EFFECT OF SOLID-SOLUTION RATIO ON ANION ADSORPTION

ON

HYDROUS METAL OXIDES

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NATIONAL UNIVERSITY OF SINGAPORE

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SUMMARY

The reactions of ions at the oxide surface are usually modeled by assuming surface complex formation with the metal ion in the solid, but some experimental results are inconsistent with this assumption. According to the surface complexation model, the reaction at the oxide surface involves one type of reaction: surface complex formation only. One of the experiment results that is inconsistent with the surface complexation model is the influence of the solids concentration on adsorption isotherm. One possible explanation for the solids concentration effect is that the sorption process involves precipitation as well as surface complex formation. Adsorption involves monolayer coverage, while multi-layer coverage occurs during precipitation as well.

Previous studies at NUS have shown that solids concentration tends to influence phosphate adsorption on goethite. Phosphate surface coverage is much higher in low solids concentration slurries than in slurries of high solids concentration at the same solution concentration. In this study, the effect of solids concentration on anion adsorption on hydrous metal oxides has been studied using two different approaches.

First, adsorption isotherms and kinetics for phosphate adsorption on goethite at various solids concentration were investigated to provide a better understanding of the reaction mechanism. Phosphate adsorption isotherms depend strongly on pH. The initial phase of this work involved the study of phosphate and arsenate adsorption on goethite at three different pH levels and two different goethite concentrations. The results give a better understanding of the effect of pH on anion adsorption on goethite and at the same time, shows that doubling the solids concentration has little effect on the surface coverage.

Second, the change in solids concentration on phosphate adsorption has been studied at varying equilibration time using a wider range of solids concentrations. A direct measurement of adsorbed phosphate on the surface was used to determine the adsorbed phosphate at very low solids concentration. This method gave more reliable results compared to the usual loss-from-solution method for samples with high phosphate concentrations or very low goethite concentrations. The results showed that solids concentration significantly impacts the adsorption isotherms at lower solids concentrations. However, the effect was only observed for surface coverage above a certain value, 70 µmol/g.

Adsorption kinetics followed a two stage process: a very rapid reaction initially, followed by a much slower stage. The transition from very rapid adsorption to a slower process occurred at around the same surface coverage as the transition point where the effect of solids concentration was observed. Both effects probably reflect the transition from adsorption to precipitation. Both results show good agreement for the point of the transition from monolayer to multilayer surface coverage. The maximum monolayer surface coverage found during the first reaction in experimental result is in good agreement with the calculated monolayer surface coverage value based on B.E.T surface area. In contrast, at a high phosphate concentration and low solids concentration, surface coverage is much higher than the calculated monolayer coverage.

These results suggest that precipitation may be occurring in the samples, and is most apparent at a very low solids concentration.

NOMENCLATURE

a, b, c	unit dimension of goethite
C	The molar electrolyte concentration (M)
CCM	Constant Capacitance Model
CD-MUSIC	Charge Distribution – Multi-site Complexation Model
DLM	Diffuse Double Layer
EDL	Electrical Double Layer
F	Faraday's constant (96490 coulomb/mol)
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma- Mass Spectrometry
iep	iso-electric point
$\mathbf{K_{ads}}$	equilibrium constant for reaction
$\mathbf{K_{intr}}$	equilibrium constant for chemical reaction between metal and the surface site
$\mathbf{K_{SPM}}$	equilibrium constant for precipitation reaction of metal ion
$\mathbf{K_{SPFe}}$	equilibrium constant for precipitation reaction of Fe^{3+} ion
P	Orthophosphate – PO_4^{3-}
PZC	point of zero charge
R	the molar gas constant (8.314 $Jmol^{-1}\ K^{-1}$)
s	specific surface area of solid
SCM	Surface Complexation Model
SEM	Scanning Electron Microscope

SPM	Surface Precipitation Model
T	the absolute temperature (K)
TEM	Transmission Electron Microscope
TLM	Triple Layer Model
XRD	X-Ray Diffraction
Z	Charge of the ion
κ^{-1}	double layer thickness (m)
Γ_{max}	Estimated Maximum Surface Coverage
ρ	Density of Goethite (α-FeOOH)
σ_p	the net total surface charge (Cm^{-2})
ψ	The electric surface potential
ε	the dielectric constant of water (dimensionless)
ε_o	the permittivity of free space ($8.854*10^{-12}$ C V^{-1} m^{-1})
α , β	Elovich's constants

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CHAPTER 1 INTRODUCTION

1.1 General Introduction

Goethite (α-FeOOH) is one of the most widespread iron oxides in natural systems and can be readily synthesized in the laboratory. Many forms of iron oxide are found in natural soil and sediment, such as hematite, ferrihydrite, lepidocrocite, alkaganeite, and goethite. Among these metal oxides, goethite is one of the most common and is widely used in ion sorption studies because of its high crystallinity and thermodynamic stability at ambient temperature.

Phosphate and arsenate are both group V elements and thus have similar chemical properties. Phosphorous is a common element and is an important plant nutrient, often being the bio-limiting nutrient in fresh water and the ocean (Krom and Berner, 1981). On the other hand, arsenic is very toxic and a health risk for humans when exposed to contaminated drinking water (Lepkowski, 1998). Both phosphorus and arsenic are released to aquatic environments through weathering of rocks or by various human activities including mining, ore processing, and industrial and agricultural use (Pierce and Moore, 1982).

Adsorption plays a major role in controlling the dissolved concentration and hence mobility of phosphate and arsenate in the environment. To facilitate describing the distribution of the anions between solution and metal oxide surfaces, adsorption models have been developed. Experimental sorption data can generally be described by the traditional Langmuir and Freundlich adsorption isotherms, however, these do not provide information of the adsorption mechanism or the speciation of surface complex (Cornell and Schwertmann, 2003). The surface complexation model (SCM) has been developed over the past several decades to describe the reaction between the ions and the surface, including the electrostatic interaction between the charged surface and ions (Dzombak and Morel, 1990).

However, some results are inconsistent with the SCM. The SCM is based on mono-layer surface coverage and equilibrium conditions. The SCM is limited in its ability to explain some experimental results, including observed reaction kinetics, lack of adsorption maxima, competitive adsorption and solid-solution ratio effects. The kinetics of phosphate adsorption on hydrous metal oxide has two phases reaction; initially the reaction is very rapid, followed by a continuous slow reaction occurring from days to weeks with no equilibrium observed at the end of the experiment (Chen, 1973a; Stanforth, 1981; Hingston, 1981). Some studies have shown that phosphate adsorption never reaches an adsorption maxima (Anderson et al., 1981). The adsorption increases with decreasing solids concentration (Li, 1998; Ler, 2000; Jaio, 2003). Increasing the solution concentration (phosphate) or decreasing the solids concentration (goethite) influences the adsorption maxima (Li, 1998; Ler, 2000). The solid-solution ratio effect plays an important role in ion sorption studies.

In the SCM, the solid to solution ratio should have no effect on the adsorption isotherm since the reaction between the anion and goethite involves a surface complex formation only. However, studies have shown that the solid solution ratio significantly influences on sorption. One suggestion that to account for the effect is that a precipitation reaction may occur at the oxide surface (Li, 1998; Ler, 2000; and Jaio, 2003). Although some studies observed the solid solution ratio effect on adsorption isotherm, the explanation of this effect on sorption isotherm is still unclear. In this study, an investigation of the solid solution ratio effect on adsorption isotherm as well as solid solution ratio effect on reaction kinetics will be investigated.

1.2 Objectives and Scope

The major objective of this study is to study the effect of solid to solution ratio on adsorption isotherms and kinetics. This study will provide a better understanding of anion adsorption mechanism as well as solid solution ratio effect on goethite. The scope of this study involves:

1) The effect of pH on anion adsorption (phosphate and arsenate) on goethite. In this portion of the study, two different solids concentration were used to obtain more reliable and accurate results.
2) The effect of solid to solution ratio on adsorption isotherm, including:
    (a) The effect on adsorption isotherm at two solid concentrations and various pH values as an initial study, and
    (b) The effect of changing solids concentrations by a factor of 1000 at pH 4.
3) The effect of solids concentrations on reaction kinetics.

CHAPTER 2 LITERATURE REVIEW

2.1 Goethite and Its Morphology

2.1.1 Goethite

Iron oxides are widespread in natural environment systems. Sixteen forms of iron oxides were observed in the natural environment (Cornell and Schwertmann, 2003), with goethite (α-FeOOH) one of the most common forms. It is occurs in nature as a component of soil and is thermodynamically stable at ambient temperature. Because of its high crystallinity, ease of formation, and stability, it has been used as adsorbent in ion adsorption experiment. Natural goethite occurs in rock and soils. Goethite is dark or brown colored in massive crystal aggregates and yellow colored in powder form. Synthetic goethite can be prepared in the laboratory with a needle-like (acicular) structure and surface areas ranging from 8 - 200 m^2/g (Cornell and Schwertmann, 2003).

2.1.2 Surface Morphology

The basic morphology of goethite crystal is acicular over the range of crystal sizes. The length of the acicular goethite ranges from a few tens of nm to several microns. The larger crystals usually consist of aggregates of smaller crystals. Synthetic acicular goethite crystals are elongated in the 100 direction and terminate on the 210 face. This morphology has a double chain of the corner shared iron octahedral running parallel to the [010] direction and dominating the crystal structure (Cornell and Schwertmann, 2003).

In general, the crystal form of goethite corresponds to a group of faces that intersect all the crystal axes. The chemical reactivity of interface is determined by the type and number of surface hydroxyl groups present. Metal oxides and hydroxides have different types of surface oxygen according to the coordination number of the metal ions in the solid. The chemical binding and reactive characteristic of the oxygens on the solid surface depend on the coordination number of the surface group. There are three types of surface oxygens on goethite: singly coordinated A-type hydroxyl group, triply coordinated B-type hydroxyl groups and doubly coordinated C-type hydroxyl groups as shown in Figure 2.1 (Sun and Doner, 1996).

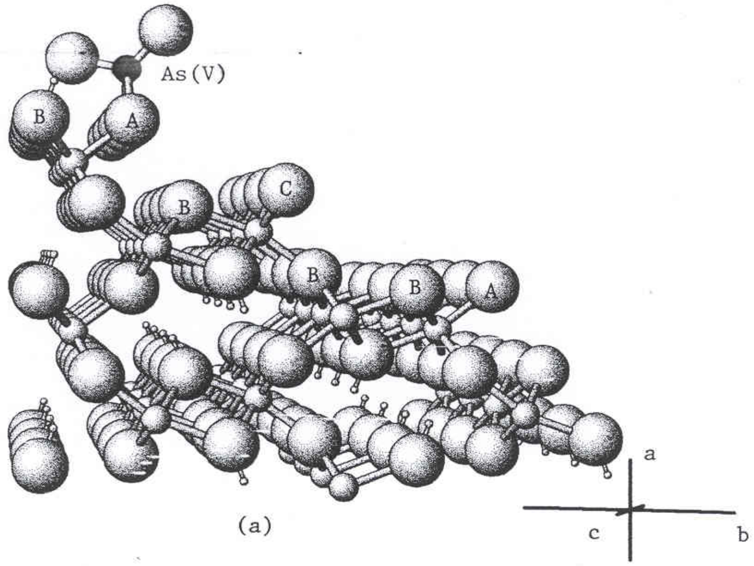


Figure 2.1 Surface groups and structure of goethite (Sun and Doner, 1996)

The reaction-dominating face in synthetic goethite is the (101) face (Cornell and Schwertmann, 2003). Phosphate and arsenate adsorption occur predominantly on the (101) face (Torrent et al., 1990) with the anion replacing two singly coordinate hydroxyl group (A type) and to form a binuclear complex as shown in Figure 2.1 (Sun and Doner, 1996).

2.2 Overview of Adsorption

Adsorption is the accumulation of a substance at an interface. The ion adsorption reaction with the solid surfaces controls the dissolved concentration and mobility of most trace elements of environmental concern (Stumm, 1992). Adsorption is important for several reasons:

1) it affects the supply of substance between aqueous phase and particulate matter.
2) it affects the electrostatic properties of suspended and colloidal particles which will sequentially influence particle aggregation and mobility.
3) it also affects the molecular structures and the reactivity of these surface which in turn control the dissolution of mineral phases, precipitation of solutes, and ion exchange processes.

Modeling ion adsorption at solid water interfaces requires an understanding of the interactions of a solute with a surface, characterizing the basic physical and chemical properties of the solute, the sorbent, and the solvent (water) (Westall, 1987).

2.2.1 Proposed Surface Reactions

All surface reactions between dissolved ions and hydrous metal oxides such as adsorption, precipitation, co-precipitation and diffusion into the crystals are generally classified as sorption when the reaction mechanism at the oxide surface is unknown. Most of the oxides surface is covered with hydroxyl groups in the presence of water.

The fundamental chemical interaction of the solute with the surface by the formation of coordinate bonds is assumed to be a surface complex formation reaction or ligand exchange reaction (surface complex formation of weak acid and metal oxides). The hydroxyl group from the metal oxide surface is replaced by the adsorbed ions and forms a surface complex.

The surface complex formation of cations and metal oxide can take several forms as follow:

(i) Monodentate surface complex

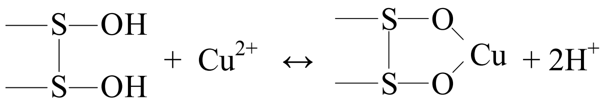
Monodentate surface complex formation involves the coordination of metal ions with the oxygen donor atoms and protons from the surface are released and formed monodentate species.

$\text{S-OH} + \text{Cu}^{2+} \Leftrightarrow \text{S-O-Cu}^{+} + \text{H}^{+}$

(ii) Bidentate species

Bidentate species can also be formed.

$2\ \text{S-OH} + \text{Cu}^{+2} = (\text{S-O})_2\ \text{Cu} + 2\ \text{H}^{+}$



(iii) Outer sphere and inner sphere surface complex

Surface complex formation reaction can be classified into two types; inner and outer sphere. In an outer surface compexation reaction, water molecules are present between the surface and adsorbed molecule while in an inner sphere surface complexation reaction, no water molecules are present between the surface and adsorbed molecules (Figure 2.2). An outer sphere surface complex formation reaction involves electrostatic coulombic interactions, and are generally weak compare to inner sphere complex formation reaction.

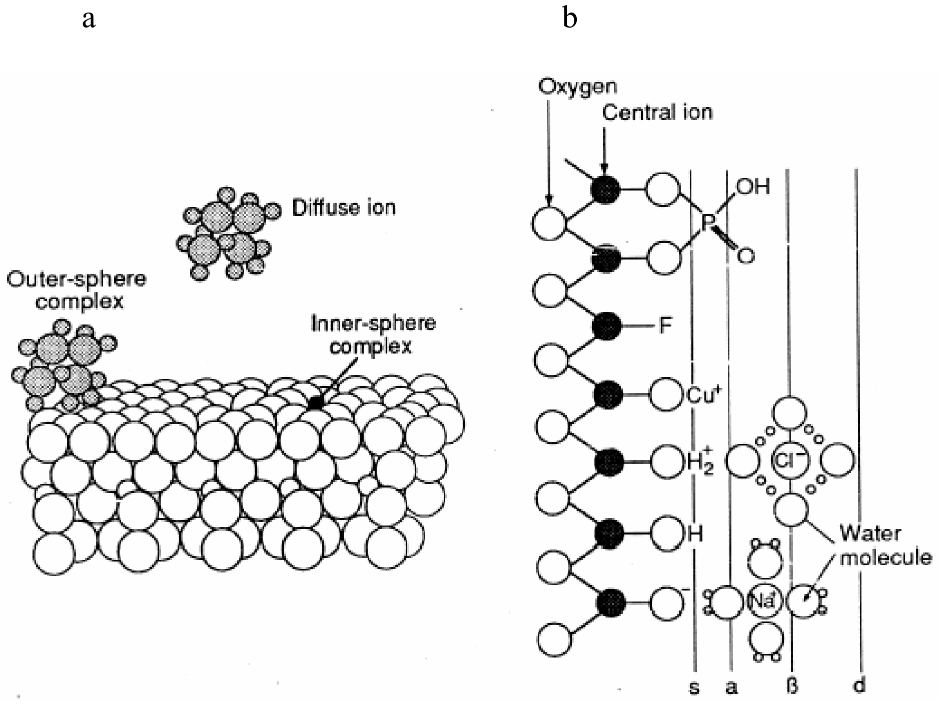


Figure 2.2 Surface complex formation of an ion [Stumm 1992]
(e.g., cation) on the hydrous oxide surface. The ion may form the inner sphere complex ("chemical bond"), an outer sphere complex (ion pair) or be in the diffuse swarm of the electric double layer. (from Sposito, 1989)
Fig. b shows a schematic portrayal of the hydrous oxide surface. showing planes associated with surface hydroxyl groups ("s") , inner-sphere complexes ("a"), outer sphere complexes ("β") and the diffuse ion swarm ("d"). Modified from Sposito, 1984)

The type of surface complex reaction also depends on the type of solutes present in the solution. In the presence of acid, the surface becomes more positive and anion adsorption is favored while cation adsorption reaction is favored in the presence of base. Table (2.1) shows the schematic representation of surface complex formation equilibria at oxide surfaces (Schindler and Stumm, 1987).

Table 2.1 Surface Complex Formation Reaction Equilibria

Acid base Equilibria

$\mathrm{S\text{-}OH} + \mathrm{H^{+}} = \mathrm{S\text{-}OH^{2+}}$

$\mathrm{S\text{-}OH} = \mathrm{S\text{-}O^{-}} + \mathrm{H^{+}}$

Metal binding

$\mathrm{S\text{-}OH} + \mathrm{M^{z+}} = \mathrm{S\text{-}OM^{(z-1)+}} + \mathrm{H^{+}}$

$\mathrm{2S\text{-}OH} + \mathrm{M^{z+}} = \mathrm{(S\text{-}O)_2M^{(z-2)+}} + \mathrm{2H^{+}}$

$\mathrm{S\text{-}OH} + \mathrm{M^{z+}} + \mathrm{H_2O} = \mathrm{S\text{-}OMOH^{(z-2)+}} + \mathrm{2H^{+}}$

Ligand exchange ($\mathrm{L^{-}}$ = ligand)

$\mathrm{S\text{-}OH} + \mathrm{L^{-}} = \mathrm{S\text{-}L} + \mathrm{OH^{-}}$

$\mathrm{2S\text{-}OH} + \mathrm{L^{-}} = \mathrm{S_2\text{-}L^{+}} + \mathrm{2OH^{-}}$

Ternary surface complex formation

$\mathrm{S\text{-}OH} + \mathrm{L^{-}} + \mathrm{M^{z+}} = \mathrm{S\text{-}L\text{-}M^{z+}} + \mathrm{OH^{-}}$

$\mathrm{S\text{-}OH} + \mathrm{L^{-}} + \mathrm{M^{z+}} = \mathrm{S\text{-}OM\text{-}L^{(z-2)+}} + \mathrm{H^{+}}$

2.2.2 Surface Complexation Modeling

Experimental ion adsorption data can be modeled by many empirical adsorption isotherms such as the Langmuir or Freundlich isotherms. However, these empirical isotherms do not explain the kind of reaction can be observed at the oxides surface or the behavior of surface charge of the oxide surface.

The Surface Complexation Model (SCM) has been one of the most powerful tools to describe the reactivity of mineral surfaces (e.g., Hingston, 1981; James and Parks, 1982; Dzombak and Morel, 1990; Stumm, 1992; Hiemstra and Van Riemsdijk, 1999). The SCM was first developed to describe ion adsorption on hydrous metal oxides system via mass law equations as a first step and explained the surface charge and potential together with ion adsorption reaction in the next step. The model uses a set of simulation equations that are solved by numerical methods using appropriate values of parameters involving the number of surface sites, the binding constants and double layer capacitance(s) using the results of a set of adsorption experiments. There are several variations of the SCM model, all based on the following fundamental concepts:

1. Sorption takes place on specific sorption sites.
2. Sorption reaction on oxides can be described quantitatively via mass law equations.
3. Surface charge results from the sorption reaction themselves.
4. The effect of surface charge on sorption can be taken into account by applying a correction factor derived from the Electrical Double Layer theory to mass law constants for the surface reaction.

Therefore, the model is based on four sets of equations (Cornell and Schwertmann 1996):

1. The mass action equation for the surface reaction.
2. The mass balance equations for the surface OH groups.
3. Equations for the calculation of surface charge.
4. Equations that describing the relationship between the charge and the potential of the electrical layer.

2.2.2.1 Variations of the Surface Complexation Model

A number of variations of the surface complexation model have been developed, such as generalized two layers model (Dzombak and Morel, 1990), the Diffuse Layer Model (DLM) (Stumm, 1970); Triple Layer Model (TLM) (Yates, 1974; Davis et al., 1978); Constant Capacitance Model (CCM) (Schindler, 1972; Goldberg, 1986) and the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996). One of the main assumptions of all these models is the formation of only monolayer surface coverage (surface complex formation only).

The main difference between these models is in the description of the electrical double layer at the oxide interface, and the locations of different adsorbing species. As a result, the relation between surface charge and surface potential of each model differs in the way in which the free energy of adsorption is divided into its chemical and electrical component.

Diffuse Layer Model (DLM)

The Diffuse Layer Model (DLM) is based on the Gouy Chapman theory and was developed by Stumm and coworkers (Stumm et al., 1970; Huang and Stumm, 1973). The DLM is often called the two-layer model and has a surface layer and a diffuse layer of counter-ion in solution. The main assumption of the DLM is that specific adsorption of ions occurred in the surface layer and non-specific adsorption of ions occurred in the diffuse layer. The simple two-layer concept of the DLM is illustrated in Figure 2.3.

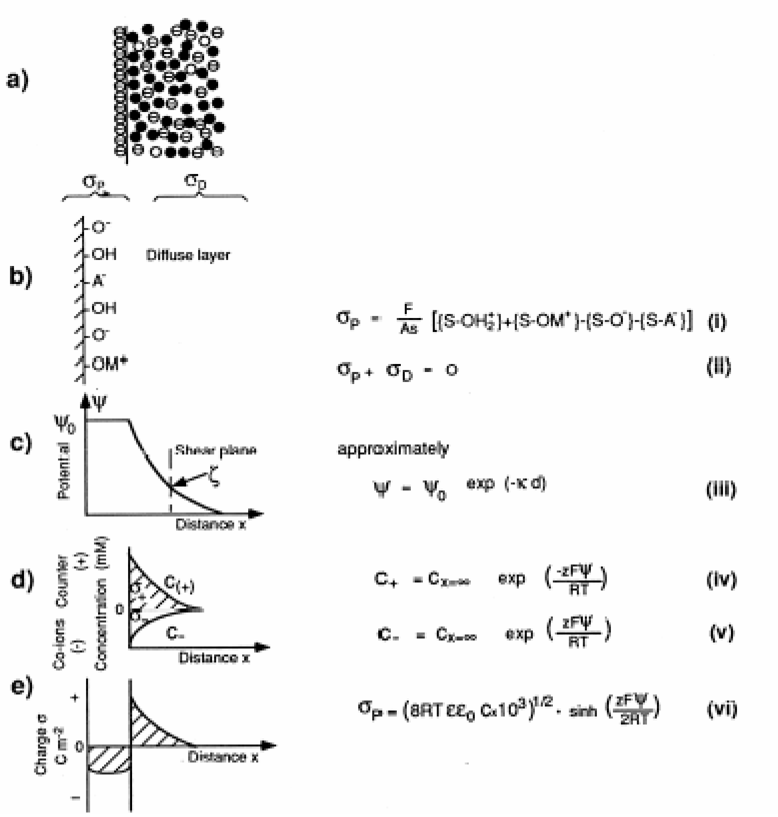


Figure 2.3 The diffuse double layer (Stumm, 1992)
a) Diffuseness results from thermal motion in solution.
b) Schematic representation of ion binding on an oxide surface on the basis of the surface
c) the electrical potential, ψ, falls off (simplified model) with distance from the surface. The decrease with distance is exponential when $\psi < 25$ mV. At a distance κ^{-1} the potential is dropped by a factor of (1/e). The distance can be used as a measure of the extension (thickness) of the double layer. At the plane of shear(moving particle), a zeta potential can be established with the help of electrophoretic mobility measurements.
d) Variation of charge distribution (concentration of positive and negative ions) with distance from the surface (Z = charge of the ion).
e) The net excess charge.

The relation between the surface charge density, σ (C/m^2) and surface charge potential, ψ is based on the Guoy-Chapman EDL theory,

$$\sigma_p = (8 RT \varepsilon_o \varepsilon c*10^3)^{1/2} \sinh (Z\psi F/2RT) \tag{2.1}$$

where

R is the molar gas constant (8.314 $Jmol^{-1} K^{-1}$)

T is the absolute temperature (K)

C is the molar electrolyte concentration (M)

ε is the dielectric constant of water (dimensionless)

ε_o is the permittivity of free space($8.854*10^{-12}$ $C V^{-1} m^{-1}$)

At low potential, the above equation can be linearlized as

$$\sigma_p = \varepsilon_o \varepsilon k\psi \tag{2.2}$$

where κ^{-1} is the double layer thikness (m)

$$\kappa = (2F^2 I* 10^3/ \varepsilon_o \varepsilon RT)^{1/2} \tag{2.3}$$

where I is the ionic strength (M).

At 25 ºC, T= 298 K, ε = 78.5, then

$$\sigma_p = 2.5 I^{1/2} \psi \tag{2.4}$$

The diffuse layer model can predict the ionic strength effect on the surface charging. It assumes that surface charge is entirely balanced by the diffuse charge. However, the diffuse layer model cannot predict the ionic effect at very low pH, although it works well for pH above the point of zero charges (pzc) (Kosmulski et al. 1999).

Constant Capacitance Model (CCM)

The Constant Capacitance Model was first developed by Stumm, Schindler and their coworkers (Stumm et al., 1970; Stumm et al., 1976; Stumm et al., 1980). It is a chemical model and explicitly defines the surface species and chemical reactions. It is a special case of the DDL model developed for the system at high ionic strength. The electrical double layer is treated as a parallel plate capacitor. In this model, all the adsorbing ions are located in one plane and are therefore at the same potential. It has been used to describe in adsorption of phosphate, arsenate, and silicate, as well as for competitive adsorption (Goldberg and Sposito, 1984; Sigg, 1981; Goldberg, 1985; Manning and Goldberg, 1996). The four essential characteristics as given by Stumm (1980) are

(i) adsorption is based on the ligand exchange mechanism
(ii) all surface complexes are inner-sphere complexes
(iii) no complex with ions in the background electrolyte is considered
(iv) the relationship between net surface charge, σ, expressed in moles of charge per cubic meter of aqueous solution, and surface potential, ψ expressed in volt, is given by the equation :

$$\sigma = (CSa/F)\,\psi \tag{2.5}$$

where C = a capacitance density parameter (F m^{-2})
S = specific surface area (m^2/kg)
a = concentration of solid in aqueous suspension (kg/m^3)
F = Faraday's constant (coulomb/mol)

Stumm et al. (1980) found that the CCM successfully described pH effect on phosphate adsorption on goethite, but it did not account for the ionic strength effects. Goldberg (1996) divided the reaction sites into two types: one site modeling and two-site modeling. Both cases showed the similar fits of CCM to experimental data, but some results did not agree with the model result at some pH values (Figure 2.4).

