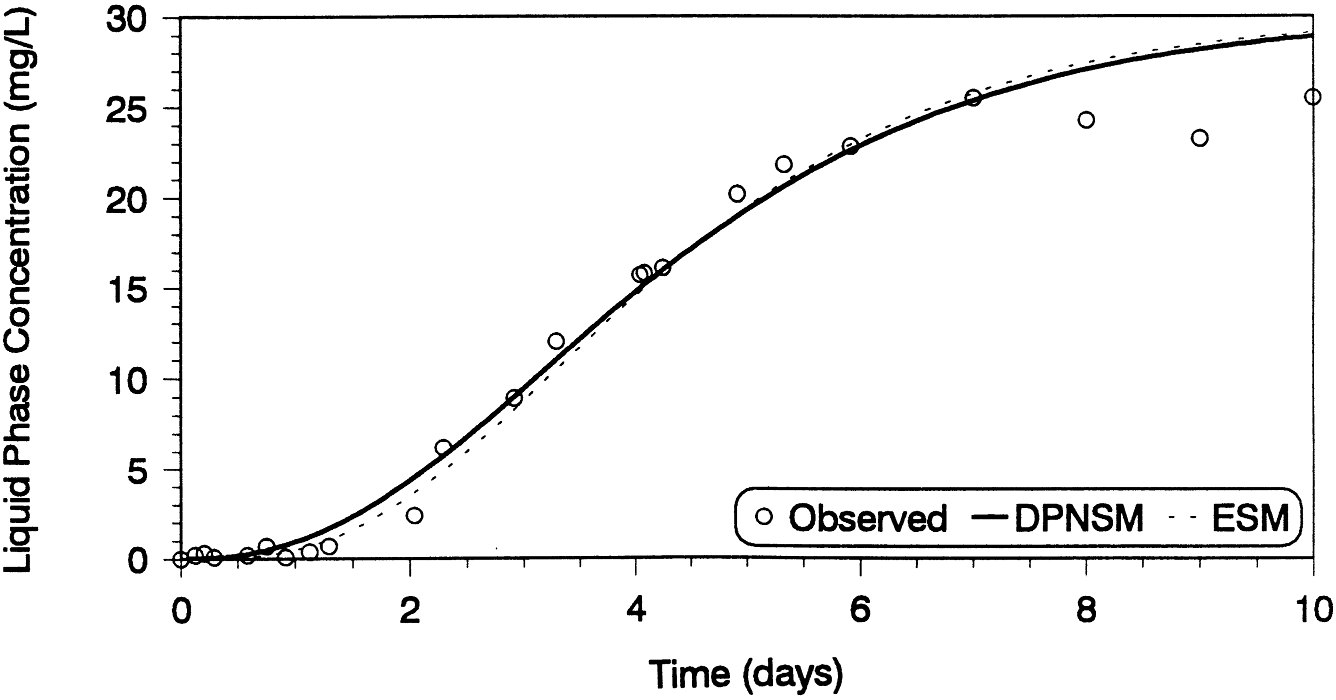
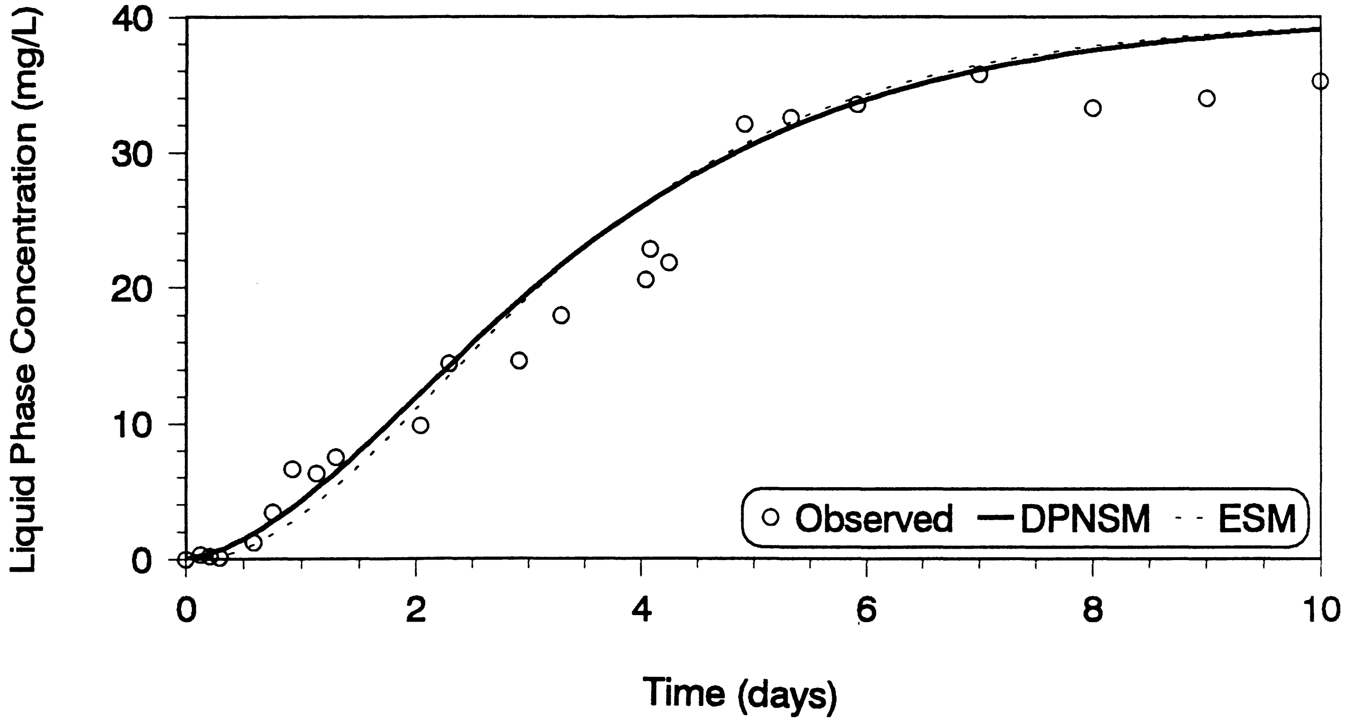


Figure 5.32(Cont'd) Phosphorus Concentration History Curves in Cake (w=15.6 cm/day for C_o=20 mg/L, w=46.0 cm/day for C_o=30 mg/L, D_s=1.42 cm^2/day, K=8.17x10^{-2} mg/g(L/mg)^N, N=1.09, α_5=0.37 day^{-1}, H=3 cm, pH=6-7)

(E) C_o=40 mg/L



(F) C_o=50 mg/L

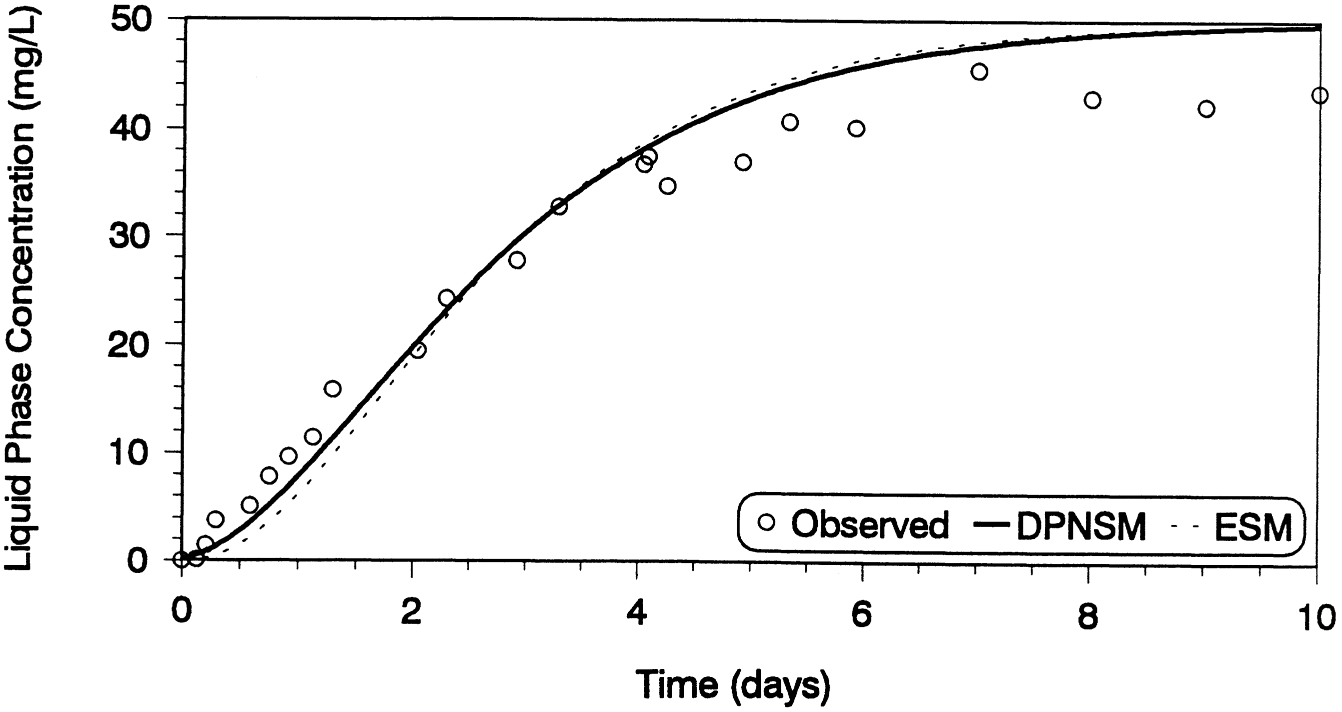


Figure 5.32(Cont'd) Phosphorus Concentration History Curves in Cake (w=54.0 cm/day for C_o=40 mg/L, w=60.0 cm/day for C_o=50 mg/L ; D_s=1.42 cm^2/day, K=8.17x10^{-2} mg/g(L/mg)^N, N=1.09, α_5=0.37 day^{-1}, H=3 cm, pH=6-7)

Table 5.30 Amount of P Adsorbed in the Batch and Column Experiments for Cake

C_o (mg/L)		5	10	20	30	40	50
S_e (mg/g)	From Column Experiment (Dynamic System)	0.36	0.68	1.28	1.85	2.41	2.96
	From Batch Experiment (Mixing System)	2.20	2.84	3.67	4.26	4.74	5.14
	From Batch Experiment (Static System)	2.15	2.80	3.66	4.27	4.77	5.19

The pore water velocity maintained was higher for higher influent P concentrations. The breakthrough time decreased as the pore water velocity and the influent P concentration increased. As the pore water velocity increases, the contact time between the P solute and the cake medium becomes less and less. The parameters K, N and a, b for Freundlich and Langmuir isotherms respectively were estimated from the solid phase concentrations of cake in the column after the saturation of cake was achieved. The isotherm constants are shown in Table 5.31. The sorption phenomenon is described better by the Freundlich isotherm than by the Langmuir isotherm. Although six points were available from the cake column experiments to calculate the isotherm constants, the variation in pore water velocities might affect the values of isotherm constants.