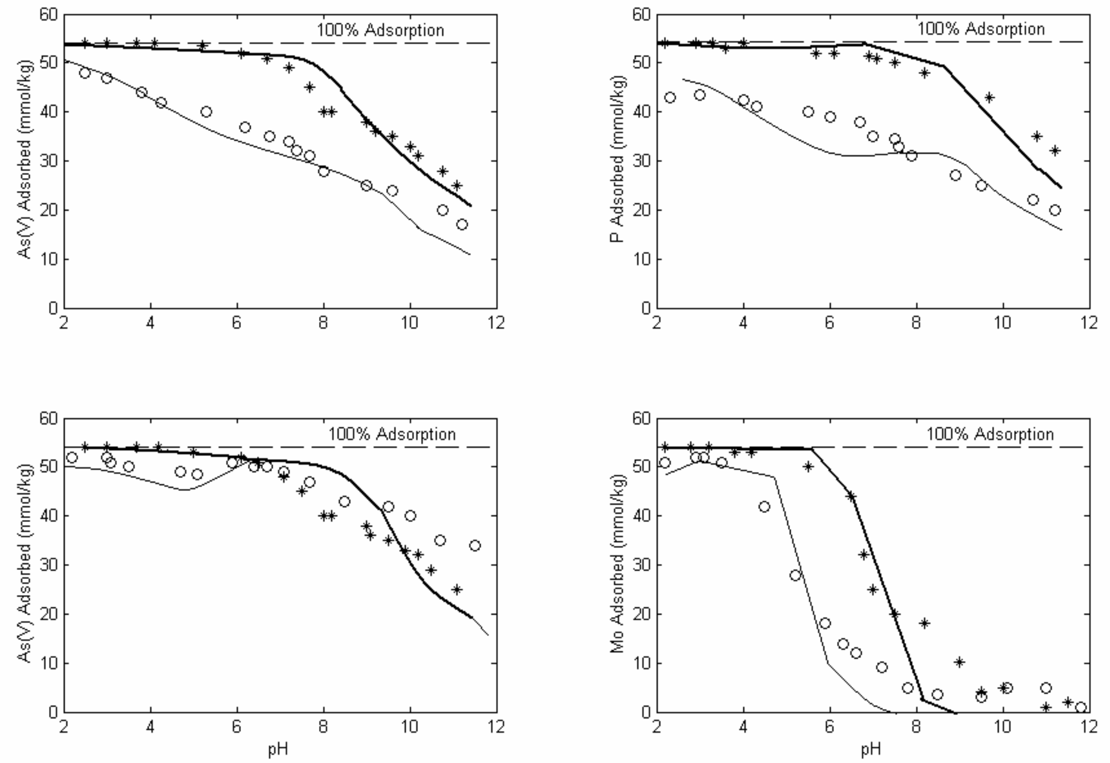


Figure 2.4 Arsenate (a and c), phosphate (b), and molybdate (d) single-anion and binary anion adsorption envelopes on goethite with CCM calculation using the one-site assumption. In all panels, symbols are: experimental single-anion data (ligend *), binary anion data (open circles), single-anion model calculations (solid lines), binary anion model calculation (dotted lines). Reaction conditions: 133 µM As(V), P or Mo (single-anion), 133 µM As(V) + 133 µM P or Mo (binary), 0.1 M NaCl, 2.5 g/l goethite, reaction time 4 h, T= 23 ºC (Goldberg, 1996).

Triple Layer Model

The Triple Layer Model (TLM) was first introduced by Yates et al. (1974) and consequently developed by Davis et al. (1978). Later, the model was further modified by Hayes and Leckie (1987). The TLM was originally based on four planes: a surface plane, an inner sphere plane (the o-plane), an outer sphere (β-plane) and the diffuse layer (d-plane). In the inner sphere complexes are formed by the adsorbing metal ion in the o-plane (surface layer); model analogs of outer sphere surface complexes are formed by the adsorbing metal ion in the β-plane. The diffuse layer d-plane represents the distance of closest approach of completely hydrated counter-ions that balance out the charging resulting from the formation of surface complexes. The schematic representation of TLM is shown in Figure 2.5.

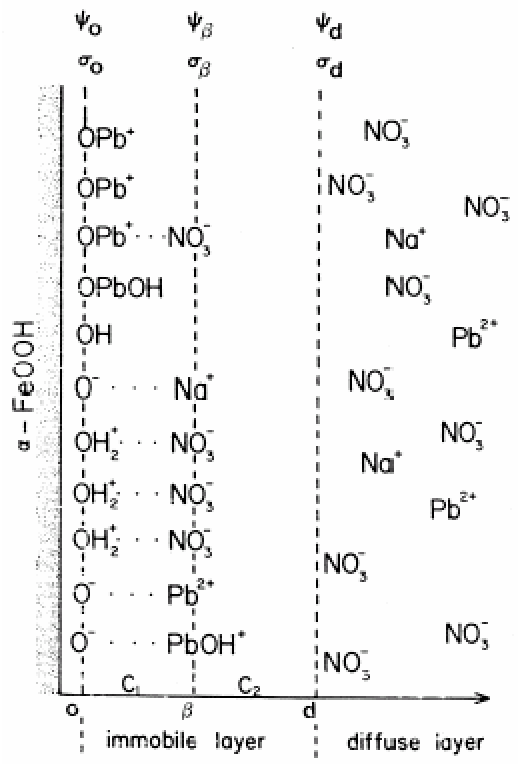


Figure 2.5 Schematic representation of TLM Model (Hayes and Leckies; 1987)

The triple layer model has been used for a number of applications including modeling inorganic anion and cation adsorption and organic compounds onto metal oxides, hydroxides, and oxyhydroxides (Hayes and Leckie, 1987, Hayes et al., 1988, 1991; Katz and Hayes 1995). Unlike the diffuse layer DLM and constant capacitance model, the TLM predicts both inner sphere and outer sphere complexation of anions and cations at the solid-liquid interface. In addition, the TLM model is applicable to various ionic strength solutions, while the DLM works well only at low ionic strength, and the CCM only at high ionic strength (Hayes et al., 1991). In the TLM, there are at least seven adjustable parameters while the DLM has two and the CCM has three parameters.

He et al. (1997) used a TLM model to describe the phosphate and sulphate adsorption on γ-Alumina and kaolinite by using both inner sphere and outer sphere complexation. Their results showed that SO_4 adsorption is consistent with outer sphere complexation, while PO_4 adsorption is consistent as an inner sphere complex. The authors emphasized that the modeling results may be consistent with the experimental data only for the use of parameters in this study, however the set of parameter values vary with the materials and methods used in the study. Even changing the site density parameter causes the modeled complexation to change from inner to outer sphere. Goldberg (1991) found a dependence on site density in evaluating the surface complex formation behavior of sulphate and borate adsorption on goethite. An inner sphere adsorption mechanism is indicated for low surface site densities, while larger value for this parameter results in outersphere complexation giving a better fit.

In addition, Katz and Hayes (1995) studied the TLM fit for the adsorption of cobalt on α-Al_2O_3 at low and high surface coverage. Their results also demonstrated that the TLM consistently underpredicted sorption at coverage in excess of 10%. In the second portion, the model was divided into three types; (1) solid solution model, (2) a surface polymer model and (3) continuum model. The modeling results indicated that all these models work reasonably well at predicting sorption data from moderate to high surface coverage. However, the first two models are inconsistent with spectroscopic data and the continuum model is the only one presented which is consistent with spectroscopic results throughout the range of surface coverages examined.

CD-MUSIC Model and Others

The SCMs discussed thus far assume that there is one sorption site on the surface, responsible for both ion adsorption and surface charging. However, goethite has several types of oxygens on the surface, which may have different protonation and adsorption behavior. Hiemstra and Van Riemsdijk developed the Charge distribution- multisite (CD-MUSIC) model to account for these differences (Hiemstra and Van Riemsdijk, 1996). The CD-MUSIC model takes into account different types of surface functional groups on the predominant crystal plane of the adsorbent. A major characteristic of this model is that the charge is distributed over several electrostatic planes. The difference between the CD-MUSIC and other models is that this model emphasizes the nature and arrangement of the adsorbent's surface functional groups. As a result, the CD-MUSIC model is able to incorporate more experimental information such as pH, ionic strength dependency, shift in isoelectric point (iep) and change in zeta potential and proton ion stoichiometry upon adsorption.

Initially, Van Riemsdijk and his co-worker suggested that surface hydroxyl groups are involved in a protonation reaction over the fairly narrow pH range and the different group had the same pKa value (Van Riemsdijk et al., 1986). Later, Boily (2001) suggested that the different surface oxygen may have different pK_a values. The pK_a values in the MUSIC model are derived from both ligand exchange interaction and Pauling bond valence. Unlike other model, the pK_a values in MUSIC model are based on fractional charge. However, the MUSIC model is not completely successful in describing surface charging behavior (Cornell and Schwertmann, 2003).

2.2.2.2 Surface Precipitation Reaction

Adsorption and precipitation are similar processes, with the major difference between these two processes being that adsorption is a two dimensional process and precipitation is a three dimensional process (Corey, 1981). The transition from adsorption to precipitation is not a simple process, with a number of reactions being involved in the precipitation process. Precipitation of adsorbed anions in general, involves at least two major reaction steps: first, the dissolution of mineral from oxide adsorbent and second, re-adsorption of the dissolved metal on the adsorbed anion to form multi-layer surface coverage.

Another way of considering precipitation is as the formation of a solid solution. At high concentrations of sorbing ion, surface precipitation may occur via formation of solid solution whose composition varies between that of the original solid and pure precipitate of sorbing ions (Corey, 1981).

2.2.2.3 Surface Precipitation Model (SPM)

One model of surface precipitation, the surface precipitation model (SPM), is an extended form of the surface complexation model (SCM). The SCM model is based on the assumption of monolayer coverage and often fails to describe adsorption at higher concentrations. Farley et al. (1985) and Dzombak and Morel (1990) developed a new chemical equilibrium model for metal cation sorption as an extended form of SCM. Their model considered both adsorption and precipitation on the solid by describing the formation of a surface phase whose composition varies continuously between that of the original solid and a pure precipitate of the sorbing cation (i.e., a solid solution). Precipitation does not start until the solution is saturated with respect to the solid being formed. Metal ion adsorption on mineral oxides is typically pH dependent and follows a pattern in which the percentage of total solute adsorbed increases rapidly from 0 to 100% over a moderately narrow pH range. In general, as the ratio of solute to solid concentration increases, the surface coverage increases and approaches 100% close to the pH range where bulk solution precipitation occurs.

However, all surface precipitation models consider that mono-layer adsorption is dominant at low solute concentrations and a surface phase formation becomes dominant when the sorbate concentration is increased to saturate the solution. The SPM of Farley (1985) postulated that the adsorption and precipitation reaction mechanisms of cation on ferrous hydroxide occur as follows:

Adsorption of M^{2+} on $Fe(OH)_3$ (s)

$$\equiv FeOH^0 + M^{2+} + H_2O \rightarrow FeO\text{-}MOH_2^+ + H^+ \qquad K_{ads} \qquad (2.6)$$

Precipitation of M^{2+}

$$=MOH_2^+ + M^{2+} + 2H_2O \rightarrow M(OH)_2\,(s) + =MOH_2^+ + 2H^+ \quad 1/K_{SPM} \qquad (2.7)$$

Adsorption of Fe on $M(OH)_2$ (s)

$$=MOH_2^+ + Fe^{3+} + 3H_2O \rightarrow M(OH)_2\,(s) + \equiv FeOH^0 + 4H^+ \quad K'_{ads}=1/K_{ads}K_{SPM}\,K_{SPFe} \qquad (2.8)$$

Precipitation of Fe^{3+}

$$\equiv FeOH^0 + Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\,(s) + \equiv FeOH^0 + 3H^+ \quad 1/\,K_{SPFe} \qquad (2.9)$$

The SPM model gives a better fit for the experiment result rather than SCM, but the model is not consistent with spectroscopic results. Charlet and Manceau (1992) have also applied that model to their results for sorption of chromium but their spectroscopic evidence was also not consistent with the formation of solid solution.

Katz and Hayes (1995) suggested several modified triple layer surface complexation models that allows for the comparison between the formation of multinuclear surface complexes and precipitates. These models are based on the ability of cobalt sorption on α-Al_2O_3 and include (1) a surface solid solution model (2) a surface polymer model and (3) a surface continuum model. The authors, however, suggested that while all of these models could be used to describe sorption data over a wide range of surface coverage, only the continuum model was consistent with the spectroscopic results.

The SPM model can be used in modeling anion adsorption on oxide surfaces (Farley, 1985; Dzombak and Morel, 1990). The major difference between the sorption of anions and cations is that the surface reactions of anion adsorption involve an exchange with surface hydroxyl groups (Stumm et al., 1980) and the precipitation step involves the dissolution of the adsorbent.

2.3 Kinetics Studies and Reaction Mechanism

Reactions at solid surfaces are time-dependent. The complete understanding of the dynamic interaction of metals with soil or metal oxides surface requires the knowledge of the kinetics of these reactions.

Kinetic analysis of phosphate adsorption on soils and soil constituents or hydrous metal oxides showed that the reaction is initially fast, followed by a slow and continuous reaction (Barrow, 1978; Barrow et al., 1981). Phosphate adsorption reaction on goethite does not reach equilibrium for months (Anderson et al., 1985). Shaking, temperature and solid/ solution ratio affect the observed reaction rate (White, 1980).

The modeling and interpretation of the slower reaction is varied. The relationship between the amount of phosphate adsorbed or released and time has been described by first order kinetics (Chen et al. 1973a), a combination of two or three instantaneous first order reactions, a parabolic diffusion law, a two constant rate equation (Chien, 1977), a second order kinetic reaction (Kuo and Lotse, 1972) and an exponential Elovich equation. The Elovich equation has general application to sorption kinetics (Low, 1960), the kinetics of heterogeneous exchange reaction (Atkinson et al., 1970), application of phosphate sorption kinetic (Stanforth, 1981) and ion adsorption on soil (Sparks, 1989).

2.3.1 Elovich Equation

The Elovich equation was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surfaces (Low, 1960). The Elovich equation has also been used to described the kinetics of heterogeneous isotopic exchange reaction (Atkinson, 1970), the kinetics of phosphate adsorption and desorption reaction at goethite (Stanforth, 1981; Torrent et al., 1990) and the kinetics of sorption and desorption of various inorganic material on soils (Pavlatou and Polyzopoulos, 1988; Sparks, 1989).

The Elovich equation is generally expressed as

$$d\Gamma/dt = \alpha \exp(-\beta\Gamma) \qquad (2.10)$$

where

Γ = surface coverage at time t

α , β = constants

t = equilibrating time

The equation can be simplified according to Chien and Clayton (1980) as follows:

$$\Gamma = (1/\beta) \ln(\alpha/\beta) + (1/\beta) \ln t \qquad (2.11)$$

A plot of Γ versus ln (t) should give a straight line.

Stanforth (1981) found that P adsorption kinetics data fit an Elovich plot of log time vs Γ (Figure 2.6). A change in Elovich slope occurred at low phosphate concentration as the system became P limited. His studies also suggested that the reaction is neither first order nor second order. The reaction did not reach equilibrium up to the end of experiment i.e., after 12 days reaction. The kinetic pattern showed that reaction is rapid at first followed by a continuous slow reaction.

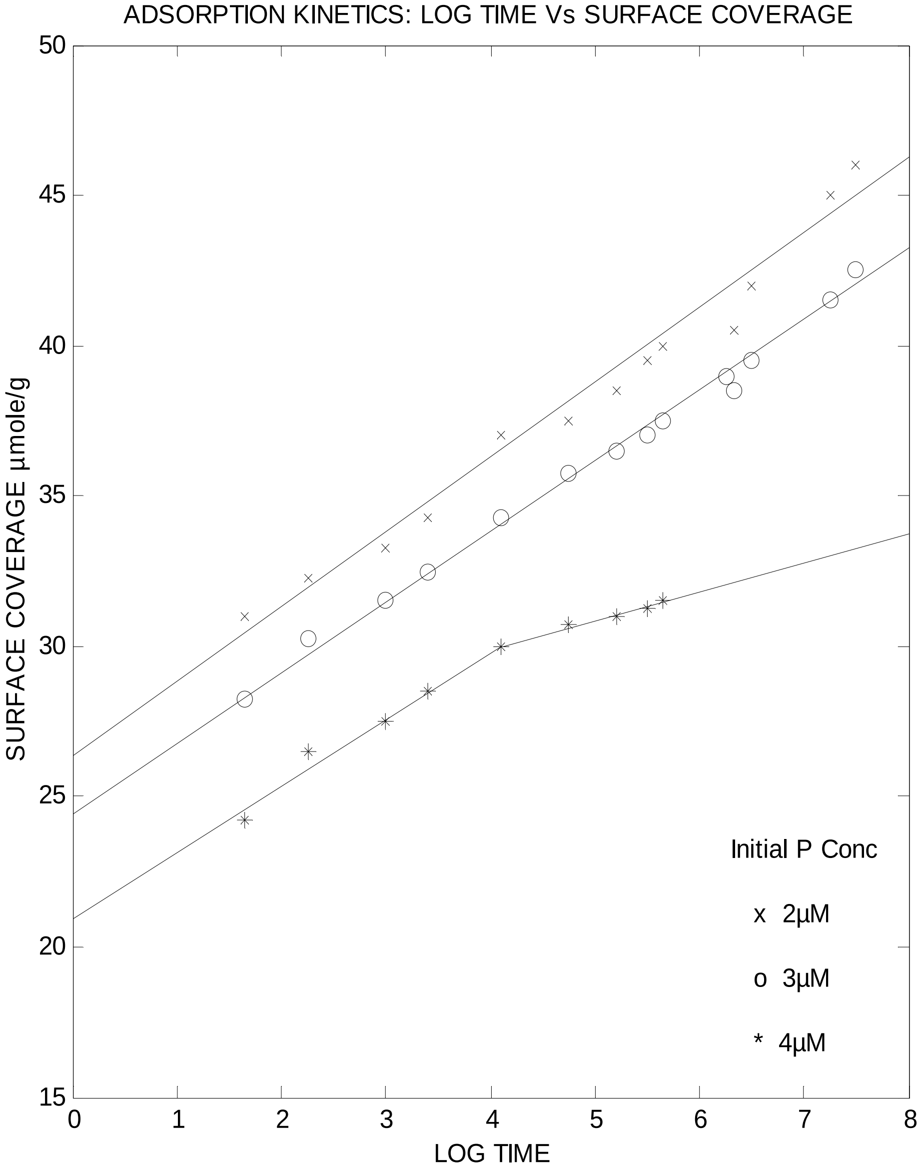


Figure 2.6 Elovich analysis of phosphate adsorption kinetics data pH 4.5 and 0.595 g/l Goethite concentration (redrawn from Stanforth, 1981).

2.4 Effect of Solid Solution Ratio

If the reaction at the solid water interface involves only surface complex formation, the effect of solid-solution ratio should not influence the adsorption isotherm. In practice, the P adsorption isotherm significantly increases at lower solids concentrations. Li (1998) (Figure 2.7) and Ler (2001) (Figure 2.8) showed the effect of solids concentration of phosphate adsorption on goethite. Both studies suggested that the solids concentrations influence the sorption isotherm.

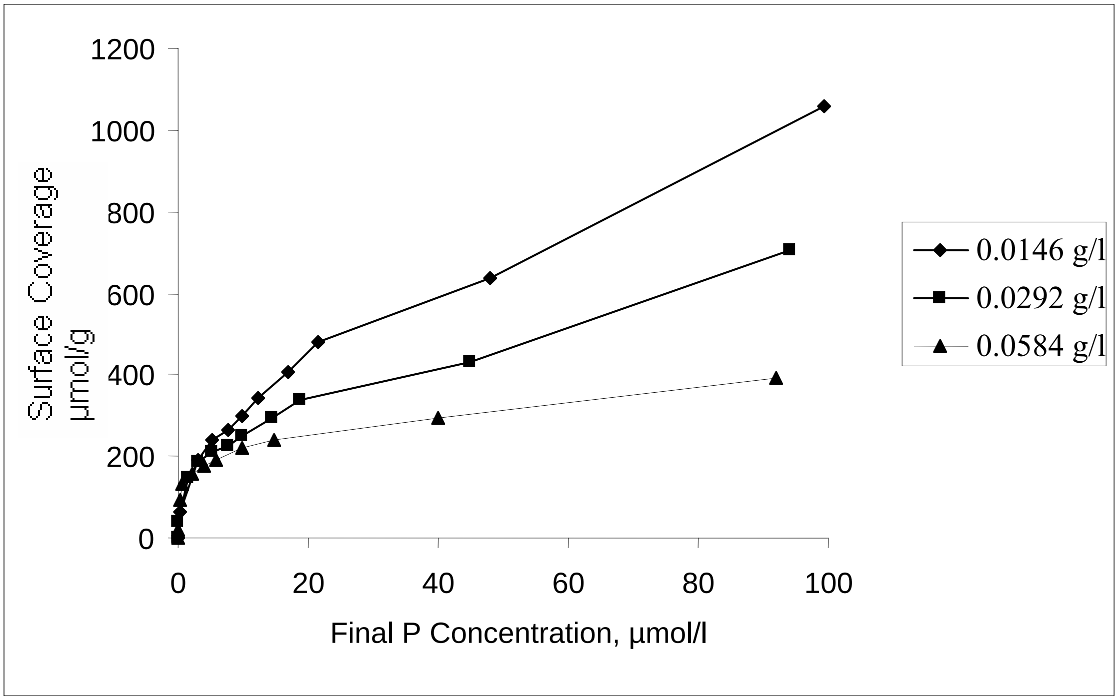


Figure 2.7 Effect of solids concentration on phosphate adsorption on goethite (Li, 1998).

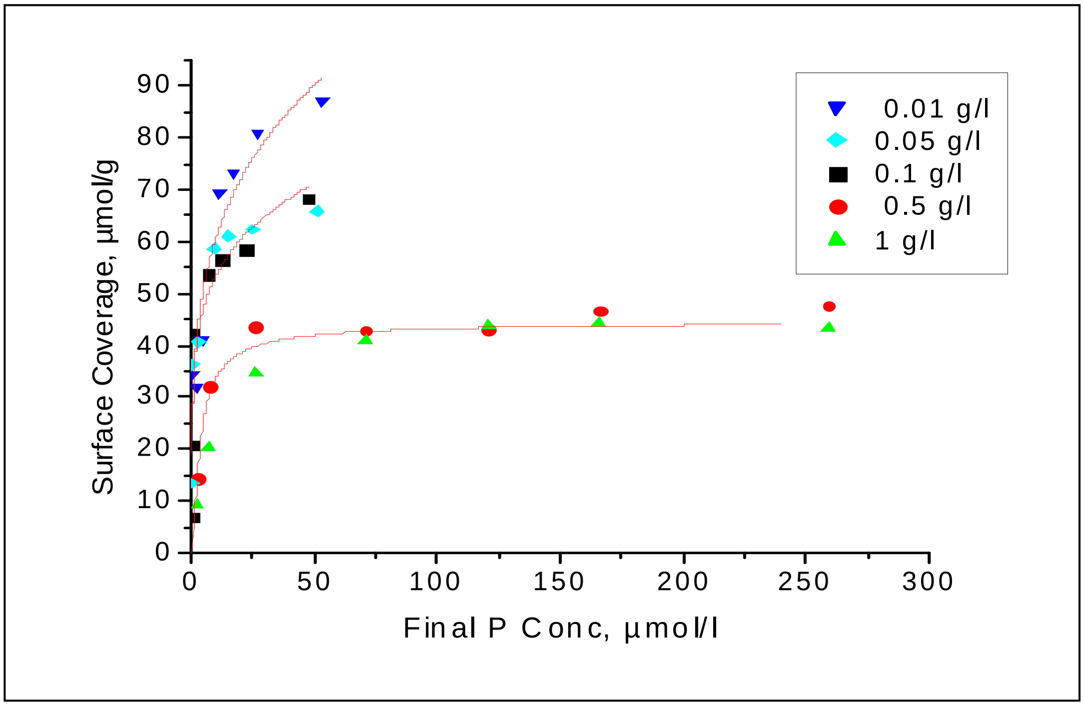


Figure 2.8 Effect of solids concentration on phosphate adsorption on goethite (Ler, 2001).

In addition, Jaio (2003) showed that solids concentrations effects phosphate adsorption on gibbsite. The phosphate adsorption on gibbsite significantly increased when the solids concentration decreased from 1.48 to 0.0148 g/l.

Many studies using soil have demonstrated that the adsorption constant varies at different solid–water (S/W) ratios (O'Connor and Conolly, 1980; Voice et al., 1983; Di Toro, 1985; Cox et al., 1993; You et al., 1999). This has been described as the solids effect (Grover and Hance, 1970; Servo and Muir 1989; Plus et al., 1991; You et al., 1999). The effect of solid to solution ratio is a major experimental parameter in determining the adsorption constant (McDonald and Evangelou, 1997). The adsorbed amount decreases with increasing S/W ratio at the same initial concentration (Chang and Wang 2002).

Although the solid to solution ratio has been found to play an important process in adsorption studies, reasons for the solid-solution ratios effect on adsorption are still unclear. Li (1998) and Ler (2001) suggested that the effect could be due to precipitation reaction. Adsorption maximum cannot be found at lower solids concentration and no plateau is observed even when the surface coverage exceeds the calculated maximum sorption capacity (Li, 1998). The adsorption of phosphate significantly increases with decreasing solids concentration. Again, Jaio (2003) also found the effect of solid solution ratio of phosphate adsorption on gibbsite. His studies demonstrated the dissolution of aluminum during adsorption reaction and suggested that the solubility of adsorbent (metal oxide) cannot be neglected in evaluating adsorption process.

CHAPTER 3 MATERIALS AND EXPERIMENTAL DETAILS

In this research, the adsorption of phosphate and arsenate on goethite was investigated. This study covers the following specific areas:

1. Individual adsorption isotherms of phosphate and arsenate at pH values of 3, 7 and 10.
2. Initial studies of anion adsorption isotherms of phosphate and arsenate at different solid concentrations of 0.5 g/l and 1 g/l at the same total initial anion concentrations.
3. Direct analysis of phosphate on the solid surface (goethite).
4. Phosphate adsorption isotherms at solids concentration of 0.01, 0.1, 1.0, 10.0 g/l at pH 4.
5. The effect of solid concentrations on phosphate adsorption kinetics.

3.1 Goethite Preparations and Characterizations

Goethite (α-FeOOH) was prepared using the procedure of Atkinson et al. (1968). First an iron solution of 72.7 g $Fe(NO_3)_3 \cdot 9H_2O$ in 400ml distilled deionized water was added to a base solution of 23.35 g NaOH in 400 ml distilled deionized water to form iron hydroxide. This suspension was then aged at 60˚C in a plastic bottle for 72 hours, with periodic shaking, during which time a change in color from red to orange was observed. The goethite was filtered once, then washed by placing it in a 4 L plastic bottle with DI water. When the goethite had settled, the supernatant solution was decanted. Washing was continued until the supernatant conductivity was less than twice that of DI water and pH was near 7. At least six or seven washings were needed to remove impurities. After washing, the suspension was filtered and allowed to dried at 60˚C, then ground into a powder form.

The morphology of the prepared goethite was characterized with Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and X-ray Diffraction (XRD). Also the surface area was determined by BET method of N_2 adsorption.

3.2 Individual Anion Adsorption Isotherms for Phosphate and Arsenate at Varying pH

The individual anion adsorption isotherms for phosphate and arsenate were determined using different initial anion concentrations. The experiments were conducted at constant pH values of 3, 7, 10 and solids concentration of 0.5 g/l and 1 g/l. A background electrolyte of 0.001 M $NaNO_3$ was used in these experiments. The goethite slurry was ultrasonicated for 20 minutes to separate the goethite particles, followed by continuous magnetic stirring of the slurry to the end of the experiment to ensure a uniform slurry. Phosphate and arsenate stock solutions were prepared with “Merck” GR grade $NaH_2PO_4{\bullet}H_2O$ and BDH Analar Grade $Na_2HAsO_4{\bullet}7H_2O$. Phosphate and arsenate stock solutions of 0.001 M were prepared for all the adsorption experiments.

The samples were prepared as follows:

First: 5 ml of 0.01 M $NaNO_3$ solution was added to 50 ml volumetric flasks. Goethite stock solutions of 2 g/l and 1 g/l were prepared for these experiments. Appropriate volumes of the stock anion solutions were then added. The initial concentrations were 5, 10, 20, 40, 50, 75, 100, 150 and 200 μM of each anion. DI water is added to bring the volume to 25 mL. Twenty-five mL of goethite slurry (2 g/l) was added and the sample brought to volume and transferred to 50 mL polyethylene bottle. The pH value was adjusted to the desired pH value (3 or 7 or 10) using 0.01 to 1.0 M HNO_3 or NaOH solutions to minimize the volume changes in solution concentration. The pH was measured using an Orion Model 420A pH meter. The mixtures were then agitated continuously on a rotating shaker. An equilibrating time of 24 hours was used. The samples were removed after 24 hours reaction time and filtered through a 0.45 μm pore size PTFE membrane filter (Whatman Autovial). Dissolved anion concentrations were analyzed by using a Perkin Elmer ICP (Inductively Couple Plasma) Optical Emission Spectrometer Optima 3000 DV. When the anion concentrations were lower than the Optima 3000 detection limit, ICP-MS (Inductively Couple Plasma Mass Spectrometer) was used to measure the anion concentrations.

3.3 Phosphate Adsorption Isotherm at Different Solids Concentrations

To study the effect of solid to solution ratio, phosphate adsorption experiments were conducted at pH 4 at different solids concentration. Solids concentration used in this study were 10 g/l, 1 g/l, 0.5 g/l, 0.1 g/l and 0.01 g/l. An ionic strength of 0.001 M $NaNO_3$

was used in all of the experiments. Samples were collected at different reaction times of 1, 24, 72, 168 and 720 hours respectively to study the reaction kinetic for each experiment. Initial phosphate concentrations used were range from 50 µM to 2000 µM for 10 g/l solids concentrations and 1 µM to 1000 µM for 1 g/l, 0.1 g/l and 0.01 g/l solids concentrations.

To account for the error induced by the volume change after the addition of P stock, and to measure the initial P concentration, the same volume of a blank P solutions were also prepared. Samples were removed after 1 hour, 24 hours, 72 hours, 168 hours and 720 hours respectively to analyze for surface coverage. The pH were regularly checked and readjusted if its changes more than ±0.05 pH unit.

3.4 Measurement of Surface Coverage

The measurement of surface coverage can be done by two different methods: indirectly using loss from solution or directly by measuring the amount on the solid. The direct measurement may involve desorption of the sorbed anions, or digestion of the solid itself. The “Loss from Solution Method” is the most common method. Although this method is quite accurate at moderate and high solids concentration, it may not give accurate result when the change in solution concentration is very small, such as when a very low solids concentration is used or at a high phosphate concentration. Under these conditions, direct measurement of surface coverage will give more accurate results than the indirect method.

3.4.1 Loss From Solution Method

The surface coverage can be determined by dividing the change in solution concentration by the solids concentration (loss from solution). Most studies use this method for determining surface coverage. While this method is generally satisfactory, the uncertainty is high when the change in solution concentration is small. The method is as follows:

Samples preparation for anion adsorption isotherm has been described in section (3.2). After equilibrating with anion solution, 10 ml of individual samples at different solids concentration were removed. The samples were then filtered with a Whatman Autovial 0.45 µm pore size PTFE membrane filter. The filtrate was then acidified and anion concentrations of both initial and final solution were analyzed by using Perkin Elmer ICP (Inductively Couple Plasma) Emission Spectrometer Optima 3000 DV. When the anion concentrations were lower than detection limit, ICPMS (Inductively Couple Plasma Mass Spectrometer) was used in measuring anion concentrations.

3.4.2 Direct Analysis

Direct analysis can be done using one of the two methods: a desorption method or an acid digestion method. In the desorption method, the phosphate released from solid surface have been determined by raising the pH. In the acid digestion method, the goethite is dissolved in a hot acid solution and both Fe and P concentration were analyzed.

3.4.2.1 Desorption Method

A phosphated goethite was prepared for use in these experiments using an initial concentration of 134 μM. The goethite concentration is 1 g/l at pH 4. The resultant surface coverage was 89 μM.

Desorption of phosphate from the phosphated-goethite was carried out using six different desorbing solutions [0.01M HNO_3, 1 M HNO_3, 6M HNO_3, 0.01M NaOH, 1M NaOH, 6M NaOH]. 50 mg of each of phosphated goethite were suspended in 50 ml of each desorbing solution. The bottles were put on the rotating shaker for the experiment. Samples were taken at 6 hours, 24 hours, 2 days, 3 days, 4 days, 7 days, 10 days and 13 days. The phosphate concentrations were measured using ICP-AES (Inductively Couple Plasma Atomic Emission Spectrometry).

3.4.2.2 Acid Digestion Method

In the acid digestion method, samples were filtered using a Whatman cellulose acetate filter of pore size 0.45 μm to obtain around 5 milligram of phosphated goethite. The solid was dried for 1 day, weighed and put in a beaker. Twenty milliliter of DI water, 1 ml of concentrated hydrochloric acid and 0.1 ml of concentrated nitric acid were added in the sample and heated to 95˚C. The temperature was maintained at 95˚C until all the goethite was dissolved. Then the samples were cooled to room temperature and stored in a refrigerator before analysis. Then P and Fe concentration were analyzed using a Perkin Elmer ICP (Inductively Couple Plasma) Emission Spectrometer Optima 3000 DV. If the phosphate concentration was lower than the ICP-OES detection limit, ICP-MS was used to measure the anion concentrations. The iron concentration was used to calculate the solids concentration.

Although this method is more complicated and have more experimental error, it is more accurate than "loss from solution" method when the solid concentration is low (< 0.1 g/l solid) and solution concentration is higher (> 20 uM). All the experiments were conducted at least four times for the acid digestion method.

3.5 Error Analysis

Duplicates of the adsorption experiments were run to examine the experimental reproducibility. The results and the variations for each experiment conducted are given in the Appendix. The experiments were repeated in duplicate for both phosphate and arsenate adsorption isotherms and for the desorption studies. For the acid digestion process, the experiments were repeated at least four times to obtain good reproducibility.

For the adsorption experiment, the mean variance (σ) normally increases with the increase of equilibrium phosphate concentration ($C_{eq,P}$). But the percentage deviation stays in the range of 5 % to 10 %. Higher percentages of deviation are found for low equilibrium phosphate concentrations. This is because low concentration of phosphate or arsenate was left after reaction. Therefore, the average concentration is small and as a result, the percentage deviation is very high. At higher equilibrium phosphate concentration, the percentage deviation becomes very low. The values at low phosphate concentrations are more sensitive to the change of instrument stability and operation conditions.

In the solid digestion method, all the experiments are repeated several times to obtain three reproducible results. The solid digestion method has several experimental errors. As both Fe and P concentration are measured by using ICP and ICP-MS, the instrumentation error may be higher than that of loss from solution method. To minimize all the error induced by experimental variation, all the experiment steps (heating, diluting, measuring P and Fe content) were carefully controlled and all the experiments were run several times until two or three reproducible results were obtained. Known solutions were measured while analyzing the sample to check the instrument stability.

Solid from solids concentration of 0.1 g/l and 0.01 g/l were analyzed by using the acid digestion method. Standard deviation and percentage deviations are calculated based on the number of runs. Selected data are calculated by average of two or three reproducible result.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Goethite Preparations and Characterizations

XRD (X ray diffraction spectroscopy) result showed the solid sample is goethite. Surface area measurement by N_2 adsorption in BET analysis gave a surface area of 36.5 m^2g^{-1}. This result is consistent with other studies of the same stoichiometric ratio and same crystallization temperature (Ler, 2001).

A scanning electron microscopy (SEM) photograph of goethite is shown in Figure 4.1. The goethite solids appear grassy, with an average length of 866 nm, and a width of 161 nm. Previous studies have shown that the cross sectional goethite under a high resolution transmission microscope exhibits a hexagonal shape.

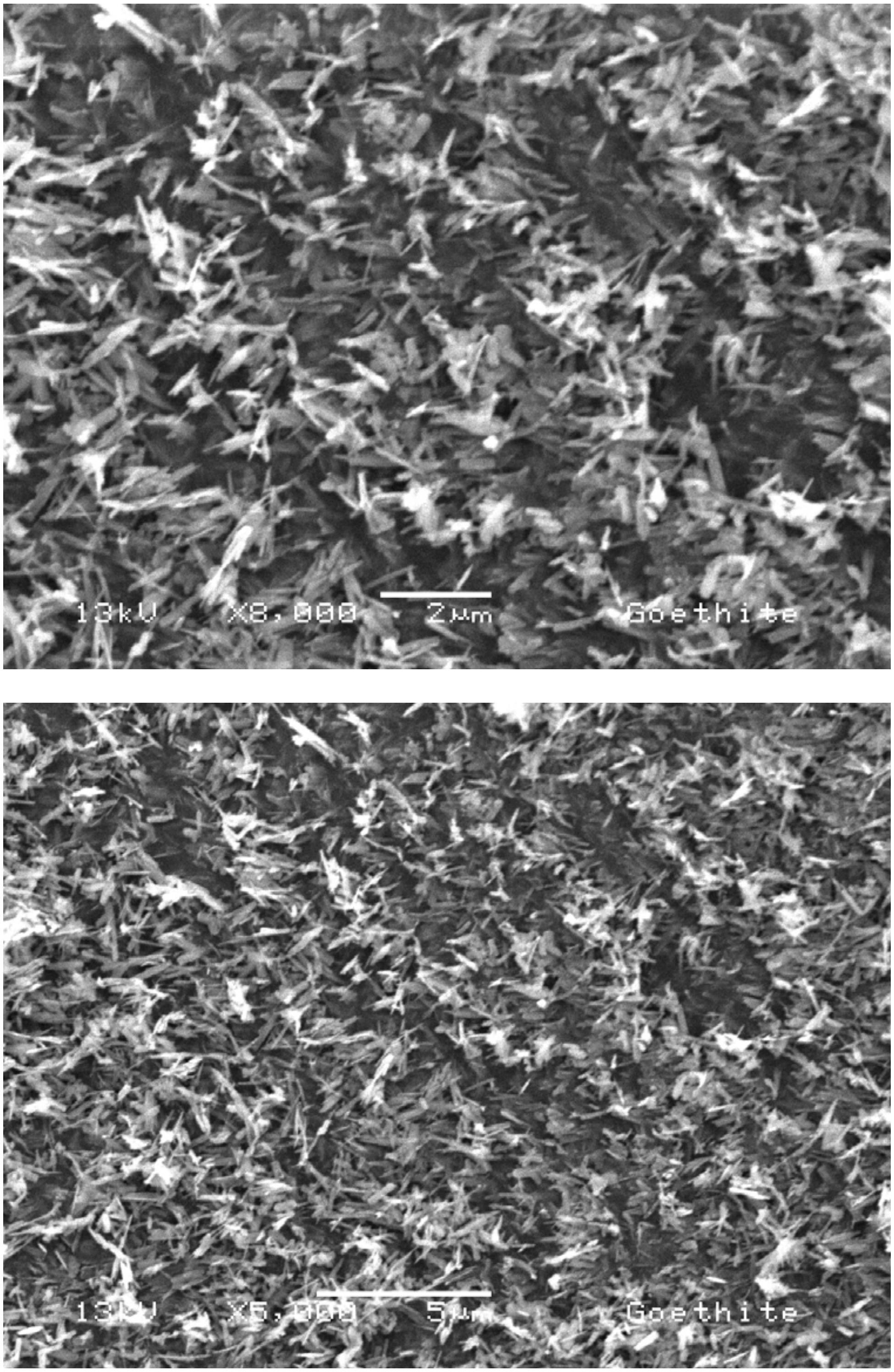


Figure 4.1 SEM image of prepared goethite

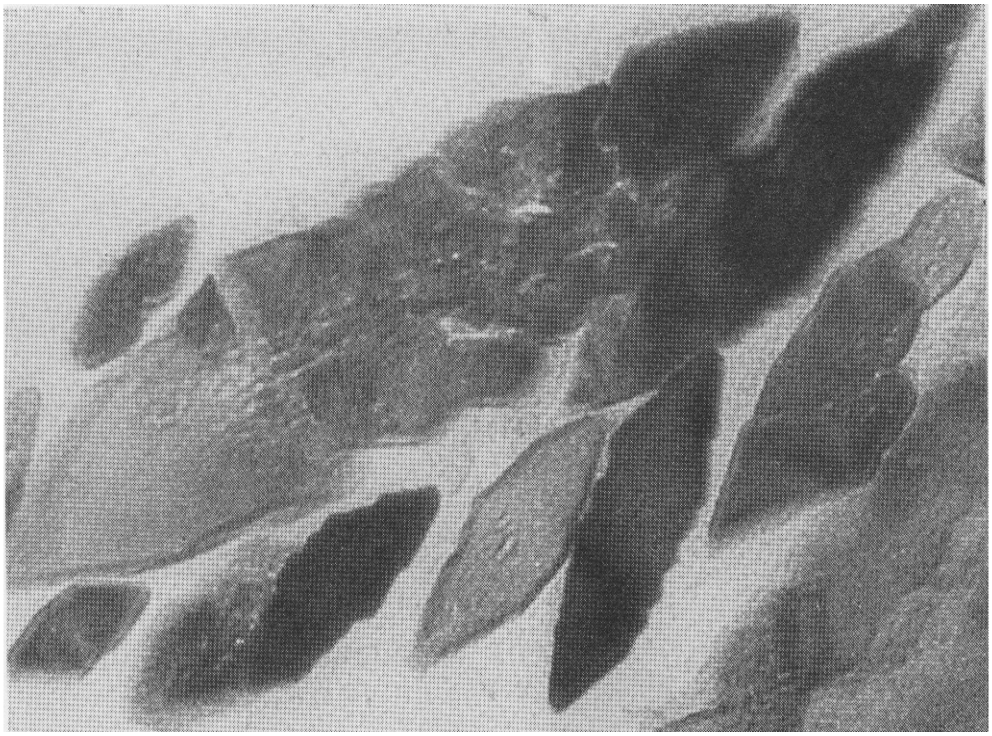


Figure 4.2 High resolution electron micrograph of synthetic goethite crystal cut perpendicular to the needle axis [010]. The crystals are bound to {101} faces (Schwertmann, 1984).

4.1.1 Calculation of Γ_{max}

The theoretical maximum surface coverage can be calculated from the dimension of goethite crystals. The comparison of the calculated data with experimental data will provide more insight into the mechanisms of the reactions occurring on the solid-solution interface. Goethite used in this experiment has a B.E.T area of 36.5 m^2/g. The specific surface area of the edge faces A_e (m^2g^{-1}) was determined by estimating the external areas and volume of particles from Figure (4.1).

Synthetic goethite crystals of size (>0.2μm) usually are acicular crystal with crystal and unit cell dimension of a= 0.9956 nm, b= 0.30215 nm and c= 0.4608 nm. Each unit cell area exposed on the 101 face has a surface area of ab= $3.01*10^{-19}$ m^2. According to Torrent (1990) adsorption of phosphate occurs on the 101 faces of goethite crystal.

$$A_e \quad = \quad (\Sigma \text{ surface area}) / (\Sigma \text{ volume x } \rho)$$

where ρ is the density of crystal (kg m^{-3}).

Using dimensional parameters of a single crystal estimated from the TEM photograph (Figure 4.2) in the calculation gives the following:

Cross sectional area = $37.6 * 10.4$ nm^2 = (assuming a rectangular shape for simplicity).

Σ surface area = $2 * (37.6*10.4 + 10.4* 866 + 37.6*866) = 83918$ $nm^2 = 8.39 * 10^{-14}$ m^2

Σ volume = $10.4* 37.6* 866 =3.39*10^5$ nm^2 $= 3.39 * 10^{-22}$ m^3

$A_e = (\Sigma \text{ surface area}) / (\Sigma \text{ volume } * \rho) = 8.39 * 10^{-14} \text{ m}^2/ (3.39 * 10^{-22} \text{ m}^3 * 4.26*10^6 \text{ gm}^{-3})$

$= 58.1 \text{ m}^2/\text{g}$.

The percentage of calculated area of the B.E.T surface area is about one and a half times larger than the measured areas, indicating that some surface area is lost as the particle aggregate into the large particles seen in the SEM photographs.

One method used in calculating the maximum adsorption density is to assume that the one P is bound per unit cell. Additional assumptions made in the calculation include

- First, all the measured B.E.T surface area is available to phosphate adsorption.
- Second, the 101 face occupies approximately 99% of the total surface area, although irregularities or imperfection may alter the proportion of the 101 face to the total surface.
- Third, only goethite is present, and no other iron hydroxide contributes to surface area.
- Fourth, a binuclear bonding mechanism is assumed.

With the assumptions, the estimation of Γ_{max} can be calculated as follows:

Number of unit cells on the 101 faces, i.e. the maximum adsorption capacity

$(36.5\ m^2g^{-1} * 99\%)/ (3.01*10^{-19}\ m^2/\text{ unit cell}) = 1.2*10^{20}$ unit cell g^{-1}

$= 1.99*10^{-4}$ mol/g

$= 199$ µmol/g

With the assumption of binuclear surface (Sigg and Stumm, 1981), the maximum adsorption would be approximately 100 µmol/g.

Torrent et al. (1990) found that the maximum adsorption of phosphate on 31 synthetic goethite with different crystal morphologies and sizes was 2.51±0.17 µmol/m^2, which is good agreement with one singly coordinated hydroxyl group per unit cell on the predominant 101 plane. Therefore,

$$\Gamma_{max} = 36.5\ m^2/g * 2.5 \mu mol/m^2 = 91\ \mu mol/g$$

The first method showed that the maximum adsorption capacity is approximately equal to 100 µmol/g. The second method showed that the maximum adsorption capacity is 90 µmol/g. The two methods are consistent with each other and therefore the maximum adsorption capacity of phosphate for the goethite used in the study is around 100 µmol/g.

4.2 Direct Analysis of Surface Coverage

Most of the adsorption studies determined surface coverage by measuring the solution concentration changes of before and after adsorption reaction (Loss From Solution method). Although this method is the most popular method in determining the surface coverage in sorption studies, the application of this method in low solids concentration is often limited. If the adsorption reaction occurs at low solid concentration and high solution concentration, the uptake of phosphate is very small with a small change in solution concentration. Surface analysis based on this small change in solution concentration has a high variance.

In this case, direct analysis of phosphate from solid can give more accurate results rather than loss from solution method.

Direct analysis can be done by two different methods.

(1) Desorption of phosphate by different desorbing solutions

(2) Acid digestion of the solid method.

4.2.1 Desorption of Phosphate by Different Desorbing Solutions

The aim of this study is to examine the percent recovery of phosphate by using different desorption solutions. Figure 4.3 shows the amount of phosphate desorbed vs time. In this study, adsorbed phosphate has been desorbed with different desorbing solutions: 6M HNO_3, 1M HNO_3, 0.01M HNO_3, 6M NaOH, 1M NaOH and 0.01M NaOH. The amount of phosphate on goethite is 89 μmol P /g of goethite. These results suggested that both strong acid and strong base do not desorb the adsorbed phosphate completely. The maximum percent recovery observed in desorbing in 0.01 M NaOH after 13 days experiment was approximated 50%, an unacceptably low value. The amount of non-exchangeable phosphate is desorbed within 6 hours reaction time and the reaction reached equilibrium when phosphate is desorbed with 1 M NaOH. These results suggest that the desorbable phosphate is released immediately. When desorbing the surface coverage in highly concentrated 6M NaOH, the amount of phosphate released is lower than that of 1M NaOH and 0.01 M NaOH (possibly due to precipitation of Na_3PO_4). Desorption did not give acceptable recovery in determining surface coverage, therefore a solid digestion method was studied.

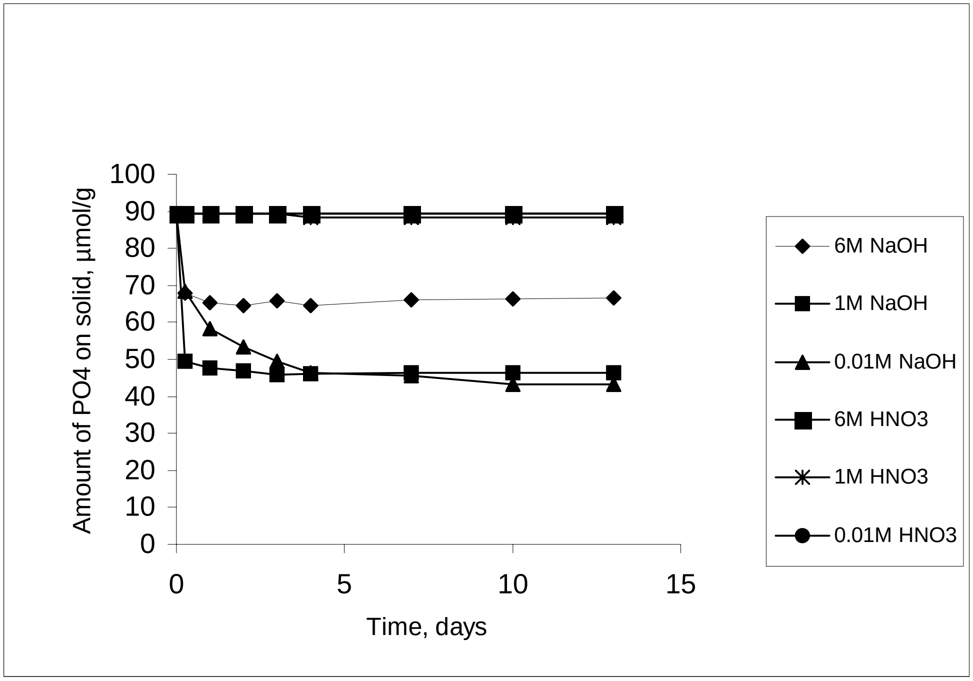


Figure 4.3 Desorption of phosphated goethite with different desorbing solutions.

4.2.2 Acid Digestion Method

Although strongly-bound phosphate cannot be completely desorbed in strong acid or strong base, the adsorbed phosphate can be analyzed by digesting the goethite in hot acid solution. In order to test the digestion method, a solid concentration of 1 g/l and phosphate concentrations of 50, 75, 100, 150 and 200 µM were first selected and adsorbed phosphate was analyzed by using both loss from solution method and acid digestion method.

Table 4.1 shows preliminary examination of the accuracy of acid digestion method. The data suggested that approximately 98 % recovery could be obtained. From this result, the acid digestion method can give approximately complete recovery.

Table 4.1 Comparison of Surface Coverage Measurement by Two Methods

Initial Conc. (mg/l)	Final Conc. (mg/l)	Adsorbed PO4 on goethite (initial - final)	Adsorbed PO4 on goethite (desorbed in hot acid solution)	% recovery
5.9	3.24	2.66	2.61	98.1
4.15	1.38	2.77	2.72	98.2
2.98	0.568	2.412	2.37	98.3
2.83	0.148	2.682	2.19	81.7
1.18	0.03	1.15	1.13	98.3

When comparing the two methods (loss from solution and digestion) at low solids concentration (0.1 g/l), more reliable results are obtained using the digestion method rather than loss from solution method (See Table 4.2). The experiments were conducted in duplicate. Although, some replicates in both methods have almost the same result, some show a significant difference. By using loss from solution method at 0.1 g/l solid concentration, the surface coverage did not increase with increasing initial P concentration. Some data fluctuations can be observed. This is because at low solids concentration the amount adsorbed P on solid surface is much smaller than that of adsorbed P in high solids concentration. In this case, the surface coverage measured by the loss from solution method may have higher uncertainty due to instrument variation than measurement using direct analysis. Therefore, there is considerable variation in the results using the loss from solution method. In the acid digestion method, the adsorption increases with increasing phosphate concentrations accordingly and the result is more reliable than that of loss from solution method. As a result, the digestion method appears to work well for low solid concentrations in the range of 0.1 g/l and 0.01 g/l.

Table 4.2 Comparison of Surface Coverage Measurement by Two Methods

Goethite concentration = 1 g/l

	Loss From Solution Method			Acid Digestion method			
Initial Conc. (mg/l)	Final Conc. (mg/l)	Adsorbed (µmol/g)	Average	Adsorbed (mg/l)	Adsorbed (µmol/l)	Adsorbed (µmol/g)	Average
0.155	0.003	4.90		0.155	5.00	5.00	
0.155	0.003	4.90	4.90	0.155	5.00	5.00	5.00
0.292	0.008	9.16		0.289	9.32	9.32	
0.292	0.006	9.23	9.19	0.287	9.26	9.26	9.29
0.52	0.007	16.55		0.353	11.39	11.39	
0.52	0.0066	16.56	16.55	0.44	14.19	14.19	12.79
1.03	0.009	32.94		0.88	28.39	28.39	
1.03	0.007	33.00	32.97	0.9	29.03	29.03	28.71
1.1	0.1	32.26		1.13	36.45	36.45	
1.1	0.1	32.26	32.26	1.15	37.10	37.10	36.77
2.3	0.167	68.81		2.19	70.65	70.65	
2.3	0.165	68.87	68.84	2.2	70.97	70.97	70.81
2.92	0.568	75.87		2.37	76.45	76.45	
2.92	0.567	75.90	75.89	2.4	77.42	77.42	76.94
5.9	3.24	85.81		2.61	84.19	84.19	
5.9	3.2	87.10	86.45	2.65	85.48	85.48	84.84

Goethite Concentration = 0.1 g/l

	Loss From Solution Method			Acid Digestion method			
Initial Conc. (mg/l)	Final Conc. (mg/l)	Adsorbed (µmol/g)	Average	Adsorbed (mg/l)	Adsorbed (µmol/l)	Adsorbed (µmol/g)	Average
0.071	0	22.90		0.067	2.16	21.61	
0.071	0	22.90	22.90	0.069	2.23	22.26	21.94
0.155	0.13	8.06		0.14	4.52	45.16	
0.155	0.14	4.84	6.45	0.15	4.84	48.39	46.77
0.292	0.135	50.65		0.277	8.94	89.36	
0.292	0.129	52.58	51.61	0.269	8.68	86.77	88.07
0.52	0.397	39.68		0.294	9.48	94.84	
0.52	0.4	38.71	39.19	0.294	9.48	94.84	94.84
1.03	0.944	27.74		0.302	9.74	97.42	
1.03	0.944	27.74	27.74	0.297	9.58	95.81	96.61
1.55	1.24	100.00		0.28	9.03	90.32	
1.55	1.21	109.68	104.84	0.35	11.29	112.90	101.61
2.92	2.57	112.90		0.297	9.58	95.81	
2.92	2.54	122.58	117.74	0.356	11.48	114.84	105.32
5.45	5.46	112.90		0.337	10.87	108.71	
5.45	5.12	106.45	109.68	0.333	10.74	107.42	108.07

4.3 Effect of pH on Phosphate and Arsenate Adsorption Isotherms

The aim of this study is to evaluate the adsorption capacity of phosphate and arsenate on goethite at different pH values.

4.3.1 Phosphate

Figure 4.4 shows the adsorption of phosphate at three different pH values with goethite concentrations of 0.5 g/l and 1 g/l. Initial phosphate concentrations used are in the range of 5 μM to 200 μM. The results show that adsorption increases with decreasing pH. A steeper isotherm is observed in the lower pH. The maximum surface coverage can be observed at pH 3 while minimum surface coverage at pH 10. These results are consistent with previous studies (Hingston, 1981; Li, 1998; Zhao, 2000 and Ler, 2001). Li (1998) studied the phosphate adsorption at constant pH values of 2.52, 3.50, 4.42, 5.45, 6.18 and 8.82. Her studies suggested that the maximum adsorption was observed at low pH and adsorption decreases with increasing pH. The adsorption curves do not reach an adsorption plateau up to initial phosphate concentration of 500 μM.

Langmuir and Frendlich isotherms have frequently been used in describing the adsorption data of phosphate adsorption on soil minerals (Barrow, 1978; Chen et al. 1973 b; Shayan and Davey, 1978). Sorption isotherms in this study follow the general shape of a Fruendlich isotherm at pH 3 and Langmuir sorption isotherm at pH 7 and pH 10. This result is consistent with Ler (2001) and her study of phosphate adsorption on goethite at constant pH value of 1, 1.5 and 2 showed that the isotherms follow Freundlich isotherms.