Table 5.31 Freundlich and Langmuir Isotherm Constants in the Batch and Column Experiment for Cake

Freundlich Isotherm Constants		Langmuir Isotherm Constants	
K[mg/g(L/mg)^N] N	8.17×10^{-2} 1.09	a(mg/g) b(L/mg)	1.56x10 4.58×10^{-3}
R^2	0.99	R^2	0.92

The DPNSM predictions using dynamic Freundlich isotherm constants are shown in the Figures 5.32A to 5.32F together with the corresponding experimental values. The dispersion coefficient (1.42 cm^2/day) and the kinetic mass transfer coefficient (0.37 day^{-1}) obtained by fitting the data was fixed in the simulation. The ESM prediction was almost the same as the DPNSM prediction especially at low influent concentrations. Table 5.32 shows the observed and predicted relative Darcy velocities of the P solution in cake corresponding to 50% of the influent concentration. The predicted relative Darcy velocities were in good agreement with the actually observed values. For the influent concentrations of 5 to 50 mg/L, the P solute in the cake medium migrated 190 to 92 times slower than water. The mobility of P is fairly restricted in the cake medium due to the fairly high sorption capacity of P in cake.

Table 5.32 Observed and Predicted Relative Darcy Velocities of P Solution in Cake

C_o (mg/L)	Observed Relative Darcy Velocity from Experiment	Predicted Relative Darcy Velocity from Cake Analysis	Retardation Factor (R_d)
5	5.25×10^{-3}	1.20×10^{-2}	83.3
10	6.68×10^{-3}	1.28×10^{-2}	78.1
20	8.74×10^{-3}	1.35×10^{-2}	74.1
30	9.32×10^{-3}	1.40×10^{-2}	71.4
40	9.26×10^{-3}	1.43×10^{-2}	69.9
50	1.09×10^{-2}	1.45×10^{-2}	69.0

5.5.4 pH changes in Column Experiments

The pH of the P solution in dynamic systems (ie. during column experiments) was observed to change with time. The pH change was monitored until the trend of change remained constant. The pH of the effluent P solution in soil columns decreased rapidly at the initial stage and remained nearly constant (pH=7.65-

7.80) after 24 hours. The pH of the effluent P solution in the dust and cake columns, on the other hand, rapidly increased at the initial stage and constantly decreased after 15 hours and 48 hours respectively. The trend of pH changes in the dynamic system was very similar to the trend in the static system. The constant (stable) pH value in the dynamic system (pH=9.3 in both dust and cake columns) was higher than the one observed in the static system (pH=7.9 both dust and cake solution). The adsorbents (soil, dust and cake media) are aggregated particles and under dynamic conditions, the solutes have more chance of getting into the structure of aggregated particles than under the static system (Tiwaree, 1989). This may be attributed to the high pH of the effluent P solution in the dynamic system. The intrinsic pH values of the soil, dust and cake (7.5, 11.8 and 9.0 respectively) also would have affected the pH of the effluent P solution. Figure 5.33 shows the pH changes with different adsorbents when a high influent concentration of P (C_o=40 and 50 mg/L) was used. The temporal variation of pH was not significant after the first day of the column experiment.

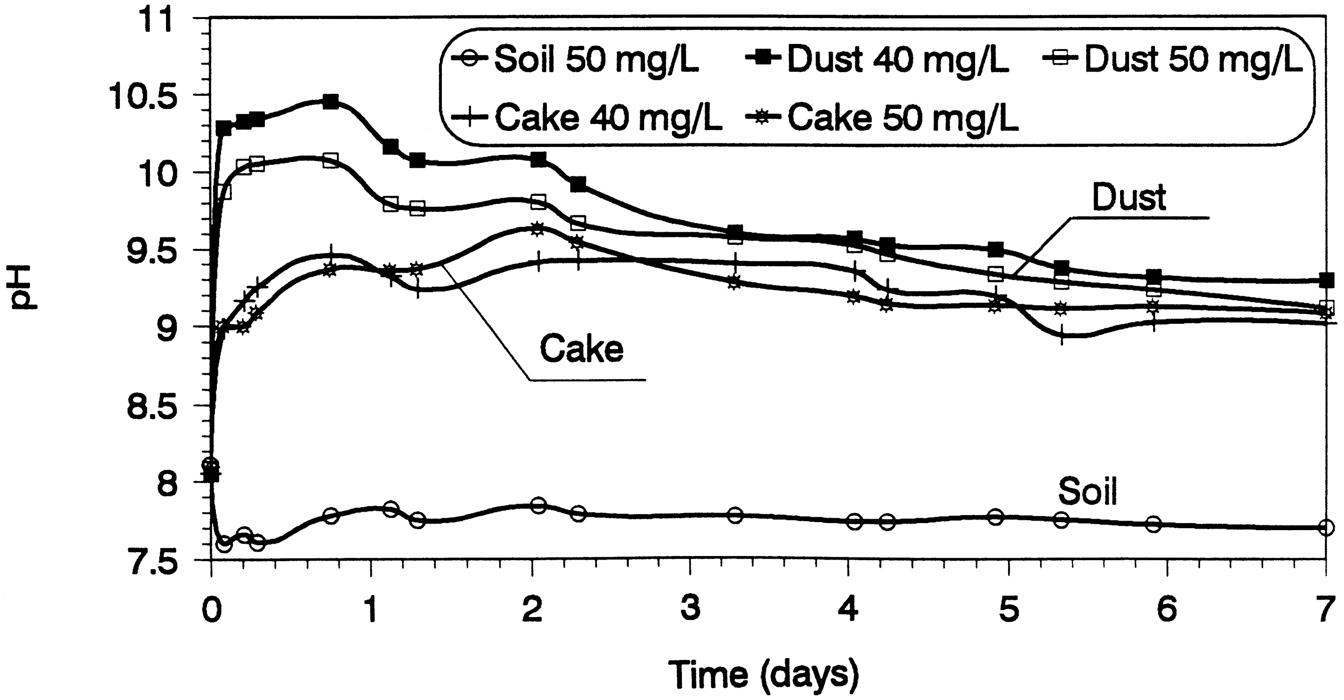


Figure 5.33 pH Changes in the Dynamic System for the Different Adsorbents (C_o=40 and 50 mg/L, H=5 cm, Initial pH=8.1)

The increase in the pH values at the initial stage of P removal (as shown in Figure 5.33) may be due to the large quantity of Mg^{2+} and Ca^{2+} ions liberated into the solution. Table 5.33 shows the concentration of Mg^{2+} and Ca^{2+} ions in the effluent P solution.

Table 5.33 Concentration of Mg and Ca ions from Effluent P Solutions

Total Elements (mg/L)	Effluent Solution from Dust Column	Effluent Solution from Cake Column
[1]Mg	8.3	13.0
Ca	2.1	7.2

[1]Total element concentrations were determined in an acidified solution by ICPAES (Method No. WSP.101, ICP.501)

The measurements of Mg^{2+} and Ca^{2+} ions were made using the effluent (collected after the breakthrough). The mechanism involved in this reaction can be explained as follows:

(i) superficial hydrolysis of MgO, according to the reaction,

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad \ldots (5.4)$$

(ii) partial solubilization of the formed hydroxide with OH^- and Mg^{2+} ions passing into the solution as a consequence,

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^- \qquad \ldots (5.5)$$

If this mechanism holds true in the present study, then the increase in pH values would be more sensitive at the liquid-solid interface than within the solution. This would favour displacing the equilibrium of the orthophosphate ions towards the PO_4^{3-} ion form and in consequence, it would favour the surface precipitation of $Ca_3(PO_4)_2$.

Figure 5.34A shows the pH changes of the P solution in the dolomite column experiments conducted by Roques et al.(1991). They used semi-burned dolomite as the medium. The amounts of NH_4^+, Ca^{2+} and Mg^{2+} in the effluent are shown in Figure 5.33B. There was a simultaneous increase in pH to a value larger than 10 which afterwards stabilised between 8 and 9. Release of Mg^{2+} ions and small uptake of Ca^{2+} ions were observed to occur during the period of intense fixation of P. They observed that even though the concentration of Mg^{2+} ions in the solution increased during the experiment, the concentration in NH_4^+ ions did not show any significant change. The amount of Mg^{2+} at the surface of the treated sample decreased, while that of Ca increased (Figure 5.34B). This matches the chemical analysis results of the present study. The simultaneous sorption of Ca^{2+} and P on the surface of the adsorbents confirms the formation of a calcium phosphate (Roques et al., 1991). The breakthrough pattern of P presented in Figure 5.34A follows a S-shape, suggesting that the mechanism for P removal was predominantly surface sorption. The fact that P removal in the dolomite was accompanied by a decrease in the concentration of Ca^{2+} ions and an increase in pH values suggested the possible precipitation of a calcium phosphate (Roques et al., 1991).

5.5.5 Effect of NH_4 on P Removal

Two column sorption experiments were conducted with dust and cake to study the effect of NH_4 as a foreign material on P removal. The influent concentrations of P were fixed at 10 and 20 mg/L for dust and cake respectively. The NH_4 concentration was maintained at 30 mg/L in both cases. The effect of NH_4 on P removal was observed by comparing the equilibrium concentration of P in the single solute and bisolute systems.