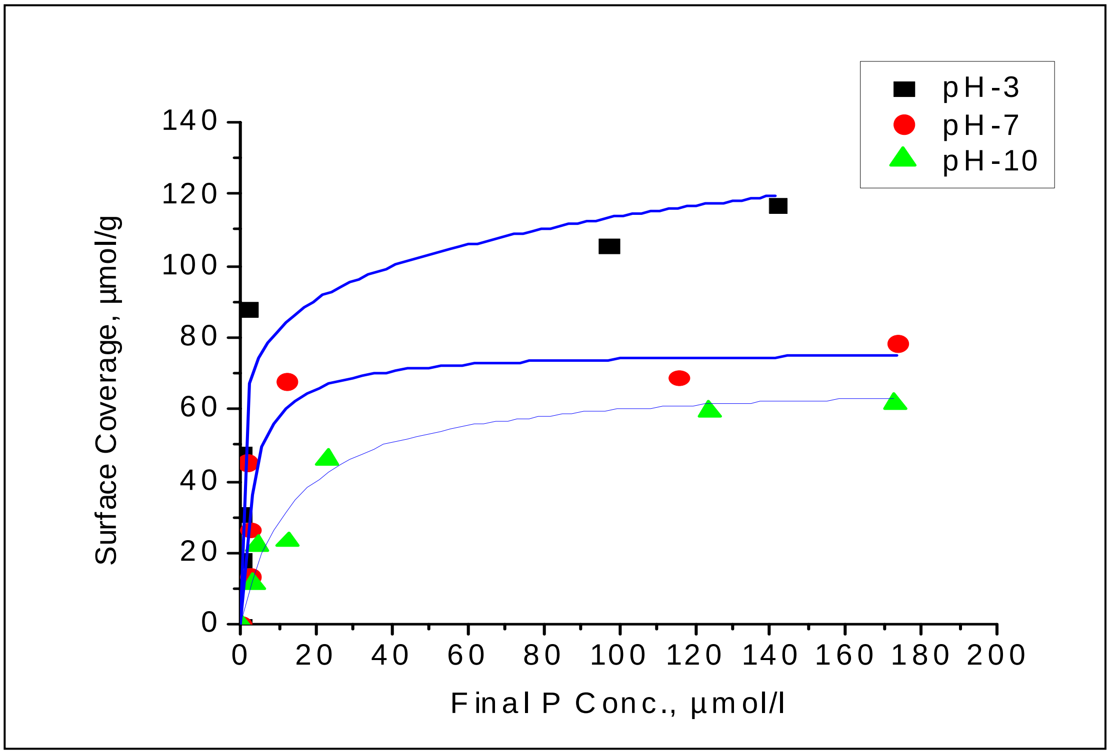


Figure 4.4a Phosphate adsorption isotherms at different pH values
Goethite concentration = 0.5 g/l, Ionic strength = 0.001 M $NaNO_3$
pH= 3, 7 and 10. Equilibrating time = 24 hours

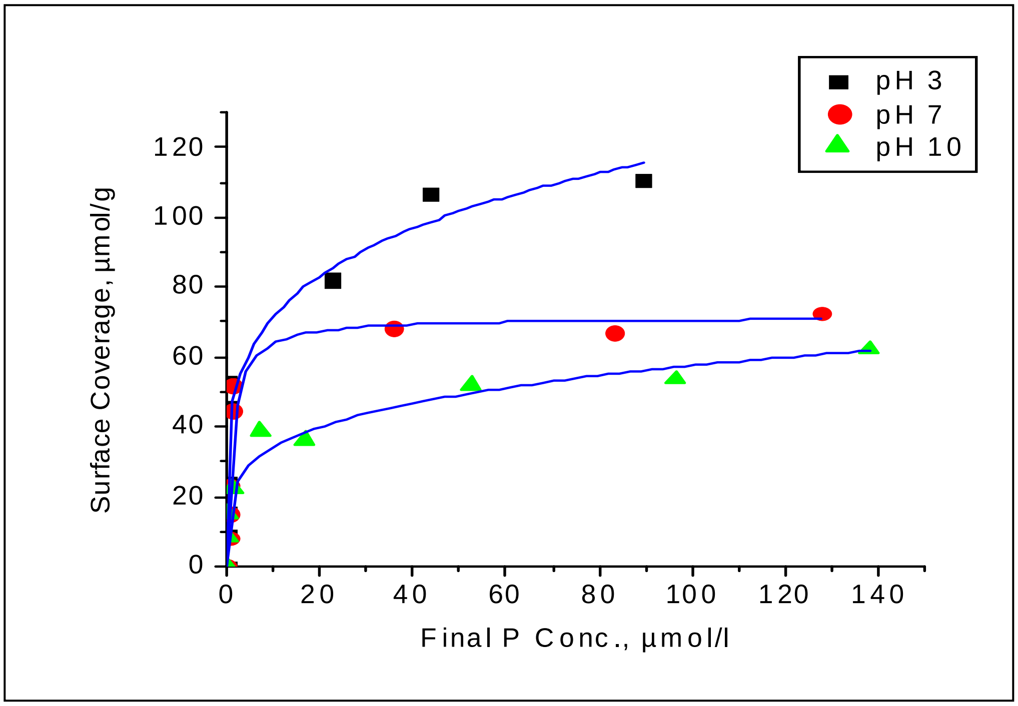


Figure 4.4b Phosphate adsorption isotherms at different pH values
Goethite concentration = 1 g/l, Ionic strength = 0.001 M $NaNO_3$
pH= 3, 7 and 10. Equilibrating time = 24 hours

4.3.2 Arsenate

Arsenate adsorption isotherms at different pH values were also studied. All the experimental conditions are the same as those of phosphate adsorption isotherms, but with initial arsenate concentrations in the range of 5 µM to 200 µM. Solids concentration used for arsenate adsorption isotherms are also 1 g/l and 0.5 g/l.

Again, Figure 4.5a and 4.5b show the arsenate adsorption at different pH values. Like phosphate adsorption, arsenate adsorption also increases with decreasing pH values. A maximum surface coverage is observed at pH 3 and minimum surface coverage is observed at pH 10. This result is in good agreement with Zhao's (2000) study of arsenate adsorption at two different pH values. The maximum surface coverage was higher in adsorption at pH 2.45 than that of pH 5.15. Zhao's study also suggested that phosphate and arsenate have similar adsorption capacity and followed similar isotherms. All the isotherm follow a Langmuir adsorption isotherm in the As concentration range of 5 to 200 µmol/l. Gao and Mucci (2001) also suggested that phosphate and arsenate have similar adsorption patterns on goethite, with adsorption increasing with decreasing pH value. Arsenate has a slightly higher affinity on goethite than phosphate.

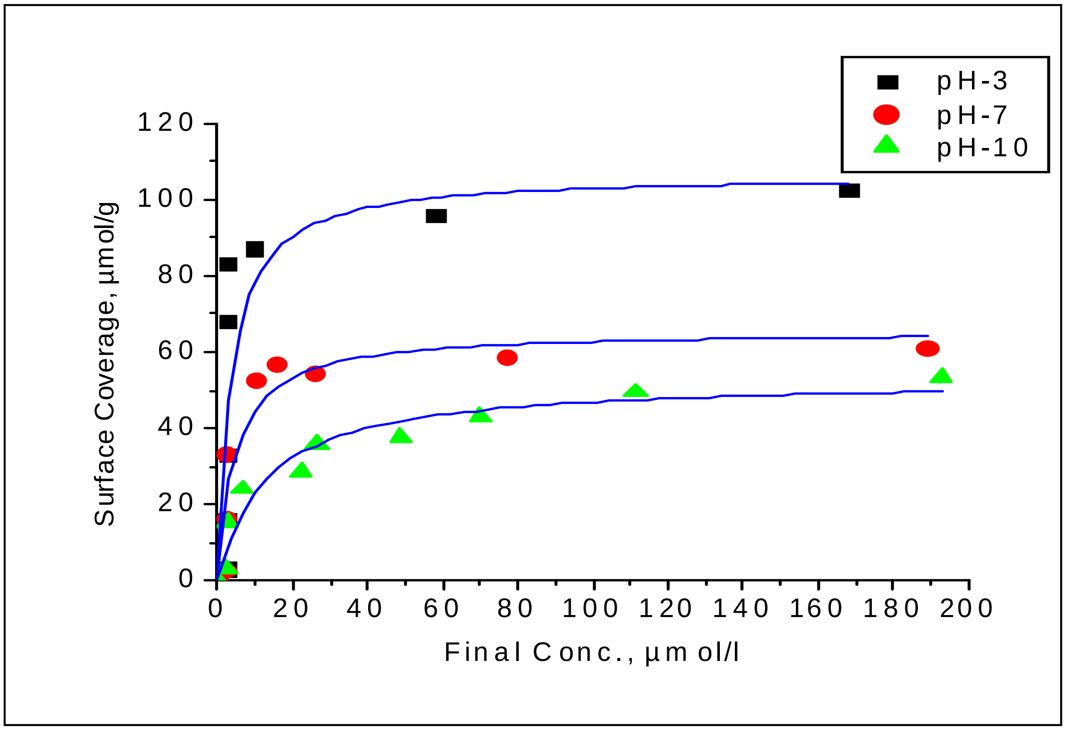


Figure 4.5a Arsenate adsorption isotherms at different pH values
Goethite concentration = 0.5 g/l, Ionic strength = 0.001 M $NaNO_3$
pH= 3, 7 and 10. Equilibrating time = 24 hours

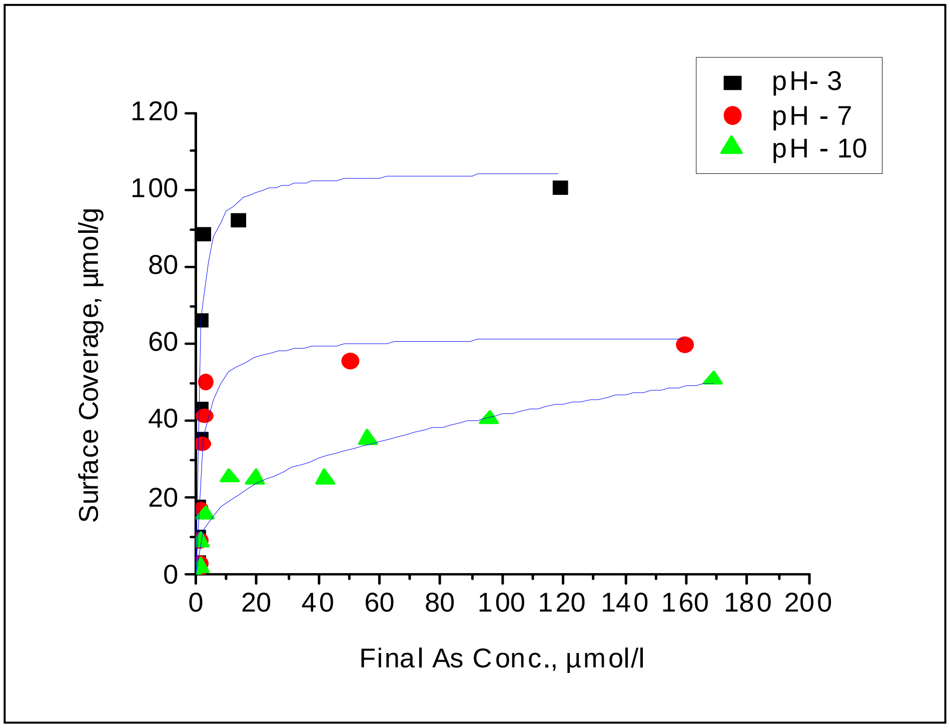


Figure 4.5b Arsenate adsorption isotherms at different pH values
Goethite concentration = 1 g/l, Ionic strength = 0.001 M $NaNO_3$
pH= 3, 7 and 10. Equilibrating time = 24 hours

4.4 Effect of Solids Concentration on Phosphate and Arsenate Adsorption

4.4.1 Initial Studies - pH 3, 7, 10

4.4.1.1 Phosphate

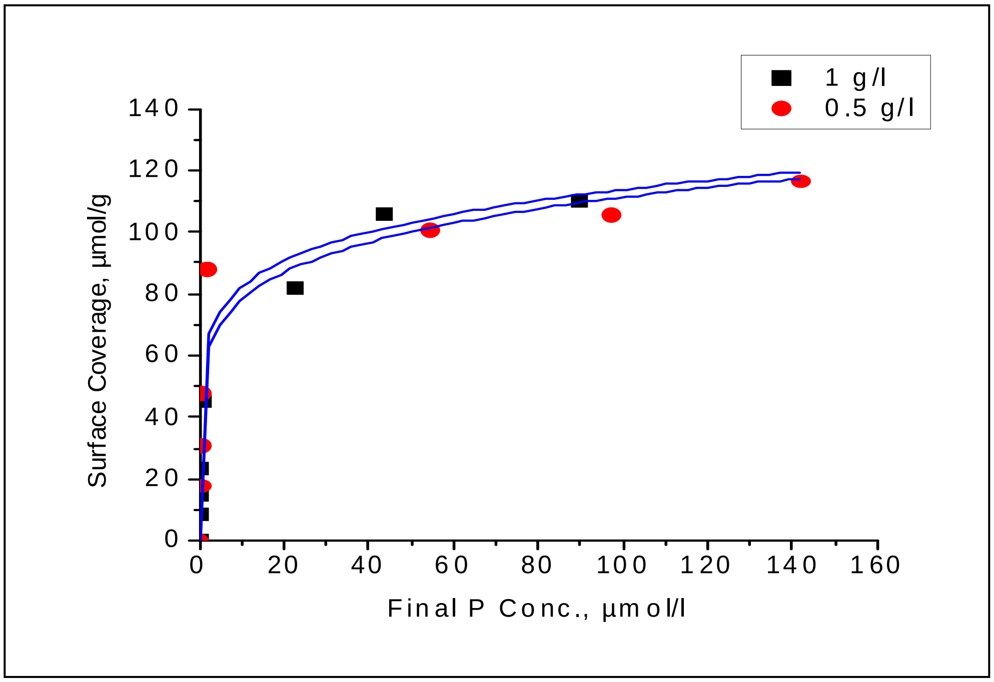
First, the effect of solids concentration on both phosphate and arsenate adsorption was studied when the solids concentration was doubled from 0.5 to 1.0 g/l. The initial studies on the doubling effect of solids concentration on both phosphate and arsenate adsorption have been performed at three different pH values.

Figure 4.6 shows the comparison of phosphate adsorption on goethite at two different solids concentration. At constant pH and comparing the surface coverage at two solids concentrations, the adsorption decreases slightly with increasing solids concentration. Even at pH 3, almost no difference in the isotherm can be observed (Figure 4.6 (a)). Very little difference in the adsorption isotherms can also be seen at constant pH values of pH 7 and 10 (Figure 4.6 (a), (b) and (c)). The similarities suggests that at high solids concentration and low phosphate concentrations the uptake is not affected by the solids concentration and the isotherms fall on the same curve within the initial P concentration range of 5 μmole/l to 200μmole/l.

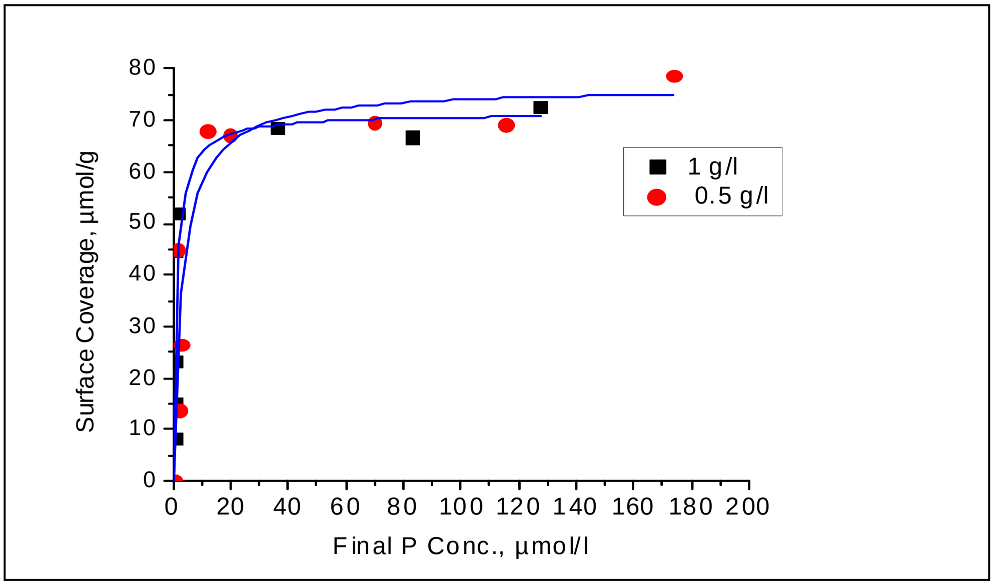
This result is in good agreement with those of previous studies Li (1998), Ler (2001) and Jaio (2003). Jaio (2003) studied the solid concentration effect of phosphate adsorption on gibbsite at different pH of 7, 8 and 10. In his study, a significant decrease in adsorption was observed when the solid concentration increased to ten times. On the other hand, his study showed that there was no effect or small effect on the adsorption isotherm when the solids concentration changed by a factor of two.

Li (1998) studied the effect of solids concentration on phosphate adsorption at low goethite concentration and moderate phosphate concentration. Her study showed the significant change of isotherms at different solids concentration of 0.0146 g/l, 0.0292 g/l and 0.0584 g/l. Her studied also showed there is no effect on adsorption isotherm at low phosphate concentration.

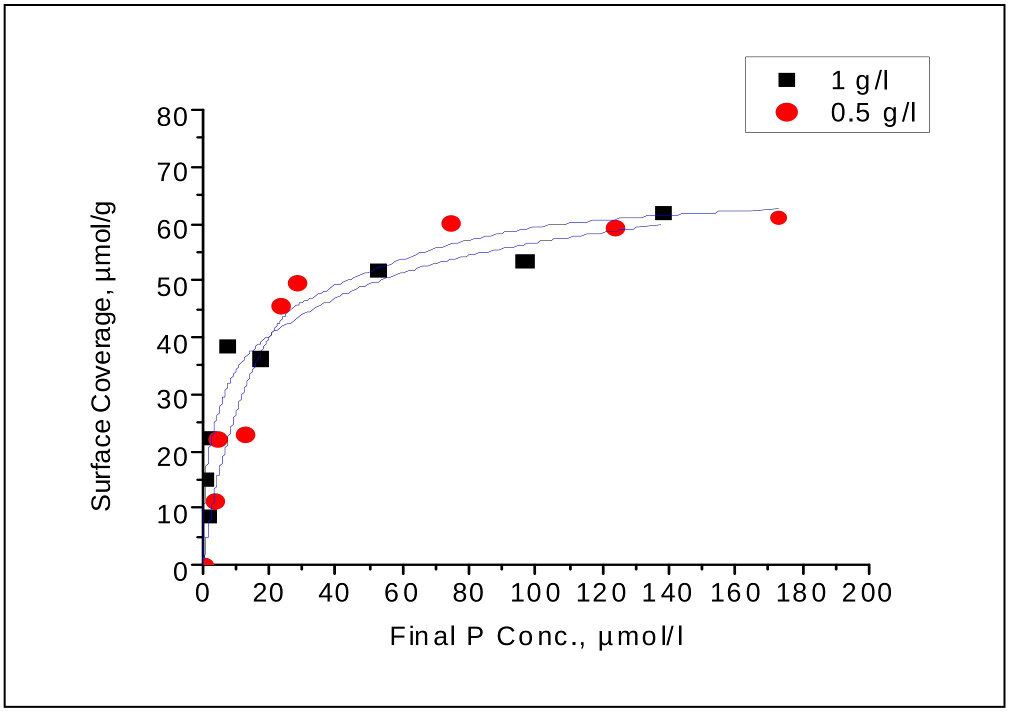
In addition, Ler (2001) studies showed a significant change of phosphate adsorption at low goethite concentration. She suggested the solids concentration has a large influence on the sorption isotherm when the solids concentration change by an order of magnitude while doubling the solids concentration has no effect on adsorption isotherm in the solids concentration range of 0.5 to 1.0 g/l.



(a)



(b)



(c)

Figure 4.6 Phosphate adsorption isotherms at different solids concentration

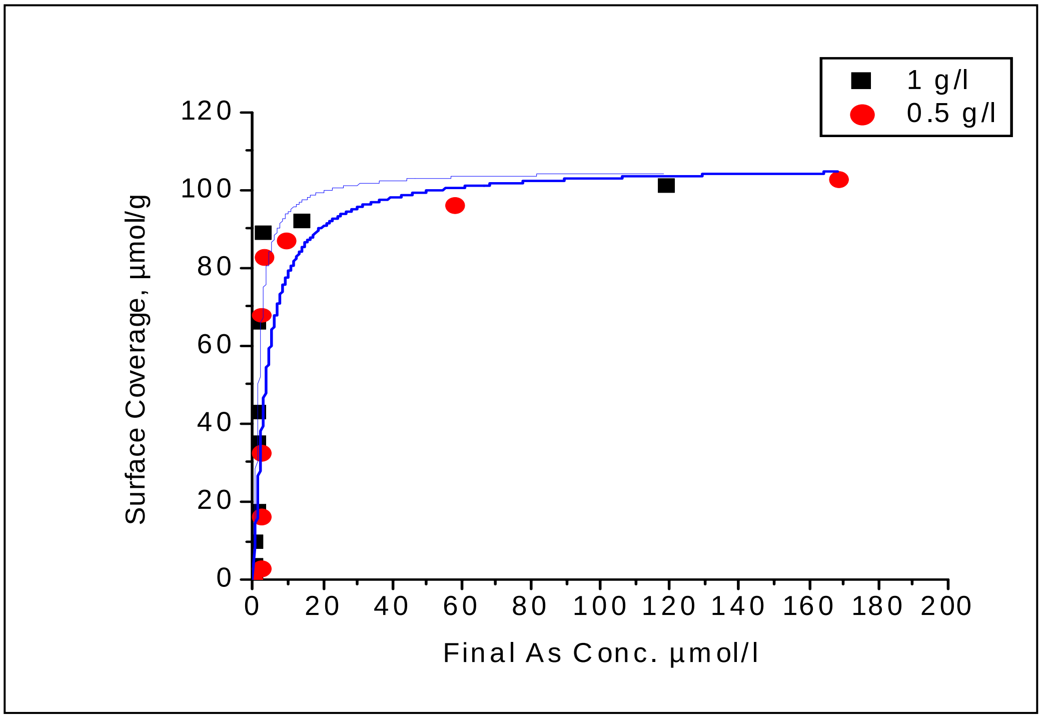
(a) at pH 3, (b) at pH 7, (c) at pH 12

Operation Conditions: Goethite concentration = 0.5 g/l, 1 g/l, Temperature = 22ºC, Ionic strength = 0.001 M $NaNO_3$, Equilibrating time = 24 hours, method used = loss from solution method.Phosphate adsorption isotherms at different solids concentration at pH 10

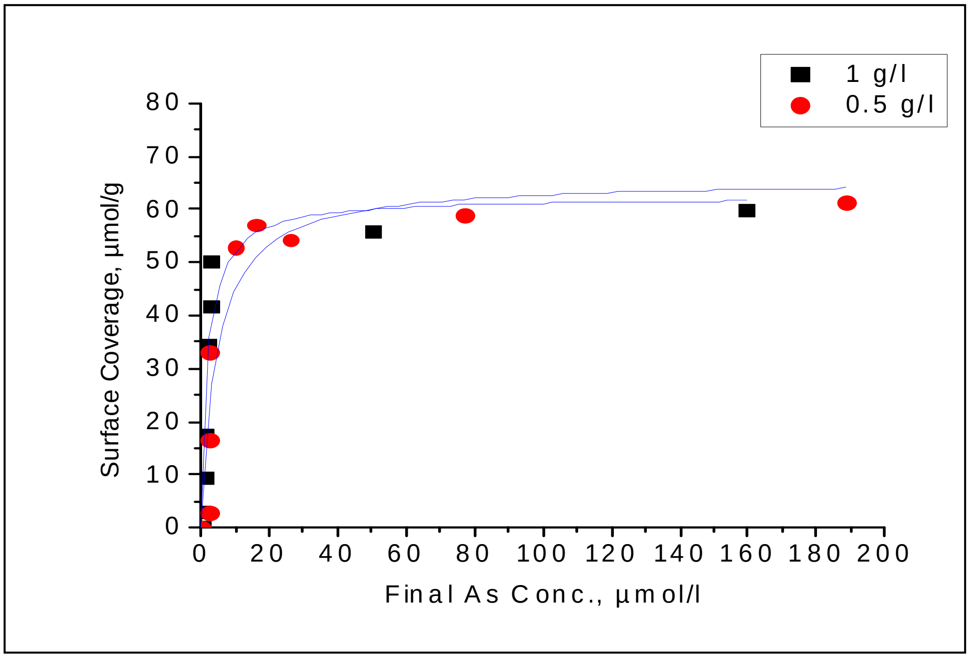
4.4.1.2 Arsenate

No significant effect of solids concentration was observed when solids concentration doubles in the arsenate adsorption isotherms. Comparing the arsenate adsorption capacity when the solids concentration is doubled also shows the solids concentration have no effect on arsenate adsorption isotherm (Figure 4.7a). Figure 4.7 shows the effects of solids concentration on arsenate concentration on goethite at three different pHs. All the experimental conditions and solids concentration used are the same as those of phosphate adsorption. Results in experiments at the three different pHs (3, & and 10) confirm that adsorption did not increase when the solids concentration was doubled.

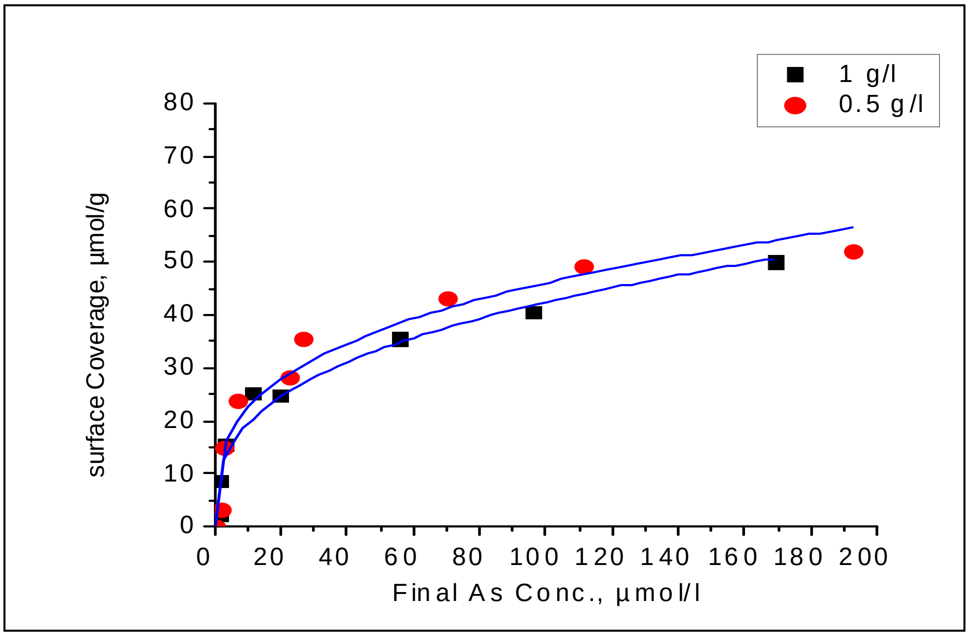
Based on these experiments, doubling the solids concentration from 0.5 to 1.0 g/l has little effect on the adsorption isotherm at the three pH values tested.



(a)



(b)



(c)

Figure 4.7 Arsenate adsorption isotherms at different solids concentration (a) at pH 3, (b) at pH 7, (c) at pH 10.

Operation Conditions: Goethite concentration = 0.5 g/l, 1 g/l, Temperature = 22ºC, Ionic strength = 0.001 M $NaNO_3$, Equilibrating time = 24 hours, method used = loss from solution method.

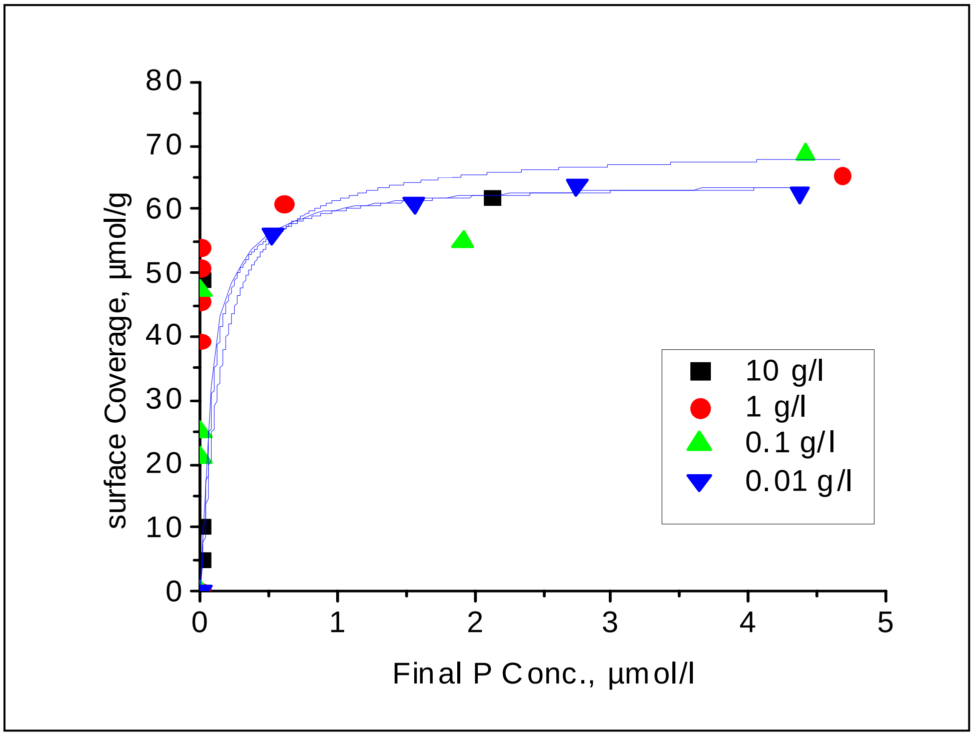
4.4.2 Adsorption at pH 4

4.4.2.1 Effect of Solids Concentration

The adsorption of phosphate at constant pH was studied to determine the effect of solids concentration over a wide range of solid and phosphate concentrations. Four different solids concentrations - 10 g/l, 1 g/l, 0.1 g/l and 0.01 g/l - were selected for this study. Surface coverage was analyzed at different time intervals.

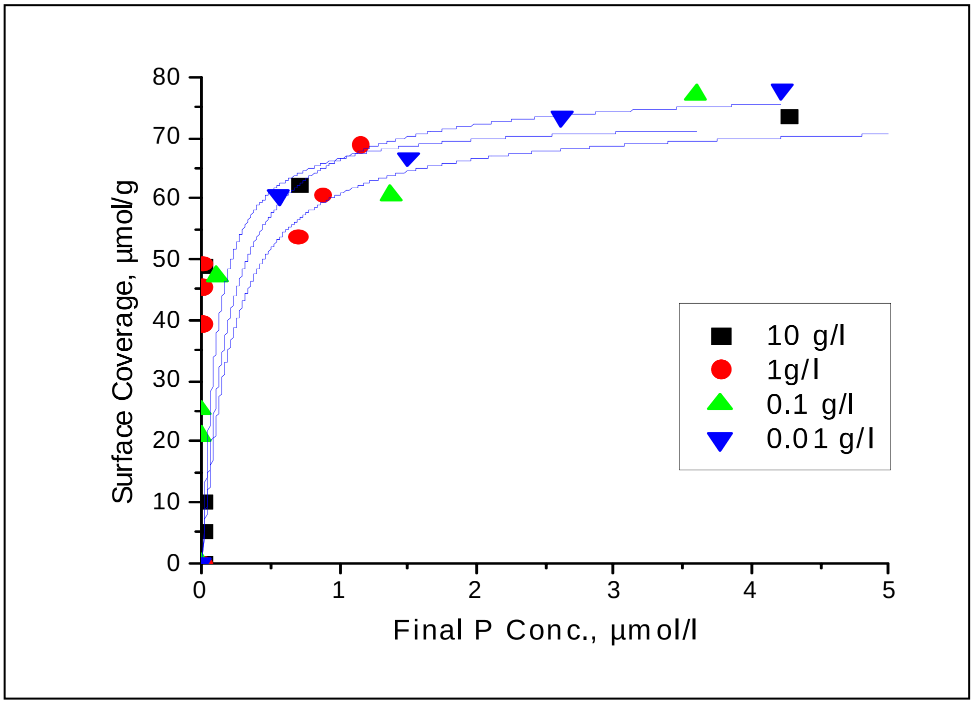
Figure 4.8 shows the effect of solids concentration on phosphate adsorption at low P concentrations. All the results lie approximately on the same curve with no obvious effect of solids concentration. Surface coverage increases rapidly to 60 ~ 65 µmol/g at all solids concentrations and all the adsorption isotherms follow a Langmuir isotherm. After a reaction time of 24 hours (see Figure 4.8 b), sorption increases slowly, with the isotherm still following Langmuir isotherm. Surface coverage increases to 70 ~ 80 µmol/g with an increase in time from 1 to 24 hours.

When the reaction continued to 72 hours, all the curves still show similar trend and no obvious effect of solids concentration is observed on the adsorption isotherm (Figure 4.8c). After 7 days experiment, the isotherm pattern of all solids concentration is more or less steeper with decreasing solid concentration and the maximum sorption is still in the range of 70 to 80 µmol/g at all solids concentration (Figure 4.8d). When adsorption is below the maximum adsorption capacity (100 µmol/g) the solids concentration does not have a significant influence on the adsorption isotherm.



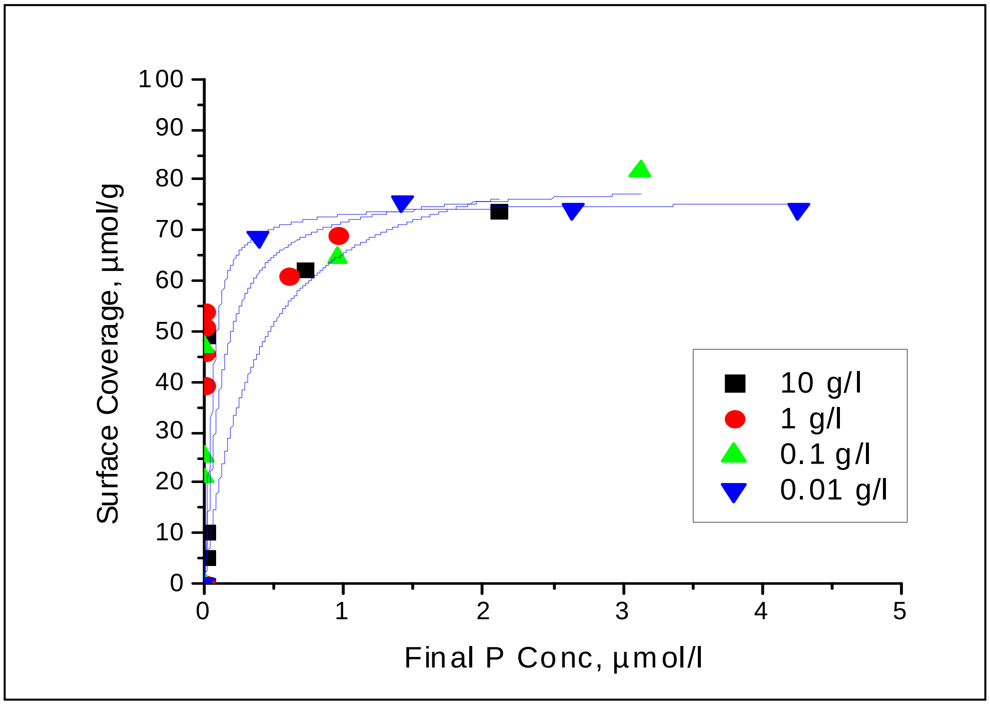
80
70
60
50
40
30
20
10
0
surface Coverage, µmol/g
0
1
2
3
4
5
Final P Conc., µmol/l
10 g/l
1 g/l
0.1 g/l
0.01 g/l

(a)

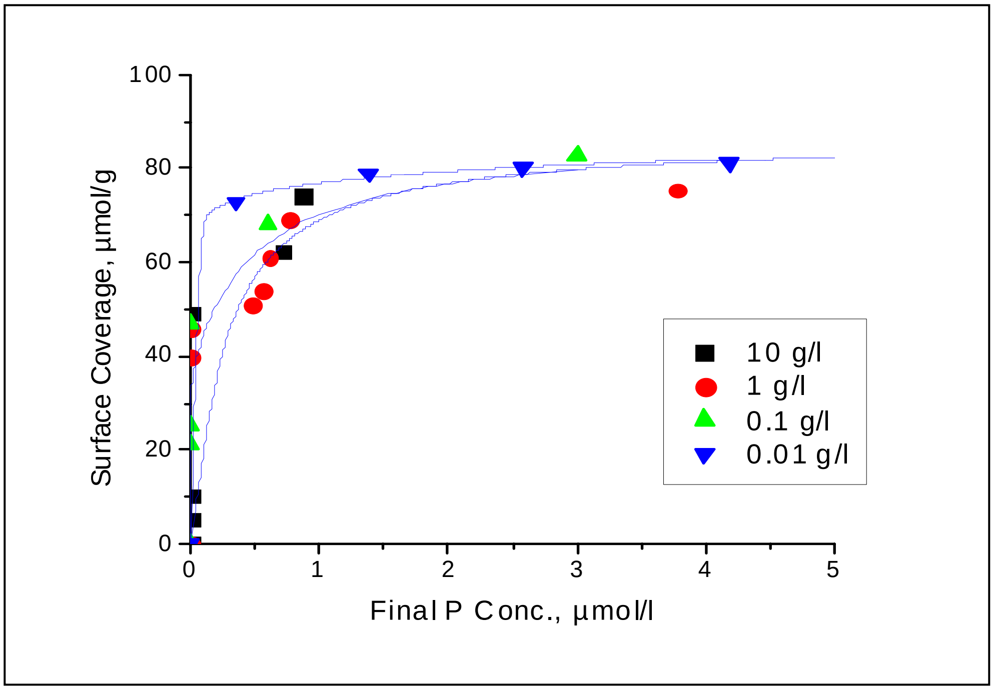


80
70
60
50
40
30
20
10
0
Surface Coverage, µmol/g
0
1
2
3
4
5
Final P Conc., µmol/l
10 g/l
1g/l
0.1 g/l
0.01 g/l

(b)



(c)



(d)

Figure 4.8 Phosphate adsorption isotherms at low phosphate concentrations.
(a) at 1 hour, (b) at 24 hours, (c) at 72 hours, (d) 168 hours.
Operation Conditions: Goethite concentration = 10 g/l, 1 g/l, 0.1 g/l and 0.01 g/l, Temperature = 22ºC, Ionic strength = 0.001 M $NaNO_3$, pH = 4, method used = loss from solution method (10 g/l, 1 g/l), acid digestion method (0.1 g/l and 0.01 g/l).

Figure 4.9 shows the adsorption of phosphate at a high phosphate concentration. The effects of solids concentration are apparent even after one hour reaction. The maximum adsorption can be seen at lowest solid concentration of 0.01 g/l. The surface coverage increases from 74 μmol/g to 153 μmol/g when the solid concentration decreases from 10 to 0.01 g/l.

After 24 hours, the difference in surface coverage at the different solids concentrations increases significantly. Although the surface coverage increase is not a significantly different between 10 g/l and 1 g/l, the differences become greater between 0.1 g/l and 0.01 g/l. At one hour reaction, the maximum surface coverage at 0.01 g/l is 20 μmol/g higher than surface coverage at 0.1 g/l. After 24 hours reaction, the difference in surface coverage between this two solids concentrations becomes 50 μmol/g.

After 72 hours, the maximum surface coverage exceeds 200 μmol/g at 0.01 g/l goethite. The amount of surface coverage increase is high, comparable to that of other three solids concentration. The surface coverage of all solids concentration increases with reaction time, and the maximum surface coverage is observed at the lowest solid concentration. A maximum surface coverage of 216 μmol/g was observed at the end of the 30-days experiment.

Based on these observations, the solids concentration strongly influences the surface coverage at high phosphate concentrations. Surface coverage increases with decreasing solids concentration. The maximum surface coverage is higher than the estimated maximum value based on crystal morphology. The estimated value of maximum surface coverage for mononuclear bonding is 200 μmol/g and for binuclear bonding is 100 μmol/g.

Phosphate adsorption on goethite is generally considered to be bidentate bonding at low pH (Hiemstra and Van Riemsdijk, 1999). Therefore, the maximum surface coverage observed of 216 µmol/g is greater than the estimated maximum monolayer coverage. Except for the 10 g/l sample, all the isotherms follow a Freundlich isotherm.

Therefore, the solids concentration has no effect at low phosphate concentration and significantly influences adsorption at higher concentration.

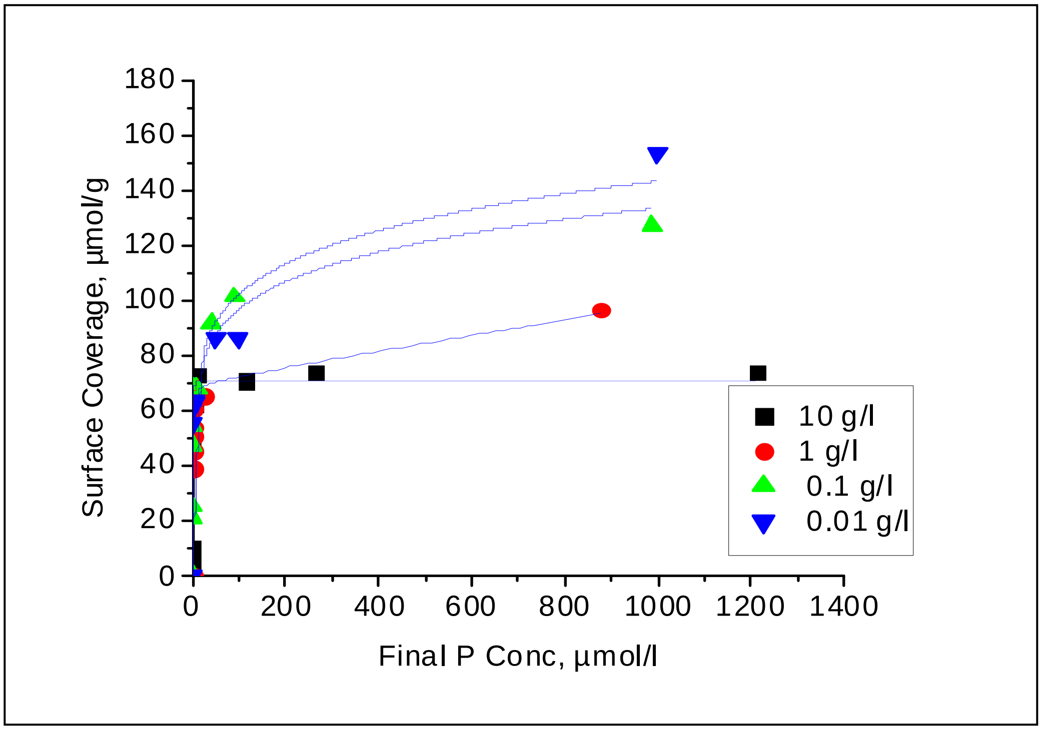


Figure 4.9 (a) Phosphate adsorption isotherms at high phosphate concentrations at 1 hour reaction.

Operation Conditions: Goethite concentration = 10 g/l, 1 g/l, 0.1 g/l and 0.01 g/l, Temperature = 22ºC, Ionic strength = 0.001 M $NaNO_3$, pH = 4, method used = loss from solution method (10 g/l, 1 g/l), acid digestion method (0.1 g/l and 0.01 g/l).

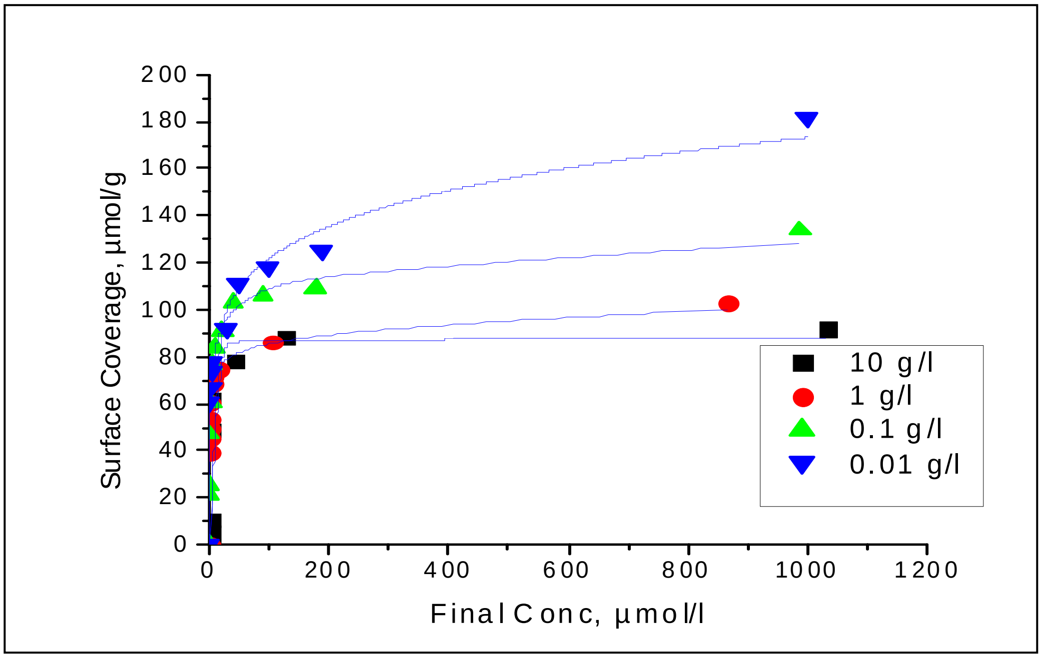


Figure 4.9 (b) Phosphate adsorption isotherms at high phosphate concentrations at 24 hour reaction.

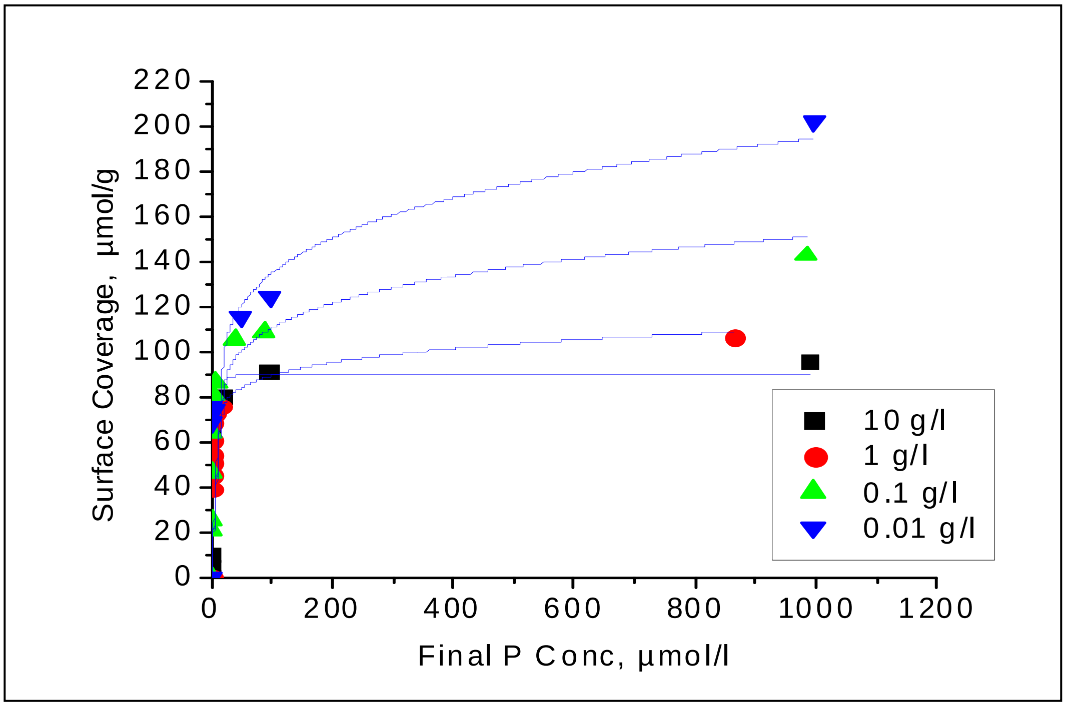


Figure 4.9 (c) Phosphate adsorption isotherms at high phosphate concentrations at 72 hour reaction.

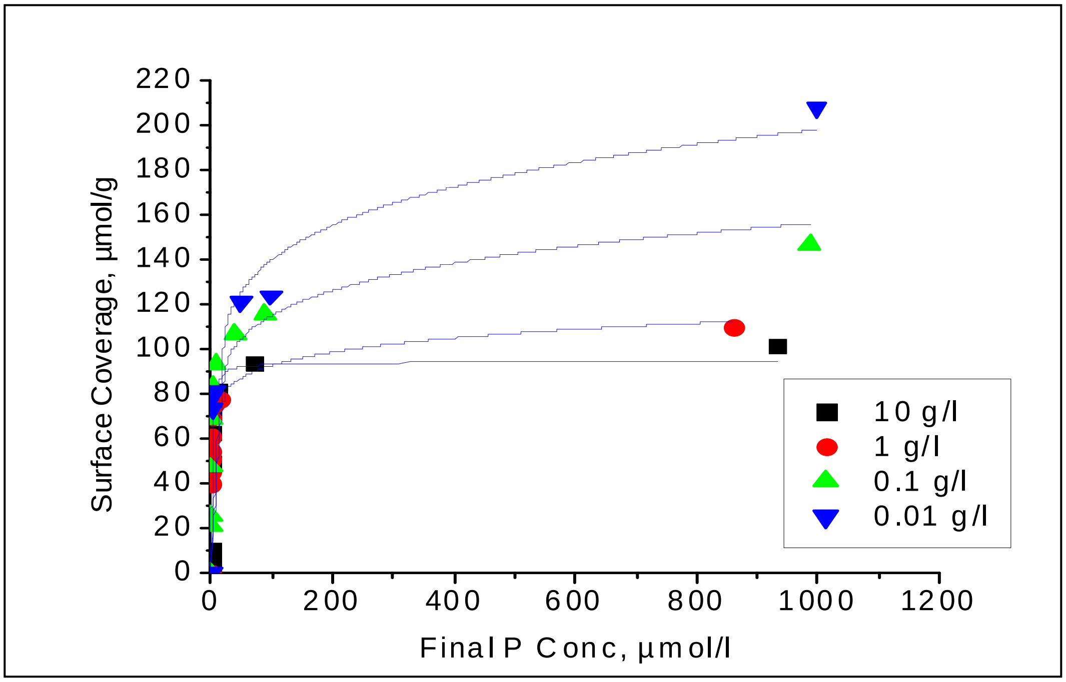


Figure 4.9 (d) Phosphate adsorption isotherms at high phosphate concentrations at 168 hour reaction.

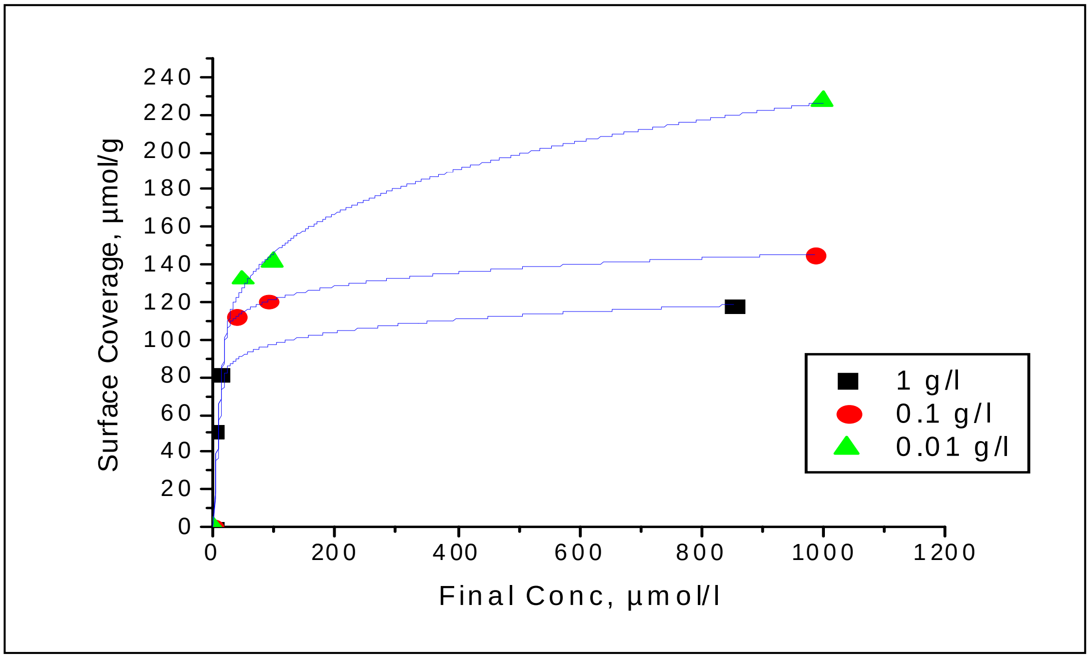


Figure 4.9 (e) Phosphate adsorption isotherms at high phosphate concentrations at 720 hour reaction.

4.4.2.2 Kinetics of Reactions

Phosphate adsorption at the various goethite concentrations follows an Elovich equation (Figures 4.10 to 4.13). The slope of Elovich equation is flat when the phosphate concentration is very low, since the phosphate is rapidly and completely adsorbed. Previous research has shown that phosphate adsorption on goethite consists of an initial rapid reaction and a continuous slow reaction (Stanforth, 1981; Barrow, 1997). In this study, the slow adsorption data are well described by an Elovich equation.

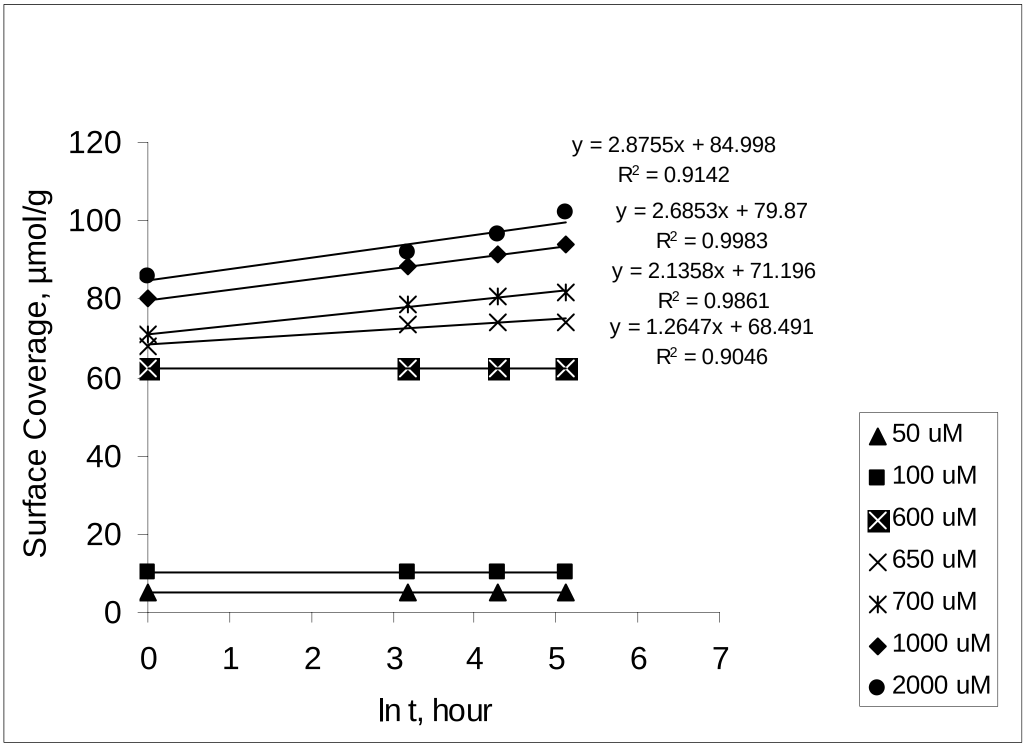


Figure 4.10 Phosphate adsorption kinetics. Goethite concentration =10 g/l, pH = 4, $NaNO_3$ = 0.001 M. Legend "50 µM" means initial phosphate concentration before reaction, and so on.

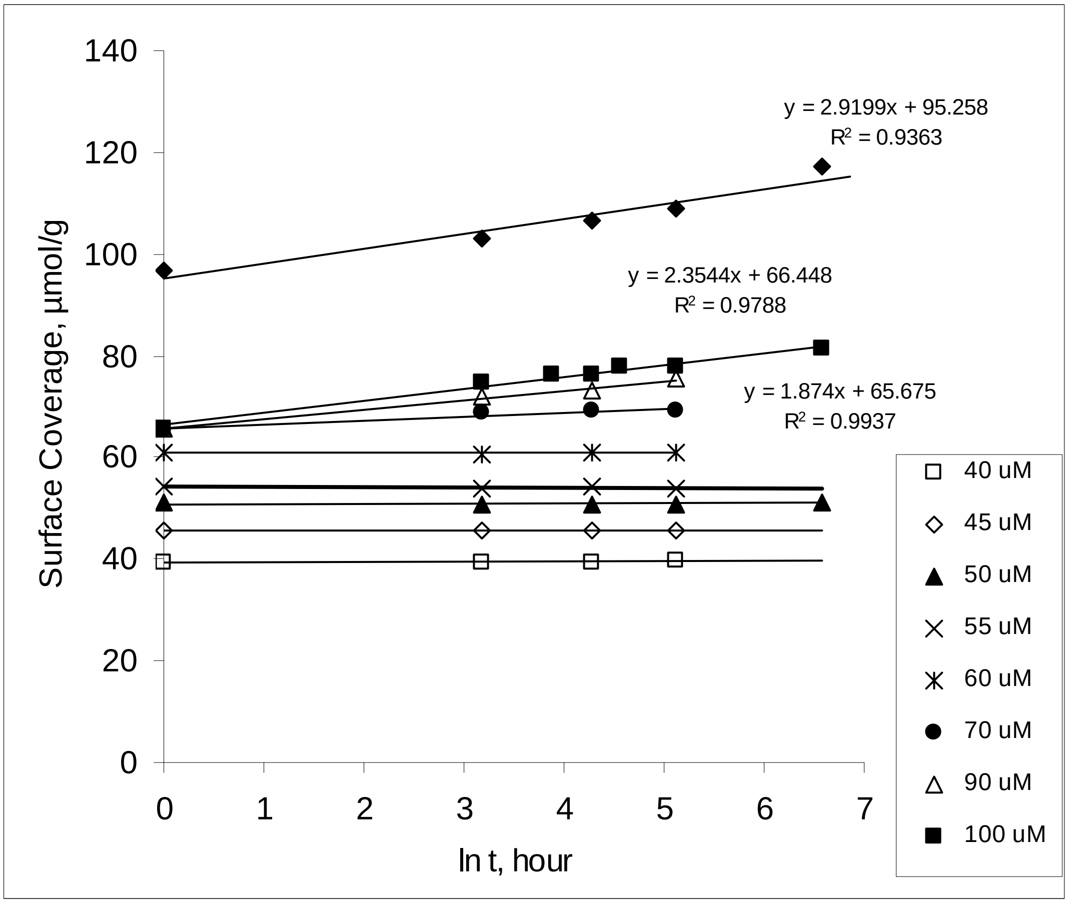


Figure 4.11 Phosphate adsorption kinetics. Goethite concentration =1 g/l, pH = 4, $NaNO_3$ = 0.001 M. Legend “40 µM” means initial phosphate concentration and so on.