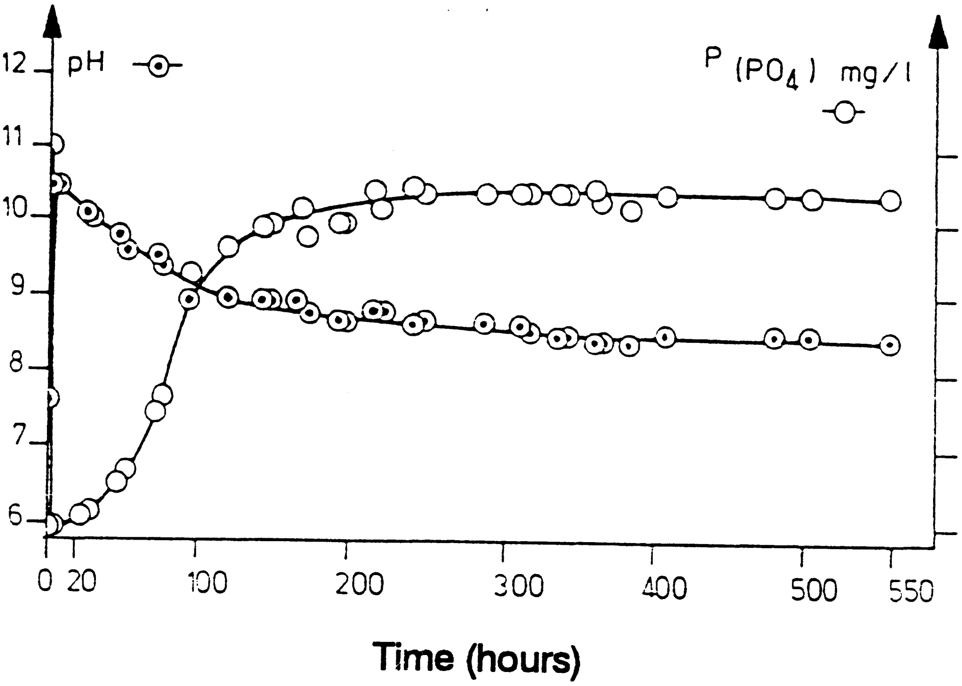


Figure 5.34A Observed Concentration History Curves and pH Change of P Solution in Dolomite Column Experiments (C_o=25 mg/L, pH=7.5-8.5) (Roques et al., 1991)

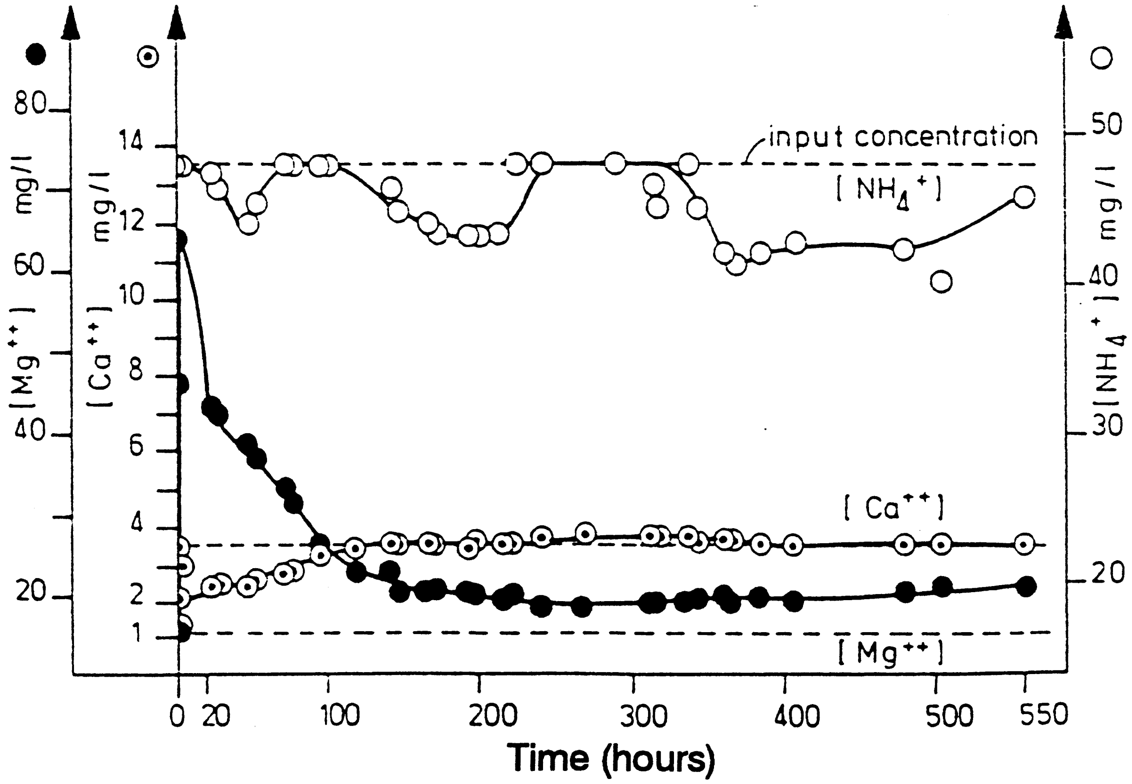


Figure 5.34B Changes of NH_4-N, Ca^{2+} and Mg^{2+} with Time in Dolomite Column Experiments (Dashed lines indicate influent concentration levels) (Roques et al., 1991)

The results obtained are presented in Figures 5.35A and 5.35B. The sorption capacity of P in dust and cake media decreased in the presence of NH_4 even though the reduced amount is not significant. Due to the competition for sorption sites, P removal decreased in both experiments. The breakthrough curves of P in the presence of NH_4 were also S-shaped, but with less spreading. Breakthrough time was shorter than the single solute system.

5.6 Field Application

Most of the chemical and advanced biological treatment technologies used for P removal in sewage treatment plants are expensive to install, difficult to operate efficiently, and produce considerable volumes of phosphorus-rich sludges requiring disposal. Most sewage treatment plants (including small community plants) in Australia are required to meet more stringent P discharge standards with limited funding. Hence, there is a need for low-cost treatment systems that are efficient, and that do not create problems of frequent sludge disposal. Because of these limitations of advanced tertiary treatment technologies, natural wetlands and ones rich in organic matter are becoming important for P removal.

Wetland treatment schemes have been successful in removing enteric bacteria, lowering biochemical oxygen demand, and decreasing nitrate concentrations in the effluent. However, they have been less effective in lowering phosphorus concentrations to acceptable levels (Finlayson, 1991; Mann and Bavor, 1993). This is due to the lack of substrata capable of adsorbing phosphorus and suppressing soil-retained P liberation from sediments to prevent it from passing into surface waters in soluble and bio-available forms. Sorption and precipitation reactions of phosphorus with iron-, aluminium- and calcium-containing materials appear to be principally responsible for phosphorus removal in wetlands (Yamada et al., 1986; Mann and Bavor, 1993; Choi and Chung, 1995).

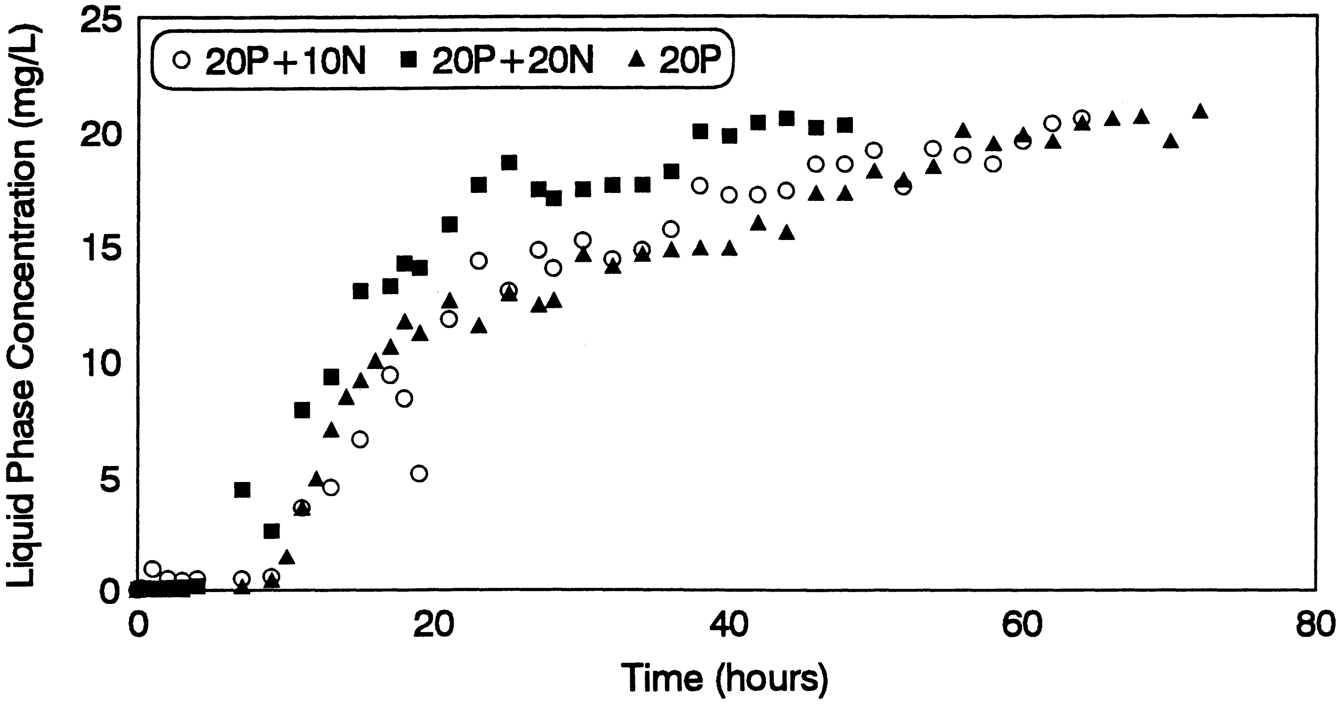


Figure 5.35A Observed Concentration History Curves of P in the Presence of NH_4 (Dust as the Adsorbent ; C_o=20 mg/L, w=305 cm/day, H=1 cm, pH=6-7)

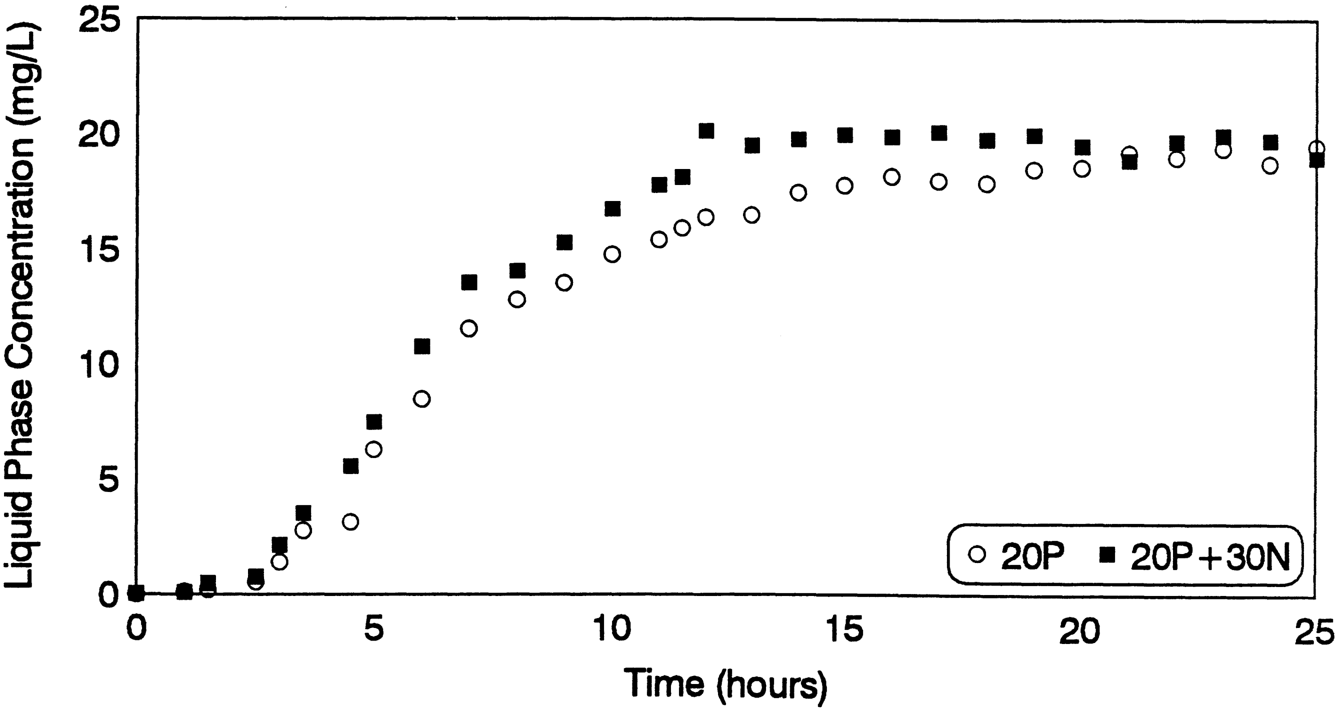


Figure 5.35B Observed Concentration History Curves of P in the Presence of NH_4 (Cake as the Adsorbent ; C_o=20 mg/L, w=890 cm/day, H=1 cm, pH=6-7)