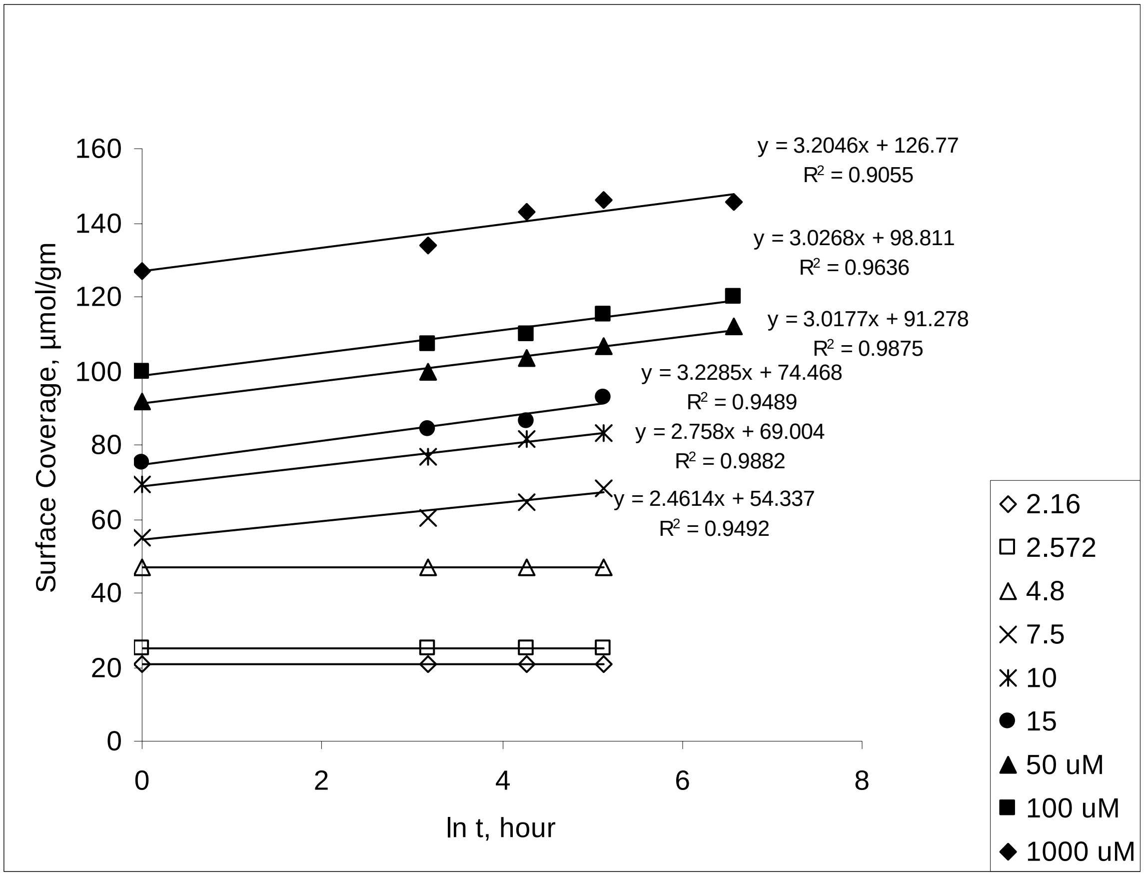


Figure 4.12 Phosphate adsorption kinetics. Goethite concentration = 0.1 g/l, pH = 4, $NaNO_3$ = 0.001 M. Legend “2.16 µM” means initial phosphate concentration and so on.

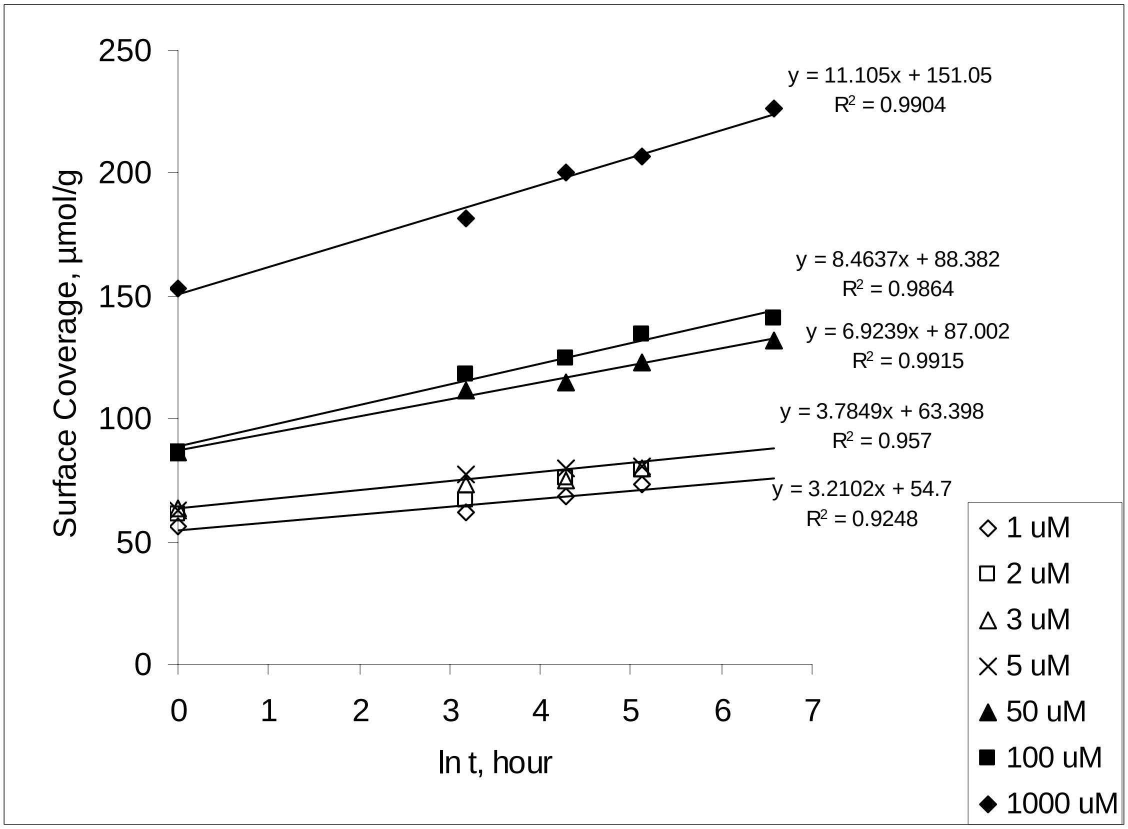


Figure 4.13 Phosphate adsorption kinetics. Goethite concentration = 0.01 g/l, pH = 4, $NaNO_3$ = 0.001 M. Legend "1 μM" means initial phosphate concentration before reaction, and so on.

At low P concentrations and relatively high solids concentration almost all the phosphate in solution is rapidly removed and the reaction becomes P-limited. The flat lines at all solids concentration indicate that the reaction is complete within a short period. Table 4.3 lists the surface coverage at which the transition from P-limited reactions to non P-limited reactions at different solids concentration occurs. The maximum flat line in the figure demonstrates the maximum adsorption capacity for the immediate removal of dissolved P. The transition from P-limited to Elovich-type reaction occurs at approximately 70 μmol/g for all solids concentrations. This result suggests that the reaction continues slowly up to days or weeks when there is enough P in solution. These results indicated that adsorption of phosphate on goethite surface may involve more than just one type of reaction, surface complexation, it may involve other kind of reactions involved as well.

Table 4.3 Surface Coverage at which Transition from P Limited to Elovich Kinetics Occurs (P< 0.5 µmol/l) after 1 hour

Solids Conc. (g/l)	Initial Conc. (µmol/l)	Conc. At 1 hour (µmol/l)	Surface Coverage (µmol/g)	Kinetic Control
10 g/l	500	0.45	49	P limited
	625	2.13	62	Elovich
1 g/l	62	0.6	61	P limited
	70	4.7	65	Elovich
0.1 g/l	4.8	0.095	47	P limited
	7.4	1.92	55	Elovich
0.01 g/l	1.1	0.52	58	Elovich
	2.16	1.56	60	Elovich

The individual graphs (Figures 4.10 to 4.13) show that the slope is steeper with increasing phosphate concentration. At higher solids concentrations (10 g/l, 1 g/l and 0.1 g/l), the Elovich lines are parallel to each other. The slope does not significantly increase with increasing phosphate concentration in high solids concentration (See Figure 4.10, 4.11 and 4.12). This suggested that change in solution concentration (phosphate) does not have an obvious effect on reaction rate at 0.1 to 10 g/l goethite concentration.

In contrast, an obvious effect of slope changes can be seen at low solids concentration (See Figure 4.13, Table 4.4). The Elovich slope significantly increases with increasing phosphate concentration at low solids concentration (0.01 g/l). The slopes increase from 3.2 to 11.1 when initial phosphate concentration increase from 1μM to 1000 μM. This result indicates that the reaction rate is faster at high phosphate concentration and slower at low phosphate concentration. Therefore, the solution concentration has a significant effect on reaction rate at very low solids concentration.

Sharpley (1983) suggested that change in Elovich slope is due to the change of solid to solution ratio, rather than the effect of reaction rate. Pavlatou and Polyzopoulos (1988) suggested that the change in slope is due to surface heterogeneity. In a study of adsorption and desorption of phosphate in four different soil, they suggested that the slope is flatter when the surface is heterogeneous and the slope is steeper when the surface is homogeneous. In this case, the same absorbent, goethite, at different concentrations was used in studying reaction kinetics. Therefore, the slope changes are not the result of surface heterogeneity. It could be the effect of other kind of reactions besides adsorption. The lower the solids concentration, the smaller the surface area available and the fewer sites are available. A maximum surface coverage, 216 μmol/g was observed at 0.01 g/l solid concentration. In this case, the slope of Elovich equation may be attributed to precipitation reaction. At a low solid concentration (0.01 g/l), Elovich slope increases linearly with increasing P concentrations (Figure 4.14). The slope of 0.01 g/l solids concentration significant increases with increasing phosphate concentration while slopes of other three solids concentration lie on the same trend. These results suggest that at higher solids concentration, the precipitation reaction is less obvious because more surface sites are available for adsorption.

Table 4.4 Comparison of Elovich Slopes at Different Solids Concentration

10 g/l goethite			1 g/l goethite			0.1 g/l goethite			0.01 g/l goethite		
PO_4 Conc. µmol/l	Elovich Slope	R^2	PO_4 Conc. µmol/l	Elovich Slope	R^2	PO_4 Conc. µmol/l	Elovich Slope	R^2	PO_4 Conc. µmol/l	Elovich Slope	R^2
50	0.0023	0.4223	40	0		2.16	0		1	3.2102	0.9248
100	0.0042	0.8738	45	0		2.572	0		2	3.474	0.8979
500	0.008	0.3731	50	0		4.8	0		3	2.9576	0.9848
600	0.034	0.8738	55	0		7.5	2.4614	0.9492	5	3.7848	0.957
650	0.222	0.9956	60	0		10	2.758	0.9882	50	6.9636	0.9671
700	2.1358	0.9861	70	0.7987	0.9225	15	3.2285	0.9489	100	8.3415	0.9963
1000	2.6853	0.9983	90	1.874	0.9937	50	3.0177	0.9875	1000	11.122	0.9885
2000	2.8755	0.9142	100	2.3309	0.9904	100	3.0268	0.9636			
			1000	2.9199	0.9363	1000	3.2046	0.9055			

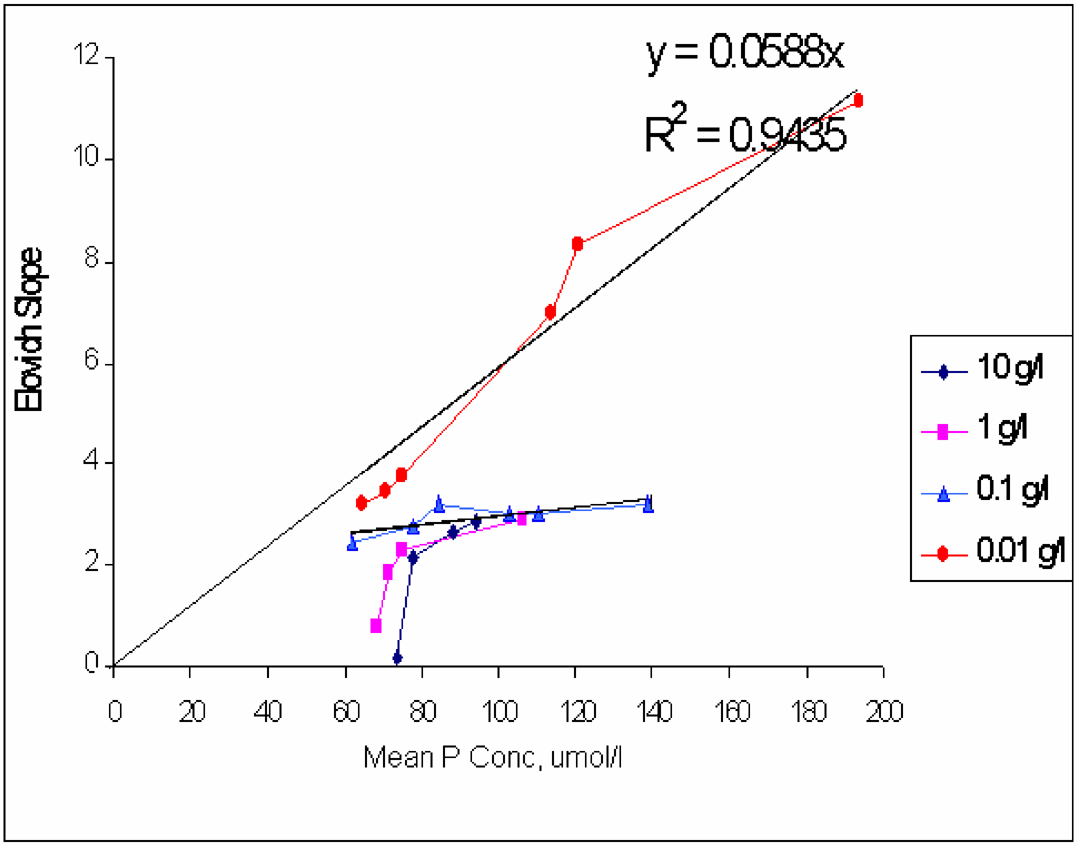


Figure 4.14 The relationship between Elovich slopes and mean adsorbed phosphate. In the legend "10 g/l" refers to the goethite concentration.

4.5 Discussion

Corey (1981) suggested that adsorption and surface precipitation coexist in the reaction between ions and solid surfaces, adsorption predominating at low ion concentration and precipitation dominating at high ion concentration. Bulk solution precipitation or new crystal formation can occur at sufficiently high ion concentration. Ler and Stanforth (2002) suggested that the adsorption-precipitation reaction of phosphate at the oxide surface occurs in four steps. First, adsorption of phosphate (surface complex formation) followed by ternary adsorption of iron (surface precipitation), the dissolution of goethite, and adsorption of phosphate on sorbed iron to continue surface precipitation. The adsorption reaction has only one step (the first step) while precipitation involves all four steps. This results in the phosphate sorption reaction at the goethite surface having two phases: a rapid adsorption step, followed by a continuous precipitation reaction.

At low phosphate concentration, the adsorption isotherms do not change with solids concentration in the range from 10 g/l to 0.01 g/l. There is no solids concentration effect on adsorption isotherm at low phosphate concentration (< 60 μmolg^{-1}) and the sorption isotherm begins to be influenced only when surface coverage exceeds 70 μmolg^{-1} (see Fig 4.7). At low phosphate concentration, the adsorption rapidly reaches 60 µmol/g. Above this surface coverage, the solids concentration begins to influence the adsorption isotherm.

A transition point can also be clearly seen in kinetic studies. There is a rapid reaction that goes to a completion up to a surface coverage of between 50 to 60 µmol/g. At high solids concentration, this reaction depletes the available P from solution (to a P concentration of < ~0.5 µM). At low solids concentration, the phosphate concentration is not significantly depleted but the reaction still goes to about the same surface coverage (Figure 4.11). This result suggests that increasing or decreasing the solids concentration has no effect on the initial adsorption reaction, which goes to completion very rapidly. Above the surface coverage of around 60 μmol/g, the reaction occurs more slowly and the surface coverage linearly increases with logarithm of time. The initial rapid reaction may be attributed to adsorption, while slow and continuous reaction may involve another kind of reaction, probably precipitation. If the reaction at the oxides surface is adsorption only, the reaction will finish when all the surface sites are saturated. The sorption isotherm will not be affected by the solids concentration. During the slow reaction, the sorption increases with time and decreasing solids concentration. The reaction has not finished up to 30 days experiment. Therefore, this phase may be due to the formation of multi-layer surface coverage (precipitation reaction). The slopes of the lines indicate the rate of precipitation reaction. Moreover, the slopes of line increase with increase in phosphate concentration and decrease in solid concentration (Table 4.4).

When comparing the Elovich slope at individual solids concentration, the slope is very high at very low solids concentration. The Elovich slopes of other three solids concentrations lie on the same trend, suggesting that the rate of reaction (precipitation) does not significantly change with decreasing the solids concentrations from 10 - 0.1 g/l. A very small slope indicates that all the phosphate is depleted before the end of the experiment. At high solids concentration, the large amount of available surface sites for phosphate sorption and dissolution of goethite may result in a slower rate of the precipitation reaction. The driving force necessary for dissolution depends on the undersaturation with respect to oxides. The rate of reaction therefore will increase with the degree of undersaturation (Bloom and Nater; 1991, Casey 1995).

However, at very low solids concentration, the Elovich slopes abruptly increase even at very low phosphate concentration. In addition, the slope is comparatively higher than those of other three solids concentrations. This result showed that the reaction rate during precipitation is significantly increased at low solids concentration.

The adsorption isotherms also show an effect of solids concentrations. The isotherms change from Langmuir to Freundlich when the solids concentrations decrease from 10 g/l to 0.01g/l. Except for the 10 g/l solids concentration, all the isotherms followed a Freundlich isotherm. This result is deviate from the major assumption of mono layer surface coverage formation of the SCM. This effect is clearly observed at sorption from high phosphate concentrations.

Although previous studies at NUS showed the solid-solution ratio effect of phosphate adsorption on goethite (Li, 1998; Ler, 2001), they used the indirect analysis of surface coverage (loss from solution method). In contrast, this study used the direct analysis from solid surface to give more accurate result for sufficiently high phosphate concentration and low solid concentration. The results are consistent with previous studies (Li, 1998; Ler, 2001).

All surface reactions should be independent of solids concentration, since surface coverage calculation is based on the amount of phosphate on solid per weight of solid in solution. However a precipitation reaction dependant on the dissolved concentrations of the ions may show an effect of the amount of solids present in the solution, as shown below:

Assume that sufficient P is added to achieve monolayer coverage (70 µmol/g). Further, assume that 1 µM of Fe from solid dissolves and precipitates on the surface, taking with it another 1µM P from solution. After precipitation, the resultant surface coverage becomes

0.01 g/l 70 µmol/g + 1 µM/0.01 g/L = 170 µmol/g
0.1 g/L 70 µmol/g + 1 µM/0.1 g/L = 80 µmol/g
1.0 g/L 70 µmol/g + 1 µM/1.0 g/l = 71 µmol/g
10.0 g/L 70 µmol/g + 1 µM/10 g/l = 70.1 µmol/g

The surface coverage for low solids concentration samples increases significantly, while the higher surface coverage samples stay almost the same. Therefore, this apparent increase in surface coverage for low solid samples may be the result of a precipitation reaction rather than surface complexation. In real samples, the amount of Fe dissolution in different solids concentration samples may not be the same. The dissolution of Fe may depend on the amount of solids in solution. As a result, the surface coverage obtained in this study at very low solids concentration is not as high as calculation based on the assumption of equal amount of Fe dissolution and surface coverage at high solids concentration are higher than calculated surface coverage based on same assumption. This result suggested that precipitation reaction can therefore occur not only at low solids concentration samples but also possibly at high solids concentration samples. But precipitation reaction can be more clearly seen at low solids concentration samples.

In conclusion, solids concentration has no effect on adsorption isotherm at low phosphate concentration, even for the reaction times of hours to weeks. The transition from adsorption to precipitation occurred at around 60-70 μmolg^{-1}. Precipitation significantly influences the isotherms at high phosphate concentrations. The solids concentration does not influence adsorption, while significantly influencing the precipitation reaction. The maximum surface coverage of 216 μmolg^{-1} is higher than estimate maximum surface coverage value of 100 μmolg^{-1}. Therefore, the reaction at the oxides surface includes not only adsorption reaction but also precipitation reaction.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this study, the reaction mechanism or behavior of ion adsorption at the solid surface was investigated. One of the main purposes of this research is to evaluate the effect of the solids concentration on the adsorption isotherm. First the surface area of goethite measured using B.E.T is 36.5 ± 0.5 m^2g^{-1}. The maximum monolayer coverage was calculated based on the surface area measurement by using different methods. The estimated maximum monolayer surface coverage based on the calculation of Torrent (1990) is 100 µmol/g.

Initially, phosphate and arsenate adsorption isotherms at three pH levels of acid, base and neutral (pH 3, 7 and 10) have been studied. The results showed that the surface coverage increases with decreasing pH. All the isotherms follow the Langmuir equation. Doubling the solids concentration did not significantly change the adsorption isotherm at low to intermediate phosphate concentrations.

The adsorption isotherms of four different solids concentrations were run at pH 4. An acid digestion method was used in measuring the phosphate adsorption at 0.1 g/l and 0.01 g/l goethite concentrations while loss from solution method was used in measuring phosphate adsorption at 10 g/l and 1 g/l solids concentration. At low phosphate concentration, the solids concentration has no effect on the adsorption isotherms in the equilibrium phosphate concentration range of 0~5 µM. All the isotherms follow a Langmuir adsorption isotherm and surface coverage at all solids concentrations increased to 60 ~ 70 µmol/g after 1 hour reaction, and adsorption increase with increasing reaction time. The solids concentration has no effect on adsorption isotherms for the low phosphate concentration up to a reaction time of 7 days and the maximum adsorption capacity does not exceed 70 ~ 80 µmol/g.

In contrast, solids concentration did have a significant influence on the adsorption isotherm at phosphate concentrations up to 1000 µM. Phosphate adsorption significantly increased with decreasing solids concentration. The isotherms of all solids concentration followed a Freundlich isotherm, except for the 10 g/l solids concentration. The surface coverage also increased with the time. The maximum surface coverage, 216 µmol/g, is significantly higher than estimated value for maximum monolayer coverage of 100 µmol/g and suggests the formation of precipitation reaction (or multilayer adsorption) at low solids concentration. Although the results are inconsistent with surface complexation model (SCM), the results are in good agreement with previous researchers Li (1998), Ler (2000), and Jaio (2003).

Maximum monolayer sorption capacity was also examined using two different approaches. Isotherms studies of low P concentration and kinetic studies at different solids concentration suggested that monolayer surface coverage may be in the range of 50 ~ 70 µmol/g (according to sorption isotherm at low P at 1 hour reaction and rapid reaction at kinetics studies) and may not exceed 80 µmol/g (according to sorption isotherm at low P at 7 days reaction). This result is also good agreement with estimated maximum adsorption based on surface area of this study.

The results are also supported by the reaction kinetics. This study suggested that two types of reaction occur at the goethite surface: an initial rapid reaction and a continuous slow reaction. The rapid reaction may be attributed to adsorption and slow and continuous reaction may be attributed to precipitation. The slow reaction kinetics follows an Elovich equation. The Elovich slope of kinetics studies may appear to suggest the possibility of precipitation reaction. The largest slope is obtained at very low solids concentration (0.01 g/l) and at the same time, maximum surface coverage of three times higher than the estimated value is also observed at same solids concentration.

Therefore, the reaction at the oxides surface is not as simple as one type of reaction in the model assumption. In practice, there may have other kind of reaction besides surface complex formation reaction. The other reactions, such as precipitation, should be considered in developing models for phosphate sorption. The actual maximum adsorption can be examined from the solids concentration effect. In addition, sorption increase with time should be also considered in modeling ion adsorption at the oxide surface.