If the substrata used in Constructed Wetland Systems (CWS) have a high sorption capacity of P solute, this treatment technology could be an attractive alternative to highly-technical sewage treatment. Based on batch equilibrium and column leaching studies, James et al. (1992) found that iron oxides and steel wool were suitable as amendment materials to enhance phosphorus removal in sewage treatment. Small amounts of preformed rust added to peat and sand greatly enhanced phosphorous sorption, and the added iron oxides were almost entirely responsible for phosphorus removal. Steel wool added to peat beds appears to be a suitable amendment material that will efficiently remove phosphorus from wastewater effluent.

Industrial waste substrata such as slag and fly ash have also been found to be suitable for use in CWS as they can adsorb P to a greater extent than the sand or gravel matrices. The fact that they contain high contents of iron, aluminium and calcium oxide implies their high sorption capacity for P. Calcium oxide assists in P complexation and precipitation of calcium hydroxy apatite at alkaline pH levels (Mann and Bavor, 1993). These researchers found out that phosphorus sorption to substrata surfaces depends on many factors such as aluminium and iron oxide concentration, particle size, porosity, redox conditions, pH and ionic strength, anaerobic and aerobic conditions, hydrologic conditions and organic matter content. Of these, the aluminium oxide was shown to play the greatest role in increasing the P sorption capacity (Sanyal and De Datta, 1991).

5.6.1 Upgrading of Sewage Treatment Plants (STPs) with CWS Using Dust

Dust can be applied as an adsorbent in STPs as well as forming the substratum in CWS because of its high sorption capacity for P (as observed in this study). This section highlights a sample application of a dust for removing P in STPs and CWS. In this application, dust is used both in a CWS and in a secondary treatment step to remove P, and soil is used in a CWS to further polish the P effluent. Figure 5.36 provides a schematic diagram of the treatment system proposed. This design is suitable for a small community wastewater treatment system (eg. 5,000 population equivalents). The free water surface system is selected for ease of maintenance. Elements of the wetlands can be isolated for harvesting or dredging if required.

5.6.1.1 Sewage Treatment Plant (STP)

In the STP, dust is used as a dosing agent in secondary treatment. Assuming a per capita wastewater production per day of 240 L and a design population of 5,000 PE, then the hydraulic loading capacity (Q) will work out to be 1.2 ML/day. Assuming the secondary influent from the STP contains 10 mg/L of P, and the removal target is 1 mg/L of P (ie. 10.8 kg of P/1.2 ML). The sorption capacity of dust based on the batch experiment in mixing system is 12.5 mg/g (for the initial concentration of 10 mg/L). In other words, about 784 kg of dust is necessary on a daily basis to adsorb this 10.8 kg of P.

At present, Spent Pickle Liquor (SPL), alum or lime is used as a dosing agent. The use of dust instead needs further study. The dust can be easily settled in the sludge lagoon (particle density=2.78 g/cm^3). Because of the presence of lead (Pb) in the dust (450 mg/kg), one should make sure that lead does not leach out with the effluent. The analysis of heavy metals conducted from the dust column effluents indicated that very little or no heavy metals is leached out (Table 5.35).

5.6.1.2 Constructed Wetland System (CWS)

The effluent after sorption with dust which contains 1 mg/L of P is directed to a CWS. Here the CWS design considered is a surface flow wetland type. The wetland made of the dust substratum (Cells 1 and 2 in Figure 5.36) is used for P removal and that with the soil substratum (Cell 3 in Figure 5.36) for polishing the secondary effluent wastewater.

Assume that the removal efficiency of P by the dust substratum (in Cell 1 or 2) in the CWS is 30% (ie. P concentration will be reduced from 1.0 mg/L to 0.7 mg/L). Assume also that plant and associated bio-film have an additional removal efficiency of 80% in Cell 3; then the P will further be reduced from 0.7 mg/L to 0.14 mg/L. The macrophytes usually planted in the CWS are *phragmites* and *scirpus sp.* and the density of planting is 8 plants/m^2. Assuming a further 20% removal by the flow through Cell 3, the effluent P concentration will be reduced to 0.112 mg/L.

The effluent P concentration can be calculated from the following equation which takes into account only the P uptake (Brix, 1987). The P uptake constant for this type of CWS is of the order of 13 m^3/(m^2.year).

$$\ln [\, C_{out}/\, C_{in}] = -k/\mathrm{HLR} \qquad \text{... (5.6)}$$

where, C_{in} = Concentration in the wetland inlet.

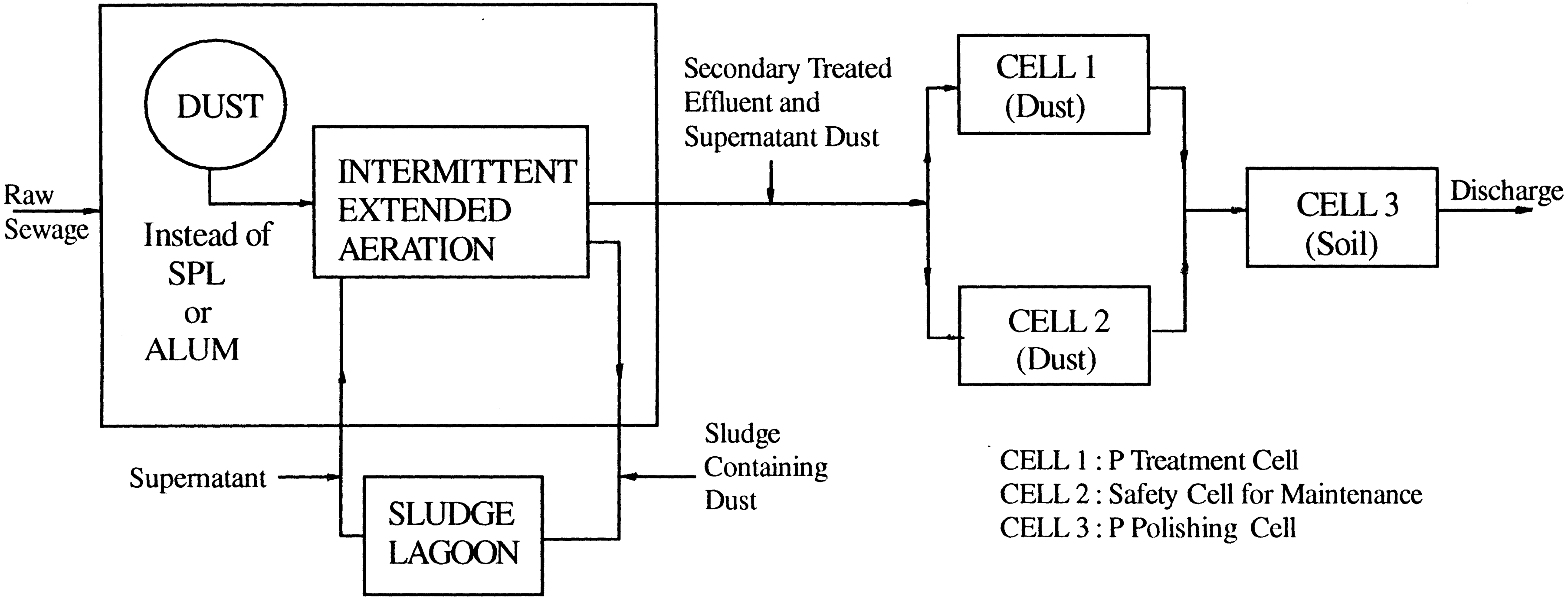
C_{out} = Concentration in the wetland outlet.

HLR = Hydraulic Loading Rate [m^3/(m^2.year)]

k = P uptake constant [m^3/(m^2.year)]

If the inlet P concentration of 1.0 mg/L at the CWS were to be reduced to 0.112 mg/L with a densely vegetated marsh, the design HLR would be:

$$\mathrm{HLR} = \frac{-13}{\ln(0.112/1.00)} = 5.94\ \mathrm{m}^3/(\mathrm{m}^2.\mathrm{year}) \qquad \text{... (5.7)}$$



CELL 1 : P Treatment Cell
CELL 2 : Safety Cell for Maintenance
CELL 3 : P Polishing Cell

Figure 5.36 Schematic Diagram of Extended STP with CWS for Wastewater Treatment (Not to Scale)

Modifications to Eqn. 5.7 are required if there are significant changes in flow through the wetland due to rainfall, evaporation, or seepage (Brix, 1987). Assuming that the average depth of the CWS to be 500 mm and that there is no short-circuiting in the flow, then the detention time will be 30.7 days [500 mm/(5940 mm / 365 days)]. To treat the wastewater quantity of 1.2 ML/day, the surface area necessary will be 6,145 m^2 [365,000 (m^3/year) /5.94 (m/year)]. That is, a well designed CWS would reduce the effluent P concentration from 1.00 mg/L to 0.112 mg/L over an area of 6,145 m^2. In winter time the P removal efficiency could be enhanced by increasing the detention time or by decreasing the flow rate.

Additional factors to be considered in the design of the extended-STP with CWS are the slope of pond, facilities to control mosquitoes in ponds, and frequency of vegetation removal (1-5 years). The economic feasibility of the application of this system might be the most crucial factor. The cost of construction of the CWS will vary according to the type, area, place of wetland and number of plants and detention time of the wastewater (Illungkoo, 1994).