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APPENDIX A

Experimental Data for Direct Analysis of Phosphate Adsorption

Table A.1 Experimental Data for Acid Digestion Method

Goethite Concentration = 1 g/l									
Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (µmol/l)	Average	mean variance (%)	Adsorbed (mg/l)	Adsorbed (µmol/l)	Adsorbed µmol/g	Average	Mean variance (%)
0.155	0.000	0.000			0.155	5.00	5.00		
0.155	0.000	0.000	0.000	0.000	0.155	5.00	5.00	5.00	0.000
0.292	0.003	0.097			0.289	9.32	9.32		
0.292	0.005	0.161	0.129	49.6	0.287	9.26	9.26	9.29	0.700
0.520	0.167	5.39			0.353	11.4	11.4		
0.520	0.080	2.58	3.98	70.4	0.440	14.2	14.2	12.8	21.95
1.03	0.150	4.84			0.880	28.4	28.4		
1.03	0.130	4.19	4.52	14.3	0.900	29.0	29.0	28.7	2.25
1.10	0.000	0.000			1.10	35.5	35.5		
1.10	0.050	1.61	0.807	200.	1.05	33.9	33.9	34.7	4.65
2.30	0.110	3.55			2.19	70.7	70.7		
2.30	0.100	3.23	3.39	9.51	2.20	70.9	70.9	70.8	0.456
2.92	0.550	17.7			2.37	76.5	76.5		
2.92	0.520	16.8	17.5	5.61	2.40	77.4	77.4	76.9	1.26
5.90	3.29	106			2.61	84.2	84.2		
5.90	3.25	105	106	1.22	2.65	85.5	85.5	84.8	1.52

For duplicate samples, percent variance can be calculated as follows:

$$\text{Mean Variance (\%)} = \left| (\text{Replicate})_1 - (\text{Replicate})_2 \right| / \text{average} * 100$$

Table A.2 Experimental Data for Acid Digestion Method

Initial Conc mg/l	Final Conc mg/l	Final Conc µmol/l	Average	Mean variance %	Adsorb-ed mg/l	Adsorb-ed µmol/l	Adsorb-ed µmol/g	Average	Mean variance %
0.071	0.004	0.129			0.067	2.16	21.6		
0.071	0.002	0.065	0.097	66.0	0.069	2.23	22.3	21.9	2.94
0.155	0.015	0.484			0.140	4.52	45.2		
0.155	0.005	0.161	0.323	100.	0.150	4.84	48.4	46.8	6.9
0.292	0.015	0.484			0.277	8.94	89.4		
0.292	0.023	0.742	0.613	42.1	0.269	8.68	86.8	88.1	2.93
0.520	0.226	7.29			0.294	9.48	94.8		
0.520	0.226	7.29	7.29	0.000	0.294	9.48	94.8	94.8	0.000
1.03	0.728	23.5			0.302	9.74	97.4		
1.03	0.733	23.7	23.6	0.683	0.297	9.58	95.8	96.6	1.67
1.55	1.27	41.0			0.280	9.03	90.3		
1.55	1.20	38.7	39.8	5.67	0.350	11.3	113.	102.	22.2
2.92	2.62	84.6			0.297	9.58	95.8		
2.92	2.56	82.7	83.7	2.28	0.356	11.5	115.	105	18.1
5.45	5.11	165.			0.337	10.9	109.		
5.45	5.12	165.	165.	0.079	0.333	10.7	107.	108.	1.2

Mean Variance (%) = $\left| (\text{Replicate})_1 - (\text{Replicate})_2 \right|$ / average*100 %

Table A.3 Experimental Data for PO_4 Desorption in 6 M NaOH Solution

	Desorbing Solution	6mol/l NaOH				
	Initial PO4 (mg/l)	4.15				
	Adsorbed PO4 (mg/l)	2.77				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	0.673	0.657	0.665	0.02406	2.41
	1	0.708	0.784	0.746	0.102	10.2
	2	0.735	0.8	0.768	0.085	8.47
	3	0.687	0.776	0.732	0.122	12.2
	4	0.753	0.786	0.769	0.043	4.29
	7	0.67	0.780	0.725	0.152	15.2
	10	0.642	0.780	0.711	0.194	19.4
	13	0.628	0.780	0.704	0.216	21.6
Amount of PO4 on solid (µmol/gm)	0	89.4	89.4	89.4	0.000	0.000
	0.25	67.6	68.2	67.9	0.008	0.760
	1	66.5	64.1	65.3	0.038	3.76
	2	65.6	63.5	64.6	0.032	3.25
	3	67.2	64.3	65.6	0.044	4.37
	4	65.1	64.0	64.5	0.016	1.65
	7	67.7	64.2	66.0	0.054	5.38
	10	68.6	64.2	66.4	0.067	6.7
	13	69.1	64.2	66.6	0.074	0.11

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average
% variance = mean variance * 100%

Table A.4 Experimental Data for PO_4 Desorption in 1 M NaOH Solution

	Desorbing Solution	1mol/l NaOH				
	Initial PO4 (mg/l)	4.150				
	Adsorbed PO4 (mg/l)	2.770				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	1.24	1.24	1.24	0.000	0.000
	1	1.29	1.30	1.29	0.008	0.77
	2	1.28	1.36	1.32	0.061	6.06
	3	1.23	1.47	1.35	0.178	17.8
	4	1.26	1.34	1.30	0.062	6.15
	7	1.17	1.30	1.24	0.105	10.53
	10	1.27	1.25	1.26	0.016	1.59
	13	1.33	1.34	1.34	0.007	0.749
Amount of PO4 on solid (µmol/gm)	0	89.4	89.4	89.4	0.000	0.000
	0.25	49.4	49.4	49.4	0.000	0.000
	1	47.7	47.4	47.6	0.007	0.678
	2	48.1	45.5	46.8	0.055	5.52
	3	49.7	41.9	45.8	0.169	16.9
	4	48.7	46.1	47.4	0.054	5.44
	7	51.6	47.4	49.5	0.085	8.47
	10	48.4	49.0	48.7	0.013	1.33
	13	46.5	46.1	46.3	0.007	0.697

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average

% variance = mean variance * 100%

Table A.5 Experimental Data for PO_4 Desorption in 0.01 M NaOH Solution

	Desorbing Solution	0.01mol/l NaOH				
	Initial PO4 (mg/l)	4.150				
	Adsorbed PO4 (mg/l)	2.770				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	0.633	0.671	0.652	0.058	5.83
	1	0.91	1.02	0.967	0.110	11.0
	2	1.05	1.18	1.12	0.117	11.7
	3	1.11	1.37	1.24	0.210	21
	4	1.22	1.45	1.34	0.172	17.2
	7	1.27	1.44	1.36	0.125	12.5
	10	1.38	1.48	1.43	0.070	7.0
	13	1.38	1.48	1.43	0.070	7.0
Amount of PO4 on solid (µmol/gm)	0	89.4	89.3	89.4	0.000	0.000
	0.25	68.9	67.7	68.3	0.018	1.79
	1	59.9	56.5	58.2	0.059	5.9
	2	55.5	51.3	53.4	0.079	7.86
	3	53.5	45.1	49.4	0.170	17.0
	4	50.0	42.6	46.3	0.160	16.0
	7	48.4	42.9	45.6	0.120	12.0
	10	44.8	41.6	43.2	0.075	7.46
	13	44.8	41.6	43.2	0.075	7.46

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average
% variance = mean variance * 100%

Table A.6 Experimental Data for PO_4 Desorption in 6 M HNO_3 Solution

	Desorbing Solution	6mol/l HNO3				
	Initial PO4 (mg/l)	4.150				
	Adsorbed PO4 (mg/l)	2.770				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	0.000	0.000	0.000	0.000	0.000
	1	0.000	0.000	0.000	0.000	0.000
	2	0.000	0.000	0.000	0.000	0.000
	3	0.000	0.000	0.000	0.000	0.000
	4	0.000	0.000	0.000	0.000	0.000
	7	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000
	13	0.000	0.000	0.000	0.000	0.000
Amount of PO4 on solid (µmol/gm)	0.000	89.4	89.4	89.4	0.000	0.000
	0.25	89.4	89.4	89.4	0.000	0.000
	1	89.4	89.4	89.4	0.000	0.000
	2	89.4	89.4	89.4	0.000	0.000
	3	89.4	89.4	89.4	0.000	0.000
	4	89.4	89.4	89.4	0.000	0.000
	7	89.4	89.4	89.4	0.000	0.000
	10	89.4	89.4	89.4	0.000	0.000
	13	89.4	89.4	89.4	0.000	0.000

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average
% variance = mean variance * 100%

Table A.7 Experimental Data for PO_4 Desorption in 1 M HNO_3 Solution

	Desorbing Solution	1mol/l HNO3				
	Initial PO4 (mg/l)	4.150				
	Adsorbed PO4 (mg/l)	2.770				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	0.000	0.000	0.000	0.000	0.000
	1	0.000	0.000	0.000	0.000	0.000
	2	0.000	0.000	0.000	0.000	0.000
	3	0.000	0.000	0.000	0.000	0.000
	4	0.030	0.033	0.032	0.095	9.524
	7	0.030	0.030	0.030	0.000	0.000
	10	0.030	0.030	0.030	0.000	0.000
	13	0.030	0.030	0.030	0.000	0.000
Amount of PO4 on solid (µmol/gm)	0.000	89.4	89.4	89.4	0.000	0.000
	0.25	89.4	89.4	89.4	0.000	0.000
	1	89.4	89.4	89.4	0.000	0.000
	2	89.4	89.4	89.4	0.000	0.000
	3	89.4	89.4	89.4	0.000	0.000
	4	89.4	89.4	89.4	0.001	0.110
	7	89.4	89.4	89.4	0.000	0.000
	10	89.4	89.4	89.4	0.000	0.000
	13	89.4	89.4	89.4	0.000	0.000

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average
% variance = mean variance * 100%

Table A.8 Experimental Data for PO_4 Desorption in 0.01 M HNO_3 Solution

	Desorbing Solution	0.01mol/l HNO3				
	Initial PO4 (mg/l)	4.150				
	Adsorbed PO4 (mg/l)	2.770				
	Time (day)	Exp # 1	Exp #2	Average	Mean Variance	%
Amount of PO4 desorbed in solution (mg/l)	0.25	0.000	0.000	0.000	0.000	0.000
	1	0.000	0.000	0.000	0.000	0.000
	2	0.000	0.000	0.000	0.000	0.000
	3	0.000	0.000	0.000	0.000	0.000
	4	0.000	0.000	0.000	0.000	0.000
	7	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000
	13	0.000	0.000	0.000	0.000	0.000
Amount of PO4 on solid (µmol/gm)	0.25	89.4	89.4	89.4	0.000	0.000
	1	89.4	89.4	89.4	0.000	0.000
	2	89.4	89.4	89.4	0.000	0.000
	3	89.4	89.4	89.4	0.000	0.000
	4	89.4	89.4	89.4	0.000	0.000
	7	89.4	89.4	89.4	0.000	0.000
	10	89.4	89.4	89.4	0.000	0.000
	13	89.4	89.4	89.4	0.000	0.000
	0.25	89.4	89.4	89.4	0.000	0.000

Mean Variance = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average

% variance = mean variance * 100%

APPENDIX B

Experimental Data for Phosphate and Arsenate Adsorption at Different pH

Table B.1 Experimental Data for Phosphate Adsorption Isotherm at pH 3, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	Mean variance (%)
0.283	0.000	0.000		9.02	9.02		
0.283	0.000	0.000	0.000	9.02	9.02	9.02	0.000
0.488	0.000	0.000		15.6	15.6		
0.488	0.000	0.000	0.000	15.5	15.5	15.6	0.124
0.747	0.000	0.000		23.9	23.9		
0.747	0.000	0.000	0.000	23.9	23.9	23.9	0.000
1.42	0.000	0.000		45.5	45.5		
1.42	0.000	0.000	0.000	45.5	45.5	45.5	0.000
1.65	0.000	0.000		53.0	53.0		
1.65	0.000	0.000	0.000	53.1	53.1	53.1	0.061
3.24	0.691	22.3		82.2	82.2		
3.24	0.70	22.5	22.4	81.9	81.9	82.1	0.354
4.65	1.40	45.2		105	105		
4.65	1.30	41.9	43.6	108	108	107	3.03
6.20	2.74	88.4		111	111		
6.20	2.80	90.3	89.4	110	110	111	1.75

Note : Loss From Solution Method was used in table B.1 to B.12

Loss From Solution Method

Adsorbed PO4 (µmol/gm) = [Initial PO4 Conc. – Final Conc.]/ Adsorbent Conc.

Mean Variance (%) = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average * 100

Table B.2 Experimental Data for Phosphate Adsorption Isotherm at pH 7, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

At pH 7							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.028	0.903		8.21	8.21		
0.283	0.020	0.645	0.774	8.47	8.47	8.34	3.095
0.488	0.018	0.581		15.2	15.2		
0.488	0.022	0.710	0.645	15.0	15.0	15.1	0.855
0.747	0.020	0.645		23.5	23.5		
0.747	0.022	0.710	0.677	23.4	23.4	23.4	0.275
1.42	0.030	0.968		44.8	44.8		
1.42	0.031	1.000	0.984	44.8	44.8	44.8	0.072
1.65	0.038	1.23		52.0	52.0		
1.65	0.033	1.07	1.15	52.2	52.2	52.08	0.310
3.24	1.11	35.8		68.7	68.7		
3.24	1.12	36.1	36.0	68.4	68.4	68.5	0.47
4.65	2.58	83.2		66.8	66.8		
4.65	2.58	83.2	83.2	66.8	66.8	66.8	0.00
6.20	4.00	129		71.0	71.0		
6.20	3.90	126	127	74.1	74.1	72.6	4.44

Table B.3 Experimental Data for Phosphate Adsorption Isotherm at pH 10, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

At pH 10							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.016	0.516		8.60	8.60		
0.283	0.000	0.000	0.258	9.11	9.11	8.86	5.83
0.488	0.020	0.645		15.10	15.10		
0.488	0.000	0.000	0.323	15.7	15.7	15.4	4.18
0.747	0.056	1.806		22.3	22.3		
0.747	0.037	1.194	1.500	22.9	22.9	22.6	2.71
1.42	0.224	7.226		38.6	38.6		
1.42	0.221	7.129	7.18	38.7	38.7	38.6	0.251
1.65	0.501	16.2		37.1	37.1		
1.65	0.540	17.4	16.8	35.8	35.8	36.4	3.45
3.24	1.67	53.9		50.6	50.6		
3.24	1.63	52.6	53.2	51.9	51.9	51.3	2.52
4.65	2.97	95.8		54.2	54.2		
4.65	3.01	97.1	96.5	52.9	52.9	53.6	2.41
6.20	4.25	137		62.9	62.9		
6.20	4.30	139	138	61.2	61.2	62.1	2.6

Table B.4 Experimental Data for Phosphate Adsorption Isotherm at pH 3, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

At pH 3							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.000	0.000		9.02	18.0		
0.283	0.000	0.000	0.000	8.95	17.9	18.0	0.718
0.488	0.000	0.000		15.6	31.2		
0.488	0.000	0.000	0.000	15.6	31.1	31.1	0.207
0.747	0.000	0.000		23.8	47.6		
0.747	0.000	0.000	0.000	24.1	48.2	47.9	1.212
1.42	0.050	1.61		44.2	88.4		
1.42	0.060	1.94	1.77	43.9	87.7	88.1	0.733
1.65	0.150	4.84		48.4	96.8		
1.65	0.130	4.19	4.52	49.0	98.1	97.4	1.33
3.24	1.70	54.8		49.7	99.4		
3.24	1.65	53.2	54.0	51.3	102	101	3.2
4.65	3.05	98.4		51.6	103		
4.65	2.97	95.8	97.1	54.2	108	106	4.88
6.20	4.38	141		58.7	117		
6.20	4.40	142	142	58.1	116	117	1.11

Table B.5 Experimental Data for Phosphate Adsorption Isotherm at pH 7, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

At pH 7							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.072	2.32		6.79	13.6		
0.283	0.066	2.13	2.23	6.98	14.0	13.8	2.81
0.488	0.077	2.48		13.3	26.5		
0.488	0.077	2.48	2.48	13.3	26.5	26.5	0.00
0.747	0.048	1.55		22.5	45.1		
0.747	0.050	1.61	1.58	22.5	45.0	45.0	0.287
1.42	0.364	11.7		34.1	68.1		
1.42	0.365	11.8	11.8	34.0	68.1	68.1	0.095
1.65	0.615	19.8		33.4	66.8		
1.65	0.600	19.4	19.6	33.9	67.7	67.3	1.44
3.24	2.16	69.7		34.8	69.7		
3.24	2.16	69.7	69.7	34.8	69.7	69.7	0.000
4.65	3.66	118		31.9	63.9		
4.65	3.50	113	116	37.1	74.2	69.0	14.9
6.60	5.38	174		39.4	78.7		
6.60	5.38	174	174	39.4	78.7	78.7	0.000

Table B.6 Experimental Data for Phosphate Adsorption Isotherm at pH 10, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

At pH 10							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.088	2.84		6.27	12.5		
0.283	0.127	4.10	3.47	5.02	10.0	11.3	22.3
0.488	0.140	4.52		11.2	22.5		
0.488	0.145	4.68	4.6	11.1	22.1	22.3	1.45
0.747	0.380	12.3		11.8	23.7		
0.747	0.390	12.6	12.4	11.5	23.0	23.4	2.76
1.42	0.700	22.6		23.2	46.5		
1.42	0.760	24.5	23.6	21.3	42.6	44.5	8.70
1.65	0.875	28.2		25.0	50.0		
1.65	0.885	28.5	28.4	24.7	49.4	49.7	1.30
3.24	2.28	73.5		30.9	61.9		
3.24	2.33	75.2	74.4	29.4	58.7	60.3	5.35
4.76	3.78	122		31.6	63.2		
4.76	3.90	126	124	27.7	55.5	59.4	13.0
6.30	5.40	174		29.0	58.1		
6.30	5.30	171	173	32.3	64.5	61.3	10.5

Table B.7 Experimental Data for Arsenate Adsorption Isotherm at pH 3, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 3							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.000	0.000		3.75	3.75		
0.283	0.000	0.000	0.000	3.74	3.74	3.744	0.357
0.770	0.000	0.000		10.2	10.2		
0.770	0.000	0.000	0.000	10.2	10.2	10.2	0.131
1.40	0.045	0.601		18.1	18.1		
1.40	0.045	0.601	0.601	18.1	18.1	18.1	0.000
2.73	0.065	0.868		35.5	35.5		
2.73	0.070	0.934	0.901	35.4	35.4	35.5	0.188
3.32	0.070	0.934		43.3	43.3		
3.32	0.078	1.04	0.988	43.2	43.2	43.3	0.247
5.05	0.090	1.20		66.2	66.2		
5.05	0.080	1.07	1.14	66.3	66.3	66.3	0.201
6.85	0.172	2.30		89.1	89.1		
6.85	0.180	2.40	2.35	89.0	89.0	89.1	0.120
7.95	0.974	13.0		93.1	93.1		
7.95	1.08	14.4	13.7	91.7	91.7	92.4	1.53
16.5	8.92	119		101	101		
16.5	8.82	118	118.5	102	102	101.0	1.32

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Table B.8 Experimental Data for Arsenate Adsorption Isotherm at pH 7, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 7							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed µmol/l	Adsorbed PO_4 µmol/g	Average PO_4 µmol/g	mean variance (%)
0.283	0.050	0.667		3.11	3.11		
0.283	0.040	0.534	0.601	3.24	3.24	3.18	4.20
0.770	0.060	0.801		9.48	9.48		
0.770	0.068	0.908	0.854	9.37	9.37	9.4	1.133
1.40	0.090	1.20		17.5	17.5		
1.40	0.100	1.34	1.27	17.4	17.4	17.4	0.766
2.73	0.146	1.95		34.4	34.4		
2.73	0.150	2.00	1.98	34.4	34.4	34.4	0.155
3.32	0.195	2.60		41.6	41.6		
3.32	0.190	2.54	2.57	41.7	41.7	41.7	0.160
3.98	0.209	2.79		50.4	50.4		
3.98	0.221	2.95	2.87	50.2	50.2	50.3	0.318
7.95	3.79	50.6		55.5	55.5		
7.95	3.72	49.7	50.12	56.5	56.5	56.0	1.67
16.5	11.9	159		60.7	60.7		
16.5	12.0	160	160	59.4	59.4	60.1	2.22

Table B.9 Experimental Data for Arsenate Adsorption Isotherm at pH 10, 1 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 10							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.113	1.51		2.27	2.27		
0.283	0.110	1.47	1.49	2.31	2.31	2.289	1.749
0.770	0.114	1.52		8.76	8.76		
0.770	0.112	1.50	1.51	8.78	8.78	8.8	0.304
1.400	0.229	3.06		15.6	15.6		
1.400	0.225	3.00	3.03	15.7	15.7	15.7	0.341
2.73	0.825	11.0		25.4	25.4		
2.73	0.830	11.1	11.05	25.3	25.3	25.3	0.264
3.32	1.46	19.5		24.8	24.8		
3.32	1.44	19.2	19.35	25.0	25.0	24.9	1.07
5.05	3.14	41.9		25.5	25.5		
5.05	3.19	42.6	42.2	24.8	24.8	25.2	2.65
6.85	4.20	56.1		35.4	35.4		
6.85	4.18	55.8	55.9	35.6	35.6	35.5	0.752
10.2	7.13	95.2		40.9	40.9		
10.2	7.21	96.2	95.7	39.9	39.9	40.4	2.64
16.5	12.7	170		49.7	49.7		
16.5	12.6	168	169	51.8	51.8	50.7	4.24

Table B.10 Experimental Data for Arsenate Adsorption Isotherm at pH 3, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 3							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed PO4 µmol/l	Adsorbed PO4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.168	2.24		1.54	3.07		
0.283	0.165	2.20	2.22	1.58	3.15	3.11	2.58
0.770	0.173	2.31		7.97	15.9		
0.770	0.156	2.08	2.19	8.19	16.4	16.16	2.81
1.40	0.173	2.31		16.4	32.7		
1.40	0.170	2.27	2.29	16.4	32.8	32.8	0.244
2.73	0.166	2.22		34.2	68.3		
2.73	0.180	2.40	2.31	33.9	67.9	68.1	0.549
3.32	0.198	2.64		41.6	83.2		
3.32	0.210	2.80	2.72	41.4	82.9	83.1	0.386
3.98	0.776	10.3		42.8	85.67		
3.98	0.656	8.76	9.56	44.4	88.87	87.3	3.67
7.95	4.30	57.4		48.7	97.4		
7.95	4.40	58.7	58.1	47.4	94.8	96.1	2.78
16.5	12.5	167		52.7	105		
16.5	12.7	169	168	50.0	100	103	5.2

Table B.11 Experimental Data for Arsenate Adsorption Isotherm at pH 7, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 7							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/g	Average µmol/g	mean variance (%)
0.283	0.178	2.38		1.40	2.80		
0.283	0.180	2.40	2.39	1.38	2.75	2.78	1.92
0.770	0.155	2.07		8.21	16.4		
0.770	0.150	2.00	2.04	8.28	16.5	16.5	0.810
1.400	0.150	2.00		16.7	33.4		
1.400	0.160	2.14	2.07	16.5	33.1	33.2	0.803
2.73	0.730	9.74		26.6	53.3		
2.73	0.766	10.2	9.98	26.1	52.3	52.8	1.82
3.32	1.20	16.0		28.2	56.5		
3.32	1.15	15.4	15.7	28.9	57.8	57.1	2.34
3.98	1.93	25.8		27.4	54.8		
3.98	1.97	26.3	26.0	26.9	53.8	54.3	1.97
7.95	5.70	76.1		30.0	60.1		
7.95	5.79	77.3	76.7	28.8	57.7	58.8	4.08
16.5	14.1	188		31.4	62.7		
16.5	14.2	190	189	30.0	60.1	61.4	4.35

Table B.12 Experimental Data for Arsenate Adsorption Isotherm at pH 10, 0.5 g/l Goethite Concentration and 0.001 M $NaNO_3$

pH 10							
Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average µmol/l	Adsorbed PO_4 µmol/l	Adsorbed PO_4 µmol/gm	Average µmol/gm	mean variance (%)
0.283	0.156	2.082		1.69	3.39		
0.283	0.160	2.136	2.11	1.64	3.28	3.34	3.200
0.770	0.225	3.00		7.27	14.6		
0.770	0.188	2.51	2.77	7.77	15.5	15.0	6.57
1.40	0.508	6.78		11.9	23.8		
1.40	0.495	6.61	6.69	12.1	24.2	24.1	1.45
2.73	1.64	21.9		14.5	29.0		
2.73	1.68	22.4	22.2	13.9	28.0	28.4	3.76
3.32	1.96	26.2		18.1	36.2		
3.32	2.00	26.7	26.4	17.6	35.1	35.6	2.99
5.05	3.68	49.1		18.3	36.6		
5.05	3.60	48.1	48.6	19.4	38.7	37.6	5.67
6.85	5.23	69.8		21.6	43.3		
6.85	5.23	69.8	69.8	21.6	43.3	43.2	0.000
10.2	8.33	111		24.9	49.9		
10.2	8.37	112	111	24.4	48.9	49.4	2.16
16.5	14.5	194		26.0	52.1		
16.5	14.4	192	193	27.4	54.7	53.4	5.000

APPENDIX C

Experimental Data for Phosphate Adsorption at Different Solids Concentration

Notes:

1. **‘**Loss from Solution method’ was used in Adsorption of Phosphate in 10 g/l and 1 g/l goethite concentration. (Table C.1 to C.11)

2. ‘Acid Digestion Method’ was used data in Table C-12 to C-22.

Loss from solution method was also used in table C-12 to C-22 at very low P concentration samples

$$\text{Adsorbed PO}_4 = \frac{measuredPO_4}{measuredFe}\frac{in}{in}\frac{hotHCl}{hotHCl}\frac{\mu mol/l}{mg/l}\,x\,\frac{55.85}{88.85}\frac{g}{g}\frac{Fe}{Goethite}\,x\,\frac{1000}{1}\frac{mg}{g}$$

Italic data in table C-12 to C-22 indicated the selected average data.

3. **For Duplicate sample, mean variance (%) can be calculated as follows:**

Mean Variance (%) = $\left|(\text{Replicate})_1 - (\text{Replicate})_2\right|$ / average * 100

Samples repeated more than three times can be calculated as follows:

Mean variance = Standard Deviation / average * 100 %

Table C-1 Experimental Data for Phosphate Adsorption Isotherm at 10 g/l Goethite Concentration. pH = 4, Reaction time = 1hour, Ionic Strength = 0.001 M NaNO$_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorbed mg/l	Adsorbed µmol/l	Adsorb-ed µmol/g	Average	mean varian-ce, σ (%)
1.64	0.000	0.000		1.63	52.7	5.27		
1.64	0.000	0.000	0.000	1.63	52.7	5.27	5.27	0.000
3.21	0.000	0.000		3.20	103.	10.3		
3.21	0.000	0.000	0.000	3.20	103.	10.3	10.3	0.014
15.3	0.000	0.000		15.2	491.	49.2		
15.3	0.000	0.000	0.000	15.2	491.	49.2	49.2	0.001
19.3	0.066	2.13		19.3	621.	62.1		
19.3	0.066	2.13	2.13	19.3	621.	62.1	62.1	0.000
22.96	0.314	10.1		22.7	731.	73.1		
22.93	0.314	10.1	10.1	22.6	730.	73.0	73.1	0.133
25.6	3.61	116		22.0	709.	70.9		
25.6	3.60	116	116.0	22.0	710.	71.0	71.0	0.045
31.2	5.00	161		26.2	845.	84.5		
31.2	5.30	171	166.0	25.9	836.	83.5	84.0	1.15
60.5	34.5	1113		26.0	839.	83.9		
60.5	33.0	1065	1089	27.5	887.	88.7	86.3	5.61

Table C-2 Experimental Data for Phosphate Adsorption Isotherm at 10 g/l Goethite Concentration. pH = 4, Reaction time = 24 hours, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. μmol/l	Average	Adsorb-ed mg/l	Adsorb-ed μmol/l	Adsorb-ed μmol/g	Avera-ge	Mean varian-ce, σ (%)
1.64	0.000	0.000		1.64	52.9	5.29		
1.64	0.000	0.000	0.000	1.64	52.9	5.29	5.30	0.000
3.21	0.000	0.000		3.21	103.5	10.4		
3.21	0.000	0.000	0.000	3.21	103.5	10.4	10.4	0.000
15.3	0.000	0.000		15.2	491.	49.1		
15.3	0.000	0.000	0.000	15.2	491.	49.1	49.1	0.020
19.3	0.022	0.710		19.3	623.	62.2		
19.3	0.022	0.710	0.710	19.3	623.	62.2	62.3	0.000
23.0	0.132	4.26		22.9	738.	73.8		
23.0	0.132	4.26	4.26	22.9	738.	73.8	73.8	0.000
25.6	1.29	41.6		24.3	784.	78.4		
25.6	1.30	41.9	41.8	24.3	784.	78.4	78.4	0.041
31.2	3.88	125.2		27.3	881.	88.1		
31.2	3.90	125.8	125.5	27.3	881.	88.1	88.1	0.073
60.5	31.6	1019.		28.9	932.	93.2		
60.5	32.4	1045.	1032	28.1	907.	90.6	91.9	2.81

Table C-3 Experimental Data for Phosphate Adsorption Isotherm at 10 g/l Goethite Concentration. PH = 4, Reaction time = 72hour, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. μmol/l	Average	Adsorb-ed mg/l	Adsorb-ed μmol/l	Adsorb-ed μmol/g	Average	Mean variance, σ (%)
1.64	0.000	0.000		1.64	52.8	5.28		
1.64	0.000	0.000	0.000	1.64	52.8	5.28	5.28	0.008
3.21	0.000	0.000		3.21	104	10.4		
3.21	0.000	0.000	0.000	3.21	104	10.4	10.4	0.000
15.3	0.000	0.000		15.3	492	49.2		
15.3	0.000	0.000	0.000	15.3	492	49.2	49.2	0.001
19.3	0.022	0.710		19.3	623	62.3		
19.3	0.022	0.710	0.710	19.3	623	62.3	62.3	0.000
23.0	0.066	2.13		22.9	740	74.0		
23.0	0.065	2.10	2.113	22.9	740	74.0	74.0	0.004
25.6	0.539	17.4		25.1	808	80.8		
25.6	0.539	17.4	17.4	25.1	808	80.8	80.8	0.000
31.2	2.91	93.9		28.3	913	91.3		
31.2	2.90	93.6	93.7	28.3	913	91.3	91.3	0.035
60.5	30.3	977		30.2	974	97.4		
60.5	31.0	1000	989	29.5	952	95.2	96.3	2.35

Table C-4 Experimental Data for Phosphate Adsorption Isotherm at 10 g/l Goethite Concentration. pH = 4, Reaction time = 168 hours, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorb-ed mg/l	Adsorb-ed µmol/l	Adsorb-ed µmol/g	Average	mean variance, σ (%)
1.64	0.000	0.000		1.64	52.8	5.28		
1.64	0.000	0.000	0.000	1.64	52.8	5.28	5.28	0.000
3.21	0.000	0.000		3.21	104	10.4		
3.21	0.000	0.000	0.000	3.21	104	10.4	10.4	0.000
15.3	0.000	0.000		15.3	492	49.2		
15.3	0.000	0.000	0.000	15.3	492	49.2	49.2	0.000
19.3	0.022	0.710		19.3	623	62.3		
19.3	0.022	0.710	0.710	19.3	623	62.3	62.3	0.000
23.0	0.026	0.839		23.0	741	74.1		
23.0	0.028	0.903	0.871	23.0	741	74.1	74.1	0.009
25.6	0.350	11.3		25.3	815	81.5		
25.6	0.350	11.3	11.3	25.3	815	81.5	81.5	0.000
31.2	2.08	67.1		29.1	939	93.9		
31.2	2.11	68.1	67.6	29.1	938	93.8	93.9	0.103
60.5	28.3	913		32.2	1039	104		
60.5	29.5	952	932	31.0	1000	100	102	3.8