5.6.2 Suppression of P Liberation from Sediments Using Dust and Cake

The accumulated P in shallow and coastal sediments plays an important role in the eutrophication of closed water bodies. The supply of P from the sediments is one of the main sources, and has an influence in the change of P concentration. The suppression of P liberation from sediments has been recognised as one of the most important measures to control the eutrophication caused by excessive P discharges into the waterways (Yamada et al., 1987).

Sediments act as a sink of P under certain circumstances, causing the accumulation of various materials. On the other hand, some conditions stimulate the release of P and produce negative effects on P removal from the water. This phenomenon, often called "internal loading", keeps the water quality unfavourable. In other words, even if there are efforts to eliminate the external source of P, there will still be a considerable amount of P released from the sediments. Raised temperature, increased pH, decrease in dissolved oxygen, along with other environmental factors are found to provide favourable conditions for P release (Davis et al., 1975). P release may take place through a diffusion and desorption process, physical turbulence, and metabolism of the microorganisms in the sediment (Forsberg, 1989). The release or internal loading of P, however, cannot be explained fully by any of the release mechanisms proposed. Many factors related to the release of P have not been fully elucidated or quantified yet. In fact, there are a number of known and unknown processes involved and often they are interrelated (Choi and Chung, 1995). According to Lee et al. (1976), Lijkleme (1976) and Banoub (1976), orthophosphate precipitate on sediment has been found in dissolved form under anaerobic conditions. Hosomi et al. (1982) divided phosphorus type (state) in lake sediments into five forms, viz., inorganic phosphorus adsorbed on clay particles; inorganic phosphorus precipitated with aluminium (Al-P), iron (Fe-P), and calcium (Ca-P); and organic phosphorus. In order to suppress the liberation of phosphorus from sediments, many kinds of substances which adsorb P have been investigated by several researchers. It was found that slag removes phosphorus from natural sea water by adsorbing P on its surface.

Kinetic results on the desorption of phosphorus from sediments showed an initial fast release, observed within 10 minutes, followed by a slower desorption. The rate and extent of release increased as the pH increased (Fox and Malati, 1985). In the case of sediments, beside sorption at the edges of the clay particles, phosphorus ions may be held in an amorphous iron and/or aluminium hydrated oxide gel on the lateral faces of the particles (Forsberg, 1989).

The suppression of phosphorus liberation can be performed by covering the sediment surface with suppressing materials or by mixing them with the sediment (Yamada et al., 1987). From Yamada et al.'s study (1987), suppression efficiency depended on the amount of slag used. The concentration of sulphide ions in the sea water was observed to decrease in the presence of slag. Sulphide ion generated under the strongly anaerobic conditions reacted with some metals (Fe, Mn) on the surface of the slag to produce metal sulphides. As the reaction of sulfide ions with precipitated phosphate was inhibited, the liberation of phosphorus was suppressed. As for the suppression mechanisms of phosphorus liberation by covering materials, the chemical effect of hydrogen sulfide generated in the anaerobic state and the sorption of P were considered (Yamada et al., 1987; Choi and Chung, 1995). Since dust and cake have most of these properties, they can be used as a suppressing material for P liberation from sediments. The suppression of phosphorus liberation by them will mainly occur due to covering and sorption effects.

5.6.3 Toxicity of the Dust and Cake

Yamada et al. (1987) studied the influence of slag on the mortality of organisms such as zooplankton and juvenile fish, on the growth rates of fish and on the biomass and fauna of benthic organisms. The materials used in their research were soft and hard granulated slag, sand and glass beads. Slag used in their study was manufactured and supplied by Nippon Kokan Co. Ltd. at Fukuyama, Japan. The concentration of several heavy metals - cadmium, lead, copper, zinc and chromium - in the four kinds of slag used are shown in Table 5.34. The concentration of cadmium was low and almost the same as that in the earth's crust. The concentrations of lead, copper, zinc and chromium were even lower than that in the earth's crust (Yamagata, 1977). The concentrations of cadmium, lead, copper and zinc in the sediments of coastal areas like Tokyo Bay, Japan were 1.2 - 3.0, 27 - 67, 18 - 87 and 130 - 440 ppm respectively (Yamada et al., 1987).

Table 5.34 Concentrations of Several Heavy Metals in Slag (Yamada et al., 1987 ;*Yamagata, 1977)

	Cd (ppm)	Pb (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
Slag-1	<0.05	0.3	1.0	6.5	29.0
Slag-2	<0.05	0.4	0.9	1.7	35.0
Slag-3	<0.05	0.9	0.6	1.9	21.0
Slag-4	<0.05	0.3	0.8	2.2	17.0
Earth's crust*	0.02	12.5	55.0	70.0	100.0

Table 5.35 shows the concentrations of different elements in the effluents from the soil, dust and cake columns. The concentrations of heavy metals - zinc, chromium, cadmium, lead, copper and so on - were much lower than the amounts found in the earth's crust (Yamagata, 1977) and the amount of heavy metals in slag estimated by Yamada et al. (1987). The effluent concentrations of heavy metals in dust and cake columns were lower than those found in the materials in the environment. Thus it can be considered that the effluent concentrations of heavy metals in dust and cake columns were too low to do harm to any living organisms, and they will not damage aquatic ecosystems.

The results reported here, however, are the effluent concentrations of heavy metals based on the vertical flow of wastewater through soil or slag media. A detailed study is warranted in other cases. For example, when dust and/or cake are used to cover sediments to suppress phosphorus liberation, the effluent concentrations of heavy metals released by them may be different from the values obtained with vertical flows and thus should be studied further. The influence of slag on the mortality of marine organisms such as rotifers and juveniles of *fascias*, and the influence of slag on the growth rate of juveniles of *oplegnathus fascias* showed that slag had no effect on these organisms (Yamada et al., 1987). In the case of covering the surface of sediment by dust or cake, however, the benthic organisms may or may not be affected. Hence, the influence of dust and cake as covering materials on biomass and fauna of bottom dwelling organisms should be studied further through pilot-scale experiments.

Table 5.35 Concentration of Total Elements from Effluent P Solutions in the Column Experiment

Total Elements (mg/L)	Effluent Solutions from Soil Column	Effluent Solutions from Dust Column	Effluent Solutions from Cake Column
[1]S	3.0	2.9	3.7
P	47.0	27.0	7.2
Mg	6.8	8.3	13.0
Ca	10.4	2.1	7.2
K	7.0	2.1	2.2
Na	87.0	73.0	38.0
Al	<0.1	<0.1	<0.1
Fe	<0.02	0.02	<0.02
B	<0.02	<0.02	<0.02
[2]Se	<0.07	<0.07	<0.07
Mo	<0.03	<0.03	<0.03
As	<0.04	<0.04	<0.04
Hg	<0.02	<0.02	<0.02
Zn	<0.01	0.03	<0.01
Cr	<0.01	<0.01	<0.01
Cd	<0.01	<0.01	<0.01
Ni	<0.03	<0.03	<0.03
Pb	<0.07	<0.07	<0.07
Cu	<0.02	<0.02	<0.02
Mn	<0.01	<0.01	<0.01

-[1]Total element concentrations determined in an acidified solution by ICPAES (Method No. WSP.101, ICP.501)

-[2]Total elements determined by acid digestion and ICPAES (Method No. EMD.101, ICP.201)

VI CONCLUSIONS

A. From the batch (static) experimental results, the following conclusions can be made:

1. P sorption in soil and slag media is a slow process. More than 90% of the P was adsorbed within 70, 12 and 60 hours in the mixing system, and 240, 24 and 120 hours in the static system for soil, dust and cake respectively, depending on the initial P concentrations. Dust adsorbed P the most, compared to the other adsorbents (220-225 times and 4-5 times of that of soil and cake respectively). Kinetic studies revealed that the amount of P adsorbed on the adsorbents increased rapidly at the initial stage and the percentage of P adsorbed decreased gradually. The changes became smaller with the increase of initial P concentration.

2. The Langmuir isotherm gave a better correlation to experimental results than the Freundlich isotherm. The Freundlich isotherm constant K in the static system was similar to the one in the mixing system, while the reciprocal exponent (N) was less. The agitation of the P solution had a significant effect on the kinetics of P. The amounts of P adsorbed in the static system were less than those in the mixing system.

3. The kinetics of P sorption are satisfactorily explained by a static physical non-equilibrium sorption model (SPNSM). The equations developed were based on the concept that the P solute is transferred by the process of film diffusion into the immobile water layer surrounding the adsorbent. The film transfer constant (α) decreased with an increase in the initial P concentration. The distribution of the film transfer constant for the mixing system was more scattered than that in the static system.

4. The pH of the P solution played a critical role in the rate of removal and the removal mechanisms of P. P removal was at a minimum at pH 2 for the soil and dust adsorbents. During the experiments, the pH of the P solution in the soil adsorbent for the static system constantly increased with time while those of the P solutions in the dust and cake adsorbents decreased. The final pH of the P solution in the soil adsorbent increased for the experiments with an initial pH < 7. For experiments with an initial pH greater than 7, the final pH decreased during the experiments. On the other hand, the final pH of the P solution in the dust adsorbent increased during the experiments for initial pH levels from 2 to 9, and decreased for initial levels beyond pH 9. In the dust adsorbent, the final pH remained constant at 9.5 for initial pH levels in the range of 4 to 10. The high intrinsic pH and high sorption capacity of P in the dust increased the final pH. The pH variation was dependent not only on the type of adsorbents but also on the initial P concentrations.

5. Batch precipitation experiments indicated that the precipitation mechanism was significant for pH levels greater than 8. P reduction by this means increased with an increase of pH. The dominant removal mechanism of P at pH levels less than 8 was sorption and at pH levels greater than 10 it was precipitation.

6. Batch flocculation experiments revealed that P removal depended on adsorbent dose, flocculation (contact) time and mixing rate. With the increase in the adsorbent dose and flocculation time, the removal efficiency of P also increased. This effect was more significant at high initial P concentrations. P complexation with Al, Ca, Fe and other chemicals was observed with the increase of time starting from high adsorbent doses. P removal by dust may be enhanced by flocculation (perikinetic and orthokinetic) and precipitation followed by sorption.

7. The sorptivity of P on dust particles was suppressed by the presence of NH_4. This is due to the competition for the available sites. The percentage reduction of P sorption ranged from 33 to 57%.

B. From the soil column (dynamic) experiments, the following conclusions can be made:

8. The solid phase concentrations using batch experimental isotherms in the static system are similar to those computed from the dynamic column experiments. The sorption phenomena in the dynamic system were described better by the Freundlich isotherm. The equilibrium stage was reached faster as the influent P concentration increased. All the columns exhibited characteristic nearly S-shaped breakthrough curves. The simulated results using a dynamic physical non-equilibrium sorption model (DPNSM) and Freundlich isotherm constants K and N (calculated from the column experiments) have satisfactorily fitted the corresponding experimental breakthrough curves.