Table C-5 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 1 hour, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc. µmol/l	Average	Adsorb-ed mg/l	Adsorb-ed µmol/l	Average	Adsorb-ed µmol/g	mean variance, σ (%)
1.23	0.000	0.000		1.22	39.4			
1.23	0.000	0.000	0.000	1.22	39.5	39.5	39.5	0.164
1.42	0.000	0.000		1.41	45.6			
1.42	0.000	0.000	0.000	1.41	45.5	45.5	45.5	0.189
1.59	0.000	0.000		1.58	51.0			
1.59	0.000	0.000	0.000	1.58	50.9	50.9	50.9	0.060
1.69	0.000	0.000		1.68	54.2			
1.69	0.000	0.000	0.000	1.68	54.1	54.1	54.1	0.119
1.91	0.000	0.000		1.89	61.0			
1.91	0.000	0.000	0.000	1.89	61.0	61.0	61.0	0.016
2.17	0.140	4.52		2.03	65.5			
2.17	0.150	4.84	4.68	2.02	65.2	65.3	65.3	0.494
2.46	0.428	13.8		2.03	65.4			
2.46	0.414	13.4	13.6	2.04	65.8	65.6	65.6	0.688
2.82	0.795	25.6		2.02	65.2			
2.82	0.757	24.4	25.0	2.06	66.3	65.8	65.8	1.86
30.1	27.2	877		2.90	93.5			
30.1	27.0	871	874	3.10	100	96.8	96.8	6.67

Table C-6 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 24 hours, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc µmol/l	Average	Adsorbed mg/l	Adsorbed µmol/l	Average	Adsorbed µmol/g	variance	mean variance, σ (%)
0.155	0.000	0.000		0.152	4.90				
0.155	0.000	0.000	0.000	0.152	4.90	4.90	4.90	0.000	0.000
0.292	0.000	0.000		0.284	9.16				
0.292	0.000	0.000	0.000	0.286	9.23	9.19	9.19	0.007	0.702
0.520	0.000	0.000		0.513	16.55				
0.520	0.000	0.000	0.000	0.513	16.56	16.6	16.6	0.001	0.078
0.970	0.000	0.000		0.960	31.0				
0.970	0.000	0.000	0.000	0.959	30.9	31.0	31.0	0.001	0.104
1.23	0.000	0.000		1.22	39.4				
1.23	0.000	0.000		1.22	39.4				
1.23	0.000	0.000		1.22	39.4				
1.23	0.000	0.000		1.22	39.5				
1.23	0.000	0.000		1.22	39.4				
1.23	0.000	0.000	0.000	1.22	39.4	39.4	39.4	0.026	0.067
1.42	0.000	0.000		1.41	45.6				
1.42	0.000	0.000	0.000	1.41	45.5	45.5	45.5	0.068	0.150
1.55	0.000	0.000		1.53	49.5				
1.55	0.000	0.000	0.000	1.54	49.5				
1.55	0.024	0.774		1.53	49.2				
1.55	0.015	0.484	0.629	1.54	49.5	49.4	49.4	0.139	0.281
1.69	0.024	0.774		1.67	53.7				
1.69	0.019	0.613	0.694	1.67	53.9	53.8	53.8	0.003	0.300
1.91	0.028	0.903		1.88	60.7				
1.91	0.026	0.839	0.871	1.88	60.8	60.7	60.7	0.001	0.106
2.17	0.038	1.23		2.13	68.8				
2.17	0.033	1.07	1.15	2.14	68.9	68.9	68.9	0.002	0.234
2.30	0.167	5.39		2.13	68.8				
2.30	0.165	5.32	5.355	2.14	68.9	68.8	68.8	0.001	0.094
2.45	0.237	7.65		2.22	71.6				
2.45	0.210	6.78	7.21	2.25	72.4	72.0	72.0	0.012	1.210
2.82	0.485	15.6		2.33	75.2				
2.82	0.519	16.7	16.2	2.30	74.1	74.6	74.6	0.015	1.470

Initial Conc. mg/l	Final Conc. mg/l	Final Conc μmol/l	Average	Adsorbed mg/l	Adsorbed μmol/l	Average	Adsorbed μmol/g	variance	mean variance, σ (%)
3.03	0.563	18.2		2.47	79.58				
3.03	0.565	18.2		2.47	79.52				
3.02	0.568	18.3		2.45	79.1				
3.02	0.567	18.3	18.3	2.45	79.1	79.3	79.3	0.023	0.029
5.90	3.25	105		2.65	85.5				
5.90	3.20	103	104	2.70	87.1	86.3	86.3	1.140	1.322
30.1	26.9	868		3.20	103.				
30.1	26.9	868	868	3.20	103	103	103.0	0.000	0.000

Table C-7 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 48 hours, Ionic Strength = 0.001 M NaNO$_3$.

Initial Conc mg/l	Final Conc mg/l	Final Conc μmol/l	Average	Adsorbed mg/l	Adsorbed μmol/l	Average	Adsorbed μmol/g	variance	mean variance, σ (%)
0.970	0.000	0.000		0.961	31.0				
0.970	0.000	0.000	0.000	0.960	30.9	31.0	31.0	0.001	0.104
1.27	0.000	0.000		1.26	40.7				
1.27	0.000	0.000	0.000	1.26	40.7	40.7	40.7	0.002	0.158
1.55	0.000	0.000		1.53	49.5				
1.55	0.000	0.000	0.000	1.54	49.5	49.5	49.5	0.001	0.052
2.82	0.440	14.2		2.38	76.6				
2.82	0.450	14.5	14.4	2.37	76.3	76.5	76.5	0.004	0.422
5.90	3.01	97.1		2.89	93.2				
5.90	3.02	97.4	97.3	2.88	92.9	93.1	93.1	0.003	0.347

Table C-8 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 72 hours, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc. mg/l	Final Conc. mg/l	Final Conc µmol/l	Aver-age	Adsorbed mg/l	Adsorbed µmol/l	Average	Adsorbed µmol/g	variance	mean variance, σ (%)
1.23	0.000	0.000		1.22	39.4				
1.23	0.000	0.000	0.000	1.22	39.5	39.5	39.5	0.002	0.164
1.42	0.000	0.000		1.42	45.8				
1.42	0.000	0.000	0.000	1.42	45.7	45.7	45.7	0.002	0.212
1.59	0.000	0.000		1.58	50.9				
1.59	0.000	0.000	0.000	1.58	50.9	50.9	50.9	0.001	0.127
1.69	0.000	0.000		1.68	54.1				
1.69	0.000	0.000	0.000	1.68	54.1	54.1	54.1	0.001	0.108
1.91	0.000	0.000		1.89	61.1				
1.91	0.020	0.645	0.597	1.89	61.0	61.0	61.0	0.002	0.159
2.17	0.026	0.823		2.15	69.2				
2.17	0.034	1.10	0.960	2.14	68.9	69.0	69.0	0.004	0.397
2.46	0.190	6.13		2.27	73.1				
2.46	0.178	5.74	5.94	2.28	73.5	73.3	73.3	0.005	0.528
2.82	0.459	14.8		2.36	76.0				
2.82	0.452	14.6	14.7	2.36	76.2	76.1	76.1	0.003	0.297
30.1	26.8	865		3.30	106				
30.1	26.8	865	865	3.30	106	106.0	106.0	0.000	0.000

Table C-9 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 96 hours, Ionic Strength = 0.001 M $NaNO_3$.

Initial Conc mg/l	Final Conc mg/l	Final Conc µmol/l	Avera-ge	Adsorbed mg/l	Adsorbed µmol/l	Average	Adsorbed µmol/g	Varian-ce	mean variance, σ (%)
0.97	0.000	0.000		0.962	31.03				
0.97	0.000	0.000	0.000	0.963	31.07	31.1	31.1	0.001	0.104
1.27	0.000	0.000		1.26	40.7				
1.27	0.000	0.000	0.000	1.26	40.8	40.7	40.7	0.001	0.119
1.55	0.000	0.000		1.54	49.5				
1.55	0.000	0.000	0.000	1.54	49.5	49.5	49.5	0.001	0.065
3.03	0.404	13.03		2.63	84.7				
3.03	0.400	12.9	13.0	2.90	93.5	89.1	89.1	0.099	9.92
5.90	2.910	93.9		2.99	96.5				
5.90	2.870	92.6	93.2	3.03	97.7	97.1	97.1	0.013	1.33

Table C-10 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 168 hours, Ionic Strength = 0.001 M $NaNO_3$

Initial Conc mg/l	Final Conc. mg/l	Final Conc µmol/l	Average	Adsorbed mg/l	Adsorbed µmol/l	Average	Adsorbed µmol/g	variance	mean variance σ (%)
1.23	0.000	0.000		1.23	39.6				
1.23	0.000	0.000	0.000	1.23	39.6	39.6	39.6	0.000	0.016
1.42	0.000	0.000		1.42	45.8				
1.42	0.000	0.000	0.000	1.42	45.8	45.8	45.8	0.000	0.014
1.59	0.000	0.000		1.57	50.8				
1.59	0.000	0.000	0.000	1.58	50.8	50.8	50.8	0.001	0.127
1.69	0.000	0.000		1.68	54.1				
1.69	0.000	0.000	0.000	1.67	53.8	53.9	53.9	0.005	0.538
1.91	0.016	0.516		1.89	61.1				
1.91	0.022	0.708	0.612	1.88	60.9	61.0	61.0	0.003	0.315
2.17	0.025	0.806		2.15	69.2				
2.17	0.023	0.742	0.774	2.15	69.3	69.2	69.2	0.001	0.093
2.46	0.117	3.77		2.34	75.4				
2.46	0.117	3.77	3.77	2.34	75.4	75.4	75.4	0.000	0.000
2.82	0.387	12.48		2.43	78.3				
2.82	0.405	13.07	12.8	2.41	77.7	78.0	78.0	0.007	0.744
30.1	26.7	861		3.40	110				
30.1	26.7	861	861	3.40	110	110	110	0.000	0.000

Table C-11 Experimental Data for Phosphate Adsorption Isotherm at 1 g/l Goethite Concentration, pH = 4, Reaction time = 720 hours, Ionic Strength = 0.001 M $NaNO_3$

Initial Conc. mg/l	Final Conc. mg/l	Final Conc µmol/l	Average	Adsorbed mg/l	Adsorbed µmol/l	Average	Adsorbed µmol/g	variance	mean variance σ (%)
1.59	0.000	0.000		1.59	51.2				
1.59	0.000	0.000	0.000	1.59	51.2	51.2	51.2	0.000	0.045
2.82	0.295	9.5		2.52	81.3				
2.82	0.298	9.6	9.55	2.52	81.2	81.2	81.2	0.001	0.119
30.1	26.5	855		3.60	116				
30.1	26.4	851	853	3.70	119	118	118	0.027	2.740

Table C-12 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 1 hour, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (µmol/l)	Average	Adsorbed (mg/l)	Adsorbed (µmol/l)	Adsorbed (µmol/g)	Average	Varia-nce	mean variance, σ (%)
	0.067	0.000	0.000		0.065	2.10	21.0			
	0.067	0.000	0.000	0.000	0.065	2.10	21.0	21.0	0	0.000
	0.080	0.000	0.000		0.078	2.52	25.2			
	0.080	0.000	0.000	0.000	0.078	2.52	25.2	25.2	0	0.000
	0.149	0.000	0.000		0.146	4.72	47.2			
	0.149	0.000	0.000	0.000	0.146	4.72	47.2	47.2	0.001	0.068
	0.230	0.0589	1.90		0.171	5.52	55.2			
	0.230	0.06	1.94	1.92	0.170	5.49	54.8	55.0	0.006	0.648
	0.350	0.139	4.48		0.211	6.81	68.1			
	0.350	0.135	4.35	4.42	0.215	6.94	69.4	68.7	0.019	1.878
	0.520	0.306	9.87		0.214	6.90	69.0			
	0.520	0.309	9.97	9.92	0.211	6.81	68.1	68.6	0.014	1.412
53.6	1.55	1.26	40.8		0.243	7.84	92.03			
53.0	1.55	1.27	40.8	40.8	0.240	7.74	91.79	91.9	0.003	0.264
49.4	3.1	2.79	89.9		0.245	7.90	101			
47.6	3.1	2.78	89.8		0.240	7.75	102			
52	3.1	2.78	89.8	89.9	0.259	8.35	102	102.0	6.248	6.16
52.4	3.1	2.75	88.6		0.293	9.45	114			
43.6	31	30.6	988		0.260	8.38	121			
49.2	31	30.6	987		0.324	10.5	134			
49.8	31	30.6	987	987	0.309	9.97	126	127	6.73	5.30

Table C-13 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 24 hours, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
	0.067	0.000	0.000		0.065	2.10	21.0			
	0.067	0.000	0.000	0.000	0.065	2.10	21.0	21.03	0	0.000
	0.080	0.000	0.000		0.078	2.52	25.2			
	0.080	0.000	0.000	0.000	0.078	2.52	25.2	25.2	0	0.000
	0.149	0.000	0.000		0.146	4.70	47.0			
	0.149	0.000	0.000	0.000	0.146	4.70	47.0	47.0	3E-04	0.034
	0.230	0.043	1.38		0.187	6.03	60.4			
	0.230	0.042	1.36	1.37	0.188	6.06	60.6	60.5	0.003	0.330
	0.350	0.111	3.59		0.239	7.70	77.0			
	0.350	0.112	3.60	3.60	0.238	7.69	76.9	76.9	8E-04	0.080
	0.520	0.266	8.58		0.254	8.19	81.9			
	0.520	0.264	8.52	8.55	0.256	8.26	82.6	82.3	0.008	0.784
	0.931	0.629	20.29		0.302	9.74	97.4			
	0.931	0.649	20.9		0.282	9.10	91.0			
	0.931	0.650	21.0	20.95	0.281	9.06	90.6	90.8	3.82	4.21
	1.55	1.25	40.2		0.273	8.82	98.0			
	1.55	1.24	40.0		0.299	9.66	99.6			
	1.55	1.24	40.0		0.310	10.0	100			
44.5	1.55	1.23	39.6		0.225	7.25	104			
46.2	1.55	1.23	39.5	39.7	0.237	7.65	105	104	2.87	2.79
50	3.10	2.75	88.8		0.276	8.90	112			
49.8	3.10	2.75	88.6		0.280	9.03	114			
48	3.10	2.77	89.4		0.254	8.21	106			
52	3.10	2.77	89.4	89.4	0.270	8.71	106	106	3.64	3.43
	3.10	2.77	89.2		0.334	10.8	108			
57	31.0	30.7	989		0.314	10.1	113			
41.6	31.0	30.6	987		0.272	8.77	133			
49.1	31.0	30.6	987	988	0.325	10.5	135	134	12.3	9.19

Table C-14 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 72 hours, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia -nce	mean variance, σ (%)
	0.067	0.000	0.000		0.065	2.10	21.0			
	0.067	0.000	0.000	0.000	0.065	2.10	21.0	21.03	0	0.000
	0.0798	0.000	0.000		0.078	2.52	25.2			
	0.0798	0.000	0.000	0.000	0.078	2.52	25.2	25.16	0	0.000
	0.1492	0.000	0.000		0.146	4.70	47.0			
	0.1492	0.000	0.000	0.000	0.146	4.70	47.0	47.03	0	0.000
	0.23	0.030	0.968		0.200	6.45	64.5			
	0.23	0.029	0.936	0.952	0.201	6.48	64.8	64.7	0.005	0.499
	0.35	0.100	3.23		0.250	8.06	80.6			
	0.35	0.094	3.04	3.13	0.256	8.25	82.5	81.6	0.023	2.303
	0.52	0.252	8.13		0.268	8.65	86.5			
	0.52	0.253	8.16	8.15	0.267	8.61	86.1	86.3	0	0.374
37.7	1.55	1.25	40.2		0.183	5.89	98.1			
37.7	1.55	1.22	39.2		0.200	6.45	107			
42.6	1.55	1.22	39.4		0.222	7.17	106			
47.7	1.55	1.24	39.8	39.5	0.239	7.70	102	105	4.25	4.05
35.9	3.1	2.77	89.5		0.186	6.00	105			
37.7	3.1	2.76	89.1		0.203	6.55	109			
50	3.1	2.76	89.1	89.08	0.269	8.68	109	109	3.12	2.86
50.8	3.1	2.75	88.7		0.280	9.03	113			
42	31	30.6	987		0.262	8.45	127			
39.6	31	30.6	986		0.274	8.84	143			
50	31	30.6	986	986	0.352	11.3	143	143	8.77	6.15
45	31	30.5	985		0.325	10.4	146			

Table C-15 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 96 hours, Ionic Strength = 0.001 M $NaNO_3$

Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
0.931	0.661	21.3		0.270	8.71	87.1			
0.931	0.639	20.6		0.292	9.42	94.2			
0.931	0.633	20.4	20.5	0.298	9.61	96.1	95.2	4.76	5.0
1.50	1.23	39.6		0.273	8.82	88.2			
1.50	1.20	38.7		0.300	9.68	96.8			
1.50	1.19	38.3	38.5	0.313	10.1	101	98.9	6.49	6.56
3.01	2.67	86.0		0.343	11.1	111			
3.01	2.68	86.3	86.2	0.335	10.8	108	109	0.024	2.4
5.86	5.57	180		0.292	9.42	94.2			
5.86	5.53	179		0.326	10.5	105			
5.86	5.51	178	178	0.346	11.2	112	108	8.8	8.12

Table C-16 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 168 hours, Ionic Strength = 0.001M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Variance	mean variance σ (%)
	0.067	0.000	0.000		0.065	2.10	21.0			
	0.067	0.000	0.000	0.000	0.065	2.10	21.0	21.03	0	0.000
	0.080	0.000	0.000		0.078	2.52	25.2			
	0.080	0.000	0.000	0.000	0.078	2.52	25.2	25.16	0	0.000
	0.149	0.000	0.000		0.146	4.70	47.0			
	0.149	0.000	0.000	0.000	0.146	4.70	47.0	47.01	7E-04	0.069
	0.230	0.021	0.684		0.209	6.74	67.4			
	0.230	0.016	0.522	0.603	0.214	6.90	69.0	68.16	0.024	2.370
	0.350	0.098	3.16		0.252	8.13	81.3			
	0.350	0.088	2.84	3	0.262	8.45	84.5	82.9	0.039	3.891
	0.520	0.230	7.42		0.290	9.35	93.5			
	0.520	0.231	7.45	7.44	0.289	9.32	93.2	93.39	0.003	0.345
40.9	1.55	1.20	38.6		0.229	7.39	114			
35.8	1.55	1.23	39.7		0.183	5.89	103			
43.5	1.55	1.22	39.4		0.228	7.33	106			
44.5	1.55	1.22	39.3	39.3	0.236	7.61	108	107	4.37	4.08
25	3.10	2.74	88.3		0.144	4.65	117			
50.3	3.10	2.75	88.6	88.5	0.283	9.13	114	116	7.66	6.63
53.6	3.10	2.71	87.3		0.336	10.8	127			
24	3.10	2.76	89.1		0.129	4.16	109			
44.7	31.0	30.6	988		0.273	8.82	124			
37	31.0	30.6	986		0.250	8.06	139			
41.5	31.0	30.5	985	986	0.313	10.1	153	146	14.5	9.9

Table C-17 Experimental Data for Phosphate Adsorption Isotherm at 0.1 g/l Goethite Concentration, pH = 4, Reaction time = 720 hours, Ionic Strength = 0.001M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
34.8	1.55	1.21	39.1		0.187	6.04	109			
32	1.55	1.19	38.4	38.8	0.183	5.90	116	113	0.058	5.8
62.8	3.10	2.73	87.9		0.374	12.06	121			
78.5	3.10	2.73	87.9	87.9	0.467	15.06	121	121	1.42	1.17
54	3.10	2.72	87.7		0.328	10.6	123			
49.6	31.0	30.5	985		0.365	11.8	150			
41.5	31.0	30.6	986	985	0.29	9.35	142	146	0.054	5.4

Table C-18 Experimental Data for Phosphate Adsorption Isotherm at 0.01 g/l Goethite Concentration, pH = 4, Reaction time = 1 hour, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
6.28	0.034	0.016	0.523		0.017	0.558	55.8			
5.35	0.034	0.019	0.519	0.521	0.015	0.477	56.2	56.0	0.265	0.671
5.45	0.067	0.051	1.56		0.017	0.532	61.462			
5.45	0.067	0.051	1.56	1.560	0.016	0.526	60.717	61.1	0.527	1.220
5.45	0.105	0.088	2.77		0.016	0.529	61.130			
5.45	0.105	0.087	2.72	2.75	0.018	0.576	66.560	63.8	3.840	8.505
5.38	0.155	0.138	4.38		0.017	0.533	62.228			
5.80	0.155	0.138	4.37	4.38	0.017	0.564	62.661	62.4	0.306	0.693
5.36	1.55	1.52	49.1		0.023	0.747	87.7			
5.16	1.55	1.52	49.2	49.1	0.022	0.694	84.6	86.2	7.7	8.91
5.03	1.55	1.52	49.0		0.024	0.789	99.2			
5.44	3.10	3.07	99.2		0.023	0.730	84.4			
5.32	3.10	3.07	99.1	99.1	0.023	0.750	88.6	86.5	7.01	8.1
5.00	3.10	3.07	99.0		0.024	0.780	98.1			
4.75	31.0	30.96	999		0.030	0.958	127			
4.71	31.0	30.96	999		0.030	0.967	127			
3.82	31.0	30.95	998		0.030	0.975	161			
4.77	31.0	30.95	999		0.036	1.16	153			
4.15	31.0	30.95	999	999	0.031	1.01	153	153.	16	10.4

Table C-19 Experimental Data for Phosphate Adsorption Isotherm at 0.01 g/l Goethite Concentration, pH = 4, Reaction time = 24 hours, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
5.03	0.034	0.017	0.419		0.016	0.529	66.1			
	0.034	0.017	0.533	0.476	0.017	0.547	54.7	60.4	0.188	18.84
	0.067	0.048	1.53		0.020	0.639	63.8			
4.97	0.067	0.050	1.47	1.50	0.017	0.551	69.7	66.8	0.088	8.8
4.97	0.105	0.083	2.68		0.022	0.703	70.3			
5.27	0.105	0.085	2.62	2.65	0.020	0.642	76.6	73.5	0.086	8.56
5.27	0.155	0.135	4.22		0.020	0.658	78.5			
5.53	0.155	0.134	4.23	4.23	0.021	0.677	77.0	77.8	0.020	1.99
5.23	0.931	0.908	29.1		0.023	0.742	89.2			
5.34	0.931	0.906	29.1	29.1	0.025	0.806	94.9	92.0	0.062	6.2
4.97	1.55	1.53	49.1		0.023	0.754	95.5			
5.04	1.55	1.52	48.8		0.031	0.993	120			
4.81	1.55	1.52	48.9		0.027	0.865	113			
3.35	1.55	1.53	48.9	48.9	0.018	0.586	110	111.5	10.2	9.15
5.04	3.10	3.07	98.8		0.032	1.019	119			
5.40	3.10	3.07	98.8	98.8	0.029	0.937	117	118	3.89	3.30
2.86	3.10	3.08	98.8		0.017	0.548	121			
5.50	3.10	3.07	98.8		0.030	0.977	112			
5.50	5.86	5.83	188		0.030	0.968	111			
5.13	5.86	5.83	188		0.033	1.06	124			
5.00	5.86	5.83	188	188	0.031	1.00	126	125	10.4	8.32
5.56	5.86	5.82	188		0.037	1.20	136			
5.00	31.0	30.95	998		0.047	1.53	179			
4.68	31.0	30.95	998		0.042	1.36	183			
5.59	31.0	30.95	998		0.050	1.60	180			
3.43	31.0	30.97	998	998	0.031	0.99	183	182	1.77	0.98

Table C-20 Experimental Data for Phosphate Adsorption Isotherm at 0.01 g/l Goethite Concentration, pH = 4, Reaction time = 72 hours, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Variance	mean variance, σ (%)
	0.034	0.012	0.376		0.022	0.705	70.5			
2.70	0.034	0.025	0.409	0.393	0.009	0.284	67.5	68.8	0.05	4.85
	0.067	0.044	1.42		0.023	0.752	75.2			
4.84	0.067	0.049	1.42		0.018	0.577	75.0			
3.33	0.067	0.055	1.40	1.42	0.013	0.407	76.9	75.7	1.050	1.39
4.15	0.105	0.082	2.66		0.015	0.479	72.5			
4.50	0.105	0.081	2.63		0.018	0.569	75.9			
4.40	0.105	0.082	2.64	2.64	0.016	0.523	74.7	74.4	1.690	2.27
4.10	0.155	0.132	4.25		0.015	0.485	74.6			
5.03	0.155	0.132	4.26	4.26	0.018	0.588	73.6	74.1	0.014	1.39
4.46	1.55	1.51	48.8		0.027	0.871	124			
4.91	1.55	1.51	48.8		0.028	0.903	116			
3.57	1.55	1.52	48.9	48.8	0.020	0.649	114	115.	5.47	4.75
4.11	3.10	3.06	98.8		0.024	0.774	118			
4.64	3.10	3.06	98.8		0.028	0.916	124			
4.33	3.10	3.06	98.7	98.8	0.027	0.865	126	125	3.73	2.99
3.39	31.0	30.9	998		0.032	1.04	192			
4.72	31.0	30.9	998		0.028	0.906	201			
4.60	31.0	30.9	999	998	0.030	0.973	203	202	5.92	2.93

Table C-21 Experimental Data for Phosphate Adsorption Isotherm at 0.01 g/l Goethite Concentration, pH = 4, Reaction time = 168 hours, Ionic Strength = 0.001M NaNO$_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
5.66	0.034	0.013	0.346		0.021	0.661	73.5			
5.66	0.034	0.013	0.358	0.352	0.020	0.651	72.3	73.00	0.016	1.61
3.95	0.067	0.053	1.421		0.015	0.472	75.0			
4.27	0.067	0.050	1.342	1.382	0.017	0.564	82.9	78.9	0.100	10.04
5.36	0.105	0.084	2.589		0.021	0.677	79.5			
3.50	0.105	0.091	2.572	2.58	0.014	0.453	81.2	80.4	0.021	2.15
4.05	0.155	0.139	4.193		0.016	0.520	80.7			
4.44	0.155	0.137	4.178	4.19	0.018	0.572	82.2	81.4	0.019	1.89
5.85	1.55	1.51	48.7		0.040	1.28	128			
5.85	1.55	1.51	48.8		0.038	1.22	122			
5.85	1.55	1.51	48.8	48.8	0.037	1.21	120	121	3.72	3.06
5.66	3.10	3.06	98.7		0.037	1.19	132			
4.71	3.10	3.06	98.7		0.042	1.34	134			
5.66	3.10	3.06	98.7	98.7	0.037	1.18	132	132	1.51	1.14
3.14	31.0	30.968	998		0.032	1.04	207			
4.88	31.0	30.950	998		0.050	1.60	206			
4.55	31.0	30.952	998	998	0.048	1.52	210	208	1.87	0.901

Table C-22 Experimental Data for Phosphate Adsorption Isotherm at 0.01 g/l goethite concentration, pH = 4, Reaction time = 720 hours, Ionic Strength = 0.001 M $NaNO_3$

Fe Conc. (mg/l)	Initial Conc. (mg/l)	Final Conc. (mg/l)	Final Conc. (μmol/l)	Average	Adsorbed (mg/l)	Adsorbed (μmol/l)	Adsorbed (μmol/g)	Average	Varia-nce	mean variance, σ (%)
3.24	1.55	1.51	48.677		0.041	1.323	132			
3.80	1.55	1.51	48.742		0.039	1.258	126			
	1.55	1.51	48.620	48.68	0.043	1.380	138	132.	6.098	4.619
3.90	3.10	3.06	98.742		0.039	1.258	126			
2.90	3.10	3.06	98.548		0.045	1.452	145			
	3.10	3.05	98.452	98.6	0.048	1.548	155	142	14.783	10.415
3.19	31.0	30.96	997.840		0.033	1.080	216			
3.92	31.0	30.95	997.622	998	0.046	1.481	238	227	0.096	9.6