9. A program to fit a generalised non-linear advection-dispersion model, MCMFIT, was used to estimate the optimum model parameter values. It was used in conjunction with a dynamic physical non-equilibrium sorption model (DPNSM) or an equilibrium sorption model (ESM). P sorption in the dynamic system was explained better by the physical non-equilibrium process than by the equilibrium process. The ESM could not predict satisfactorily the breakthrough pattern of P for high influent P concentrations (>30 and 40 mg/L). P solute movement was fast through the column at high influent P concentrations. At the influent concentrations of 10 to 40 mg/L, P migrates 25 to 16 times slower than water. The mobility of P is restricted by the soil medium.

10. The kinetic mass transfer coefficient (α_5) appearing in the model was found to decrease with the increase in the pore water velocity. The immobile film layer surrounding the soil particle becomes thinner with the increase in P diffusion. This leads to an early breakthrough. The DPNSM gave rise to satisfactory predictions, with the variation of pore water velocities, soil depths and water levels being described well. The curves are nearly S-shaped or curvilinear, with more spreading and longer breakthrough times with a decrease of pore water velocity or an increase of soil depth.

C. From the dust and cake column (dynamic) experiments, the following conclusions can be made:

11. Both dust and cake columns had a higher sorption capacity than the soil column. As noticed in the soil column, there was an early breakthrough with the increase of influent P concentration in the dust and cake columns. Unlike the case of soil, the solid phase concentrations using batch experiment isotherm constants are substantially higher than those computed from dynamic column experiments. The sorption phenomena were described better by the Freundlich isotherm.

12. The P removal process in the dust column was explained better by the physical non-equilibrium process than the equilibrium one. The DPNSM predicted the observed breakthrough data while the ESM prediction was satisfactorily only at high influent P concentrations (C_o=40 and 50 mg/L). The P solute in the dust medium migrates 250 to 685 times slower than water. The mobility of P is highly restricted in the dust medium due to its high sorption capacity of P.

13. The ESM prediction of the P concentration history in the cake column (using Freundlich isotherm constants estimated from the dynamic conditions) was almost the same as the DPNSM prediction and in both cases, one could predict the observed data satisfactorily. The breakthrough data from DPNSM and ESM both exhibited a curvilinear curve. The P solute in the cake medium migrates 92 to 190 times slower than water.

14. The trend of pH changes in the column experiment was similar to that in the batch experiment. In the case of dust and cake, an increase of pH values occurred at the initial stage of P removal. This pH change can be correlated to the quantity of Mg^{2+} and Ca^{2+} ions liberated into the solution from the dust and cake media.

15. Due to the competition for sorption sites, P removal in the dust and cake medium decreased in the presence of NH_4. The breakthrough curves of P followed a S-shape, but with less spreading and shorter breakthrough times than that in the single solute system.

16. Dust and cake, due to their high sorption capacity for P, can be applied as (i) an adsorbent in a sewage treatment plant, (ii) as a substratum in constructed wetland system and (iii) as a suppressing material for P liberation from sediments. The effluent concentrations of heavy metals in the dust and cake column were lower than those in the materials found in the environment.

VII RECOMMENDATIONS FOR FUTURE RESEARCH

One the basis of this research the following works are recommended for future study:

1. The applicability of the Freundlich and Langmuir isotherm constants derived from batch experiments of P at low initial P concentrations (less than 5 mg/L) should be investigated. In this study, the Freundlich isotherm constants derived from batch experiments were significantly different from those of column experiments and they could not predict satisfactorily the observed breakthrough data.

2. Laboratory (batch and column experiments) and field scale experiments are needed to study the mobility of nitrogen (NH_4, NO_3-N and NO_2-N) in soil and slag media. Rational mathematical models for saturated steady flow conditions need to be developed to simulate the spatial and temporal distribution of nitrogen and to predict the transport of nitrogen in soil and slag media.

3. A development of the mathematical equations for bi-solute and multi-solute systems is recommended to simulate the P sorption in the presence of foreign materials, such as NH_4-N, Ca and heavy metals.

4. In addition to the soil and slag sorption studies, desorption and precipitation-dissolution (at high pH) experiments can also be performed. This will simulate the real situation in a land treatment system, where P sorption takes place up to the equilibrium condition during the application of wastewater to land, and then desorption or dissolution of P into the wastewater and groundwater may take place.

5. The investigation into the applicability of other media such as fly ash, dolomite and another type of slag from the steel industry can also be carried out to study the possibility of using them in similar roles to the media studied here.

6. A pilot-scale experiment of the effluent concentrations of heavy metals released by the adsorbents in horizontal flow is warranted.

7. Additional experiments and mathematical modelling should be carried out under unsaturated conditions.

8. The impact of pH and characterisation of a pH related precipitant should be developed under the static and dynamic conditions.

9. The experiments conducted were with artificial suspensions and only upto the breakthrough stage. Many of processes and interactions characterised in the study are expected to be strongly influenced by biological and resultant physical/chemical changes in a wastewater treatment system. Biofilm development, accretion of biological sediments, biological uptake and dissolution all need to be recognised as playing a significant, if not predominant, role in the long term operation of soil and slag media sorption systems. Thus a long term study with wastewater effluents should be conducted to study these factors.

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APPENDICES

A1. Definitions of Abbreviations, Terms and Units
A2. FORTRAN Listing of ALPA
A3. FORTRAN Listing of SPNSM
A4. Program Description of MCMFIT

A1. Definitions of Abbreviations, Terms and Units

ABSORPTION: A surface phenomenon which is defined as an increase in concentration of a particular component (adsorbate) in the interfaces of the solid phases of a particular adsorbing medium (adsorbent) from liquid phases or solid phases. In this study, phosphorus was used as adsorbate and adsorbents were soil, dust and cake particles

ADSORPTION: A surface phenomenon which is defined as an increase in concentration of a particular component on the surface between the liquid and solid phases

ALGAL BLOOM: A sudden growth of algae, water weed or other primitive plant, which may be undesirable aesthetically or because on dying the algae decays, causing deoxygenation of the water which may kill fish

ANION EXCHANGE CAPACITY (AEC): Total amount of anions. This is the positive charge measured by Cl^- or NO_3^- retention

BLUE-GREEN ALGAE (BGA): Primitive plants called cyanobacteria. Because of their distinctive colour and characteristics, they are more commonly known as BGA. Mass aggregations of BGA cause blooms and some are toxic

^oC: Degree Celsius

CATION EXCHANGE CAPACITY (CEC): The total sum of exchangeable cations which can be can be adsorbed by adsorbents, sometimes called total-exchange, base exchange capacity or cation absorption capacity expressed in milli-equivalents per 100 g or per gram of soil (or of other materials, such as clay)

CONSTRUCTED WETLAND SYSTEM (CWS): A man-made wetland used for the purpose of water and wastewater treatment

DESORPTION: Release of sorbed P back into solution as an opposite reaction of sorption

DPNSM: Dynamic Physical Non-equilibrium Sorption Model

EFFLUENT: Liquid discharge from a sewage treatment plant after treatment

EPA: Environment Protection Authority (New South Wales, Australia). A state government agency responsible for administration of pollution control legislation [formerly the State Pollution Control Commission (SPCC)]

ESM: Equilibrium Sorption Model.

g: Gram(s)

h: Hour(s)

ICPAES: Inductively Coupled Plasma Atomic Emission Spectrometer

INFILTRATION: Groundwater which enters a sewage system through cracked pipes or defective joints

INFLOW: Water which enters a sewerage system from roofs, drains, access covers, cross connections from stormwater drains, street washing and illegal connections

INFLUENT: Fluid such as sewage or stormwater which flows into a treatment plant

NUTRIENTS: Compounds required for growth. Nitrogen and phosphorus are the most common nutrients removed in sewage treatment

L: Litre(s)

mg/L: Milligrams per litre - the concentration of a substance in liquid. If the liquid is water, then mg/L is equivalent to parts per million (ppm)

ML/d: Megalitre per day. Flow measurement units: 10^6 litres/day = 11.6 litres/second

NH_4-N: Concentration of nitrogen in the form of ammonium (NH_4^+)

NLL: Non Licence Limit

NSW: New South Wales, a state in Australia

P: Phosphorus as orthophosphate (PO_4^{3-})

PE: Population Equivalent

PERMEABILITY: The ability of a solid medium to transmit the liquid through pores, which is also called hydraulic conductivity

rpm: Revolution(s) per minute

SEWAGE: The wastewater from homes, offices, shops and factories. Most sewage comes from domestic sources such as washing clothes, dishes and using the toilet and shower

SEWAGE SYSTEM: The system of pipes in which sewage flows

SORPTION: A surface phenomenon which is defined as an increase in concentration of a particular component at the surface or interface between two phases. Here, sorption is expressed as the combination of adsorption and absorption

SORPTION EQUILIBRIUM: A state at which the rates of sorption and desorption attain an equilibrium. No charge is observed in the concentration of the solute on the solid surface or in the liquid phase

SORPTION ISOTHERM: The penetration of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution at constant temperature

SPCC: The NSW State Pollution Control Commission, presently known as the Environment Protection Authority (EPA)

SPL: Spent Pickle Liquor

SPNSM: Static Physical Non-equilibrium Sorption Model

STP: Sewage Treatment Plant

TP: Total Phosphorus concentration (mg/L)

PRI: Phosphorus Retention Index

WASTEWATER: Another word for sewage

WL: Water Level above the adsorbent in column experiments

µg: Microgram; 10^{-6} g

A2. FORTRAN Listing of ALPA

A FORTRAN program ALPA to estimate optimal α values from experimental results has been developed. The α values which demonstrate a minimum error are regarded as the optimal ones. This program is designed to make use of Freundlich, Langmuir and Sips isotherms. The Sips isotherm, a modified form of the Langmuir and Freundlich isotherms, is expressed as follows:

$$S = \frac{Q_m b C^{\frac{1}{N}}}{1 + bC^{\frac{1}{N}}} \qquad \text{... (A.1)}$$

where,

Q_m, b, N = Sips isotherm constants
C = Liquid phase concentration (mg/L)
S = Solid phase concentration (mg/g)

```
C***********************************************************************
C                    PROGRAM FOR ESTIMATING COEFFICIENT alpha
C***********************************************************************
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      CHARACTER TEXT*80, DUMMYSTRING*80, DATAFILE*12
      DIMENSION Y(50), RWORK(10000), IWORK(50), I_TIME(100), C_EXP(100)
      DIMENSION C_PRE(100)
      COMMON/LANGMUIR/RANG_QM,RANG_B
      COMMON/FREUNDRICH/FREU_K,FREU_N
      COMMON/SIPS/SIPS_QM,SIPS_B,SIPS_N
      COMMON/PARAMETER/ALPA,BETA,THETA
      COMMON/CHOICE/NUMBER
      EXTERNAL FCN,FCNJ
C-----------------------------------------------------------
      NUMARG = NARGS()
      CALL GETARG(1,DATAFILE,ISTATUS)
C-----------------------------------------------------------
      IN=4
      ICLIP=5
      IOUT=6
      OPEN (IOUT,FILE='FINDALPA.OUT')
      OPEN (IN,FILE=DATAFILE,STATUS='OLD')
      OPEN (ICLIP,FILE='CLIP')
C-----------------------------------------------------------
 12   READ (IN,'(A80)',END=13) DUMMYSTRING
      IF (DUMMYSTRING(1:1) .NE. '*') THEN
```

```
      WRITE (ICLIP,'(A80)') DUMMYSTRING
      END IF
      GOTO 12
 13   CLOSE (IN)
      REWIND (ICLIP)
C-----------------------------------------------------------
      WRITE (*,*) '[1] LANGMUIR   [2] FREUNDRICH   [3] SIPS'
      WRITE (*,*) 'WHICH ISOTHERM DO YOU WANT TO USE ?'
      READ (*,*) NUMBER
C-----------------------------------------------------------
      READ (ICLIP,'(A80)') TEXT
      READ (ICLIP,*) C0,Q0
      READ (ICLIP,*) RANG_QM, RANG_B
      READ (ICLIP,*) FREU_K, FREU_N
      READ (ICLIP,*) SIPS_QM, SIPS_B, SIPS_N
      READ (ICLIP,*) ALPA, BETA, THETA, ALPA_INC, ALPA_FINAL
      READ (ICLIP,*) DTIME, DT, DTSTEP, TINC, TFINAL, TOL
      READ (ICLIP,*) N
      READ (ICLIP,*) (I_TIME(I),C_EXP(I),I=1,N)
      WRITE(*,200)
C-----------------------------------------------------------
 11   GEAR_TIME = DTIME
      GEAR_DT = DT
      TIMESTEP = DTSTEP
      Y(1)=C0
      Y(2)=Q0
      C_PRE(1) = Y(1)
C     WRITE(IOUT,100) GEAR_TIME,Y(1),C_EXP(1)
C     WRITE(*,100) GEAR_TIME,Y(1),C_EXP(1)

  1   CALL DGEAR(2,FCN,FCNJ,GEAR_TIME,GEAR_DT,Y,TIMESTEP,TOL,
     +         2,2,1,IWORK,RWORK,IER)
      I_TCHECK = GEAR_TIME
      DO I = 2,N
      IF(I_TCHECK .EQ. I_TIME(I)) THEN
C     RROR = DABS(Y(1)-C_EXP(I))
      C_PRE(I) = Y(1)
C      WRITE(*,100) GEAR_TIME,Y(1),C_EXP(I),ERROR
C      WRITE(IOUT,100) GEAR_TIME,Y(1),C_EXP(I),ERROR
       EXIT
       ELSE
       END IF
       END DO

 66    IF (TIMESTEP .GT. TFINAL) GOTO 99
      TIMESTEP=TIMESTEP+TINC

      I = I+1
      GOTO 1
 99   CALL FIND_ERROR (N,C_EXP,C_PRE,ERR)
      WRITE(*,100) ALPA,ERR
      WRITE(IOUT,100) ALPA,ERR
C     PAUSE
```

```
      IF (ALPA .LE. ALPA_FINAL) THEN
C      WRITE(*,*) '-----------------------'
C      WRITE (*,'(F10.3)') ALPA
      ALPA = ALPA + ALPA_INC
      GOTO 11
      ELSE
      STOP
      ENDIF

 100  FORMAT(T10,F10.3,',',T25,F10.5,',',E15.7,',',F10.3 )
 200  FORMAT(T10,'Alpha',',',T25,'error[%]')
      END
C
C     PURPOSE    : TO EVALUATE MEAN ERROR
C
C                1              | ( ABS( QEXP(I) - QCAL(I) )      |
C     MEAN_ ERROR = --------------  SUM  | -------------------------- * 100 |
C            NUMBER OF DATA        |         QEXP(I)                |
C
C                              ( I = 1,2,.....,NUMBER OF DATA )
C
C    USAGE      : CALL FIND_ERROR ( N,QEXP,QCAL,ERROR )
C   ARGUMENTS  : N - NUMBER OF DATA
C          QEXP - AN AMOUNT OF ADSORBED     IN EXPERIMENT
C          QCAL - AN AMOUNT OF ADSORBED     IN PREDICTED
C          ERROR - EVALUATED MEAN_ERROR
C
C OUTPUT     : ERROR
C
      SUBROUTINE FIND_ERROR ( N,QEXP,QCAL,ERROR )
      IMPLICIT DOUBLE PRECISION ( A-H,O-Z )
      DIMENSION QEXP(50), QCAL(50), ERROR_EACH(50)
      ERROR = 0.D0
      DO I = 1,N
      ERROR_EACH(I) = ( DABS(QEXP(I)-QCAL(I) )*100.D0 ) / QEXP(I)
      ERROR = ERROR + ERROR_EACH(I)
      END DO
      ERROR = ERROR / N
      RETURN
      END

      SUBROUTINE FCN (N,T,Y,DY)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION Y(50),DY(50)
      COMMON/LANGMUIR/RANG_QM,RANG_B
      COMMON/FREUNDRICH/FREU_K,FREU_N
      COMMON/SIPS/SIPS_QM,SIPS_B,SIPS_N
      COMMON/PARAMETER/ALPA,BETA,THETA
      COMMON/CHOICE/NUMBER
C----------------------------------------------------------
      T=T
      IF (NUMBER .EQ. 1) THEN
      DY(1)=-ALPA*(Y(1)-Y(2)/(RANG_B*RANG_QM-RANG_B*Y(2)))
```

```
  DY(2)=ALPA*(THETA/BETA)*
+       (Y(1)-Y(2)/(RANG_B*RANG_QM-RANG_B*Y(2)))
  ELSE IF (NUMBER .EQ. 2) THEN
  DY(1)=-ALPA*(Y(1)-(Y(2)/FREU_K)**FREU_N)
  DY(2)=ALPA*(THETA/BETA)*(Y(1)-(Y(2)/FREU_K)**FREU_N)
  ELSE IF (NUMBER .EQ. 3) THEN
  DY(1)=-ALPA*(Y(1)-(Y(2)/(SIPS_B*(SIPS_QM-Y(2))))**SIPS_N)
  DY(2)=ALPA*(THETA/BETA)*
+       (Y(1)-(Y(2)/(SIPS_B*(SIPS_QM-Y(2))))**SIPS_N)
  ENDIF
  RETURN
  END

  SUBROUTINE FCNJ (N,T,Y,PD)
  IMPLICIT DOUBLE PRECISION (A-H,O-Z)
  DIMENSION Y(50),PD(50)
  T=T
  Y(1)=Y(1)
  PD(1)=PD(1)
  RETURN
  END
```

A3. FORTRAN Listing of SPNSM

The following FORTRAN program SPNSM has been developed to describe the kinetics of P sorption under static conditions. This program is also designed to make use of other isotherm parameters such as the Langmuir and Sips isotherm constants although all the simulated results in this study are calculated from the Freundlich isotherm constants (K, N).

```
C*************************************************************************
C                         PROGRAM FOR SPNSM
C          (STATIC PHYSICAL NON-EQUILIBRIUM SORPTION MODEL)
C*************************************************************************
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      CHARACTER TEXT*80, DUMMYSTRING*80, DATAFILE*12
      DIMENSION Y(50), RWORK(10000), IWORK(50)
      COMMON/LANGMUIR/RANG_QM,RANG_B
      COMMON/FREUNDRICH/FREU_K,FREU_N
      COMMON/SIPS/SIPS_QM,SIPS_B,SIPS_N
      COMMON/PARAMETER/ALPA,BETA,THETA
      COMMON/CHOICE/NUMBER
      EXTERNAL FCN,FCNJ
C-----------------------------------------------------------
      NUMARG = NARGS()
      CALL GETARG(1,DATAFILE,ISTATUS)
C-----------------------------------------------------------
      IN=4
      ICLIP=5
      IOUT=6
      N=2
      OPEN (IOUT,FILE='SPNAM.OUT')
      OPEN (IN,FILE=DATAFILE,STATUS='OLD')
      OPEN (ICLIP,FILE='CLIP')
C-----------------------------------------------------------
 12   READ (IN,'(A80)',END=13) DUMMYSTRING
      IF (DUMMYSTRING(1:1) .NE. '*') THEN
      WRITE (ICLIP,'(A80)') DUMMYSTRING
      END IF
      GOTO 12
 13   CLOSE (IN)
      REWIND (ICLIP)
C-----------------------------------------------------------
      WRITE (*,*) '[1] LANGMUIR   [2] FREUNDRICH   [3] SIPS'
      WRITE (*,*) 'WHICH ISOTHERM DO YOU WANT TO USE ?'
      READ (*,*) NUMBER
C-----------------------------------------------------------
```

```
      READ (ICLIP,'(A80)') TEXT
      READ (ICLIP,*) Y(1),Y(2)
      READ (ICLIP,*) RANG_QM, RANG_B
      READ (ICLIP,*) FREU_K, FREU_N
      READ (ICLIP,*) SIPS_QM, SIPS_B, SIPS_N
      READ (ICLIP,*) ALPA, BETA, THETA
      READ (ICLIP,*) DTIME, DT, DTSTEP, TINC, TFINAL, TOL
C----------------------------------------------------------------
      WRITE(*,200)
      WRITE(IOUT,200)
      WRITE(IOUT,100) DTIME,Y(1)
      WRITE(*,100) DTIME,Y(1)
C----------------------------------------------------------------
    1 CALL DGEAR(N,FCN,FCNJ,DTIME,DT,Y,DTSTEP,TOL,
     +        2,2,1,IWORK,RWORK,IER)
      WRITE(*,100) DTIME,Y(1)
      WRITE(IOUT,100) DTIME,Y(1)
      IF (DTSTEP .EQ. TFINAL) GOTO 99
      DTSTEP=DTSTEP+TINC
      GOTO 1
C----------------------------------------------------------------
   99 STOP
  100 FORMAT(T10,F10.3,',',T25,F10.5 )
  200 FORMAT(T10,'TIME',',',T25,'Concentration[mg/L]')
      END

      SUBROUTINE FCN (N,T,Y,DY)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION Y(50),DY(50)
      COMMON/LANGMUIR/RANG_QM,RANG_B
      COMMON/FREUNDRICH/FREU_K,FREU_N
      COMMON/SIPS/SIPS_QM,SIPS_B,SIPS_N
      COMMON/PARAMETER/ALPA,BETA,THETA
      COMMON/CHOICE/NUMBER
C--------------------------------------------------------------
      T=T
      IF (NUMBER .EQ. 1) THEN
      DY(1)=-ALPA*(Y(1)-Y(2)/(RANG_B*RANG_QM-RANG_B*Y(2)))
      DY(2)=ALPA*(THETA/BETA)*
     +      (Y(1)-Y(2)/(RANG_B*RANG_QM-RANG_B*Y(2)))
      ELSE IF (NUMBER .EQ. 2) THEN
      DY(1)=-ALPA*(Y(1)-(Y(2)/FREU_K)**FREU_N)
      DY(2)=ALPA*(THETA/BETA)*(Y(1)-(Y(2)/FREU_K)**FREU_N)
      ELSE IF (NUMBER .EQ. 3) THEN
      DY(1)=-ALPA*(Y(1)-(Y(2)/(SIPS_B*(SIPS_QM-Y(2))))**SIPS_N)
      DY(2)=ALPA*(THETA/BETA)*
     +      (Y(1)-(Y(2)/(SIPS_B*(SIPS_QM-Y(2))))**SIPS_N)
      ENDIF
      RETURN
      END
```

```
SUBROUTINE FCNJ (N,T,Y,PD)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION Y(50),PD(50)
T=T
Y(1)=Y(1)
PD(1)=PD(1)
RETURN
END
```

A4. Program Description of MCMFIT

A FORTRAN program to carry out the nonlinear least squares fitting of the general nonlinear transport model to generalised experimental data has been developed in MCMFIT. The program MCMFIT was based on the maximum neighbourhood method of Marquardt (1963) as implemented by van Genuchten (1980, 1981), Parker and van Genuchten (1984) and Barry et al. (1988). MCMFIT fits nine parameters, viz., the pore water velocity (VEL), dispersion coefficient (D_s), pulse duration (PULSET), the four sorption isotherm coefficients (α_1, α_2, α_3, α_4), the rate coefficient (α_5) and the fraction of sorption site (α_6). The program consists of the main program, MCMFIT, and the subroutines MATINV, MODEL, FUNC1, FUNC2, FNC2, FUNC3, FUNC4, NLSYST and ran3. The main program handles the input and output of data, generates the parameter data set for which the sum of residual squares is a minimum and implements the fitting program. MATINV performs matrix inversion as required by the fitting program for parameter estimation. MODEL organises data predicted by the system of non linear equation solver, and FUNC4. FNC2 is the function as required by NLSYST. The subroutine RAN3 generates random numbers between 0 and 1. The system time in seconds has been used as the seed for the random generator in MCMFIT.

Upon execution, MCMFIT looks for an input file (MCMFIT.DAT is the default) containing the necessary information on the model to be fitted and the experimental data. Once this file name is entered, the program prompts for the results file name. A plot file name which consists of the observed and the fitted results is created. Table A4.1 shows example parameter values required by the MCMFIT in the soil column experimental data for the influent concentration of 5 mg/L. The line by line formation of this file is presented in Table A4.2.

The output file consists of:

1. Descriptive title
2. Initial values of coefficients (obtained from the random search)
3. Iteration number and sum-of-squares for the given parameter values
4. Correlation matrix of the fitted parameters
5. The R^2 value for the regression
6. Optimised parameter values and their 95% confidence limits

7. Fitted and observed data as ordered by the input file
8. Fitted and observed data as ordered by the residual magnitude.

Table A.1 Input Data File for the Example
(Soil Column Experiment, C_o=5 mg/L)

```
  NVAR     NOB     MIT  MAXTRY      IPLOT    MODE    NRAN    NEST
      9      59     30        20        1        1      10       1
  CLEN      C01      DT        RHO     TIMET
 5.0000  10.0000  0.2000    3.0213  9999.0000
    Example 1
    Fitting soil-5 P experimental data
   vel        ds      pulset    alpha1  alpha2    alpha3   alpha4
     1         1          0        0        0         0        0
1.5000   1.1934  9999.0000  -1.0000  5.3700    0.9000   1.0000
0.5000   0.0100  9999.0000  -1.0000  5.3700    0.9000   1.0000
2.5000   1.5000  9999.0000  -1.0000  5.3700    0.9000   1.0000
alpha5.  alpha6.
     1        0
0.3252   0.0000
0.0100   0.0000
1.0000   0.0000

 Conc.   Time/Distance
 0.0000   0.0000
 0.0100   1.1700
 0.2500   1.9200
  1.0000  3.0000
  0.7500  4.9600
  0.7500  5.9600
 ......   ......
 1.0000  18.0400
 0.7500  18.9600
 0.7500  20.0800
 1.0000  21.1600
 1.2500  22.1600
 ......   ......
 4.7500  31.2500
 5.0000  33.0000
 5.2500  35.0000
 5.5000  37.0000
 4.7500  39.0000
 ......   ......
 8.0000  61.0000
 8.2500  63.0000
 8.5000  65.0000
 7.7500  69.0000
 ......   ......
  9.7500  81.0000
 10.0000  83.0000
 10.2500  85.0000
  9.7500  87.0000
 10.0000  89.0000
```

Table A.2 Format of Input File as Required by MCMFIT
(see example in Table A.1)

Line	Columns	Format	Description
2	1-10	I10	NVAR: Number of variables in the model.
	11-20	I10	NOB: Number of observations.
	21-30	I10	MIT: Maximum number of iterations allowed in the least-squares fitting. If set to 0, the program simply calculates breakthrough curve/profile using the initial parameter values.
	31-40	I10	MAXTRY: Number of trial solutions allowed at each iteration
	41-50	I10	IPLOT: 1 (0) -do (not) create plot file
	51-60	I10	MODE: codes 1 to 4 selects the model to be fitted. 1. Two site model with b.c.type 1 (breakthrough curve) 2. Two site model with b.c.type 3 (breakthrough curve) 3. Two site model with b.c.type 1 (profile) 4. Two site model with b.c.type 3 (profile)
	61-70	I10	NRAN: Number of times the random set of parameters is to be generated.
	71-80	I10	NEST: A flag to select the option between user-defined or random searches of initial parameter values. Any other integer selects random searches.
4	1-10	F10.4	CLEN: Column length
	11-20	F10.4	C01: Influent concentration
	21-30	F10.4	DT: Time step
	31-40	F10.4	RHO: Ratio of bulk density to porosity of the medium
	41-50	F10.4	TIMET: Time at which concentration profile is to be generated.
5	1-80	A80	Descriptive label
6	1-80	A80	Descriptive label
7,12	1-10	2A4	Parameter names.
	11-20 etc		VEL- pore water velocity, VEL>0.
			Ds- dispersion coefficient, Ds>0.
			PULSET - duration that solute is injected at the soil surface
			$\alpha1$, $\alpha2$,$\alpha3$, $\alpha4$ - S-curve isotherm parameters
			$\alpha5$ -kinetic mass transfer coefficient, $\alpha5 \geq 0$
			$\alpha6$-fraction of equilibrium, $0 \leq \alpha6 \leq 1$.

8,13	1-10 etc	I10	Finite code : (0) 1 - (do not) fit this parameter.
9,14	1-10 etc	F10.4	User-defined parameter values.
10,15	1-10 etc	F10.4	Lower limit allowed for parameter.
11,16	1-10 etc	F10.4	Upper limit allowed for parameter.
18	1-10 11-20	F10.4 F10.4	Value of the observed concentration Time or space of observation (Line 18 is repeated NOB times).

Table A.3 Output File for the Example (Soil Column Experiment, C_o=5 mg/L)

```
           NON-LINEAR LEAST-SQUARES ANALYSIS
           Example 1, Fitting soil-10 P experimental data

      INITIAL VALUES OF COEFFICIENTS
       NAME      INITIAL VALUE
           vel.... 1.5000E+00
            ds.... 1.1934E+00
        pulset.... 9.9990E+03
        alpha1.... -1.0000E+00
        alpha2.... 5.3700E+00
        alpha3.... 9.0000E-01
        alpha4.... 1.0000E+00
        alpha5..... 3.2520E-01
        alpha6.... 0.0000E+00

ITERATION          SSQ            vel          ds        alpha5.
        0     2.6660E+01    1.5000E+00  1.1934E+00  3.2520E-01
        1     2.6058E+01    1.5166E+00  6.1674E-01  3.7432E-01
        2     2.5481E+01    1.5146E+00  1.0825E+00  3.2059E-01
      ..................................................................
       12     2.2497E+01    1.5253E+00  5.8212E-01  2.3037E-01
       13     2.2497E+01    1.5253E+00  5.8099E-01  2.2997E-01
      ..................................................................
       19     2.2497E+01    1.5253E+00  5.7775E-01  2.2877E-01
       20     2.2497E+01    1.5253E+00  5.7775E-01  2.2877E-01

      CORRELATION MATRIX
          1       2       3
       1  1.0000
       2 -0.6073    1.0000
       3 -0.6035    0.9997    1.0000

      RSQUARE FOR REGRESSION =0.97287691

      NON-LINEAR LEAST SQUARES ANALYSIS, FINAL RESULTS

                                                        95% CONFIDENCE LIMITS
VARIABLE  NAME    VALUE   S.E.COEFF.  T-VALUE           LOWER       UPPER
     1        vel 1.5253E+00  3.8502E-02  3.9617E+01    1.4482E+00  1.6024E+00
     2         ds 5.7775E-01  3.9710E+00  1.4549E-01    -7.3745E+00 8.5300E+00
     3   alpha5 2.2877E-01  1.3394E+00  1.7080E-01     -2.4535E+00 2.9110E+00
```

```
-------------------ORDERED BY COMPUTER INPUT-------------------
                      Y        RESI-
NO    T1        OBS      FITTED      DUAL
 1  0.000E+00  0.000E+00  0.000E+00  0.000E+00
 2  1.170E+00  1.000E-02  7.052E-03  2.948E-03
 ..................................................................
27   2.912E+01   2.750E+00   3.041E+00   -2.907E-01
28   3.125E+01   4.750E+00   3.436E+00   1.314E+00
 ..................................................................
42   5.900E+01   7.250E+00   7.994E+00   -7.442E-01
43   6.100E+01   8.000E+00   8.196E+00   -1.957E-01
 ..................................................................
58   9.100E+01   1.105E+01   9.700E+00   1.350E+00
59   9.300E+01   1.100E+01   9.737E+00   1.263E+00

---------------------ORDERED BY RESIDUAL---------------------
                      Y        RESI-
NO    T1        OBS      FITTED      DUAL
58   9.100E+01   1.105E+01   9.700E+00   1.350E+00
28   3.125E+01   4.750E+00   3.436E+00   1.314E+00
 ..................................................................
 2  1.170E+00  1.000E-02  7.052E-03  2.948E-03
 1  0.000E+00  0.000E+00  0.000E+00  0.000E+00
```