# EFFECT OF HEATING ON PHOSPHATE ADSORPTION BY SOIL

JASON CHONG ZHE XIN

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# DECLARATION

I hereby declare that this dissertation is based on my original work, except for quotations and summaries each of which have been fully acknowledged.

18 April 2008

JASON CHONG ZHE XIN
(HS 2005-2297)

## VERIFICATION

**NAME:** Jason Chong Zhe Xin

**TITLE:** Effect of Heating/Burning on Phosphate Adsorption by Soil

**Prof. Madya Dr. Marcus Jopony**

**Dr. Noumie Surugau**

**Dr. Sazmal Effendi Arshad**

**Dean of School of Science and Technolgy**
**Prof. Madya Dr Shariff A. Kadir S. Omang**

8 May, 2008

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# ABSTRACT

The effect of soil heating at different temperatures (i.e 100 – 500 °C) on phosphate adsorption have been investigated. The soil was obtained within the university campus. The final concentration of phosphate in solution was determined according to ascorbic acid method. The results of the batch experiments showed that percentage removal of phosphate decreased while the amount of phosphate adsorbed increased with increase in initial phosphate concentration. At a fixed initial phosphate concentration, the percentage removal of phosphate increased with increasing heating temperature from 100°C to 500°C. The value of maximum adsorption capacity also increased with increasing heating temperature. The adsorption data fitted to Langmuir or Freundlich isotherm depending on the heating temperature. Overall, heating the soil at high temperatures have a positive effect on phosphate adsorption.

# *KESAN PEMANASAN TERHADAP JERAPAN FOSFAT OLEH TANAH*

## *ABSTRAK*

*Kesan pemanasan tanah pada suhu yang berbeza (i.e 100 – 500 °C) terhadap jerapan fosfat telah dikajikan. Tanah diperolehi dalam kampus universiti. Kepekatan akhir fosfat dalam larutan ditentukan mengikut kaedah asid askorbik. Hasil eksperimen kelompok menunjukkan peratus penyingkiran ion fosfat menurun manakala jumlah fosfat terjerap meningkat apabila kepekatan awal fosfat meningkat. Pada kepekatan awal fosfat yang tetap, peratus penyingkiran ion fosfat meningkat apabila suhu pemanasan meningkat dari 100°C hingga 500°C. Nilai kapacity jerapan maksima juga didapati meningkat apabila suhu pemanasan meningkat. Data jerapan mematuhi isotherm Langmuir atau Freundlich bergantung kepada suhu pemanasan sample. Pada keseluruhannya, pemanasan tanah memberikan kesan positif terhadap jerapan fosfat.*

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of The Study

Phosphorus in soils exists as organic-P and inorganic-P, the proportion of which is dependent on the type of soil (Cornforth, 1998). Inorganic phosphorus includes solution-P, adsorbed-P and phosphate minerals. Solution-P compresses of orthophosphates such as $H_2PO^{4-}$ and $HPO_4^{2-}$(Cornforth, 1998). These forms of phosphorus are required for the plant nutrition. Adsorbed-P refers to phosphate anion adsorbed on soil components in particular iron and aluminum oxides. Phosphate minerals include Ca-P (hydroxylapatite $Ca_5(PO_4)_3OH$), Fe-P (Dufrenite, $Fe_5(PO_4)_3(OH)_5.2H_2O$) and Al-P (alphite, $AlPO_4$).

The phosphate minerals in soil was classified in to many groups, such as berlinite group (alphite $AlPO_4$), apatite groups (apatite $Ca_2Ca_3[PO_4]_3$ (OH, F)), struvite group ( Newberryite $HMg[PO_4](H_2O)_3$ ) and many more (Dixon *et al.*,1997).

Tropical soils are known for its high ability and capacity to adsorb phosphate. This is associated with the acidic pH and high iron and aluminum oxides content of the soils (Bigham *et al.*, 1978). Other properties of the soil such as the clay and organic content will also play a part in affecting phosphate adsorption by the soil. Phosphate adsorption by soils is also dependent on other factors such as soil heating temperature (Jiang *et al.*, 2004), contact time (Ozacar, 2006) and soil pH (Luengo *et al.*, 2007). Adsorption is a process which described the accumulation of a substance or material at an interface between the solid surface and the bathing solution (Sparks, 1995). So, adsorption can lead to low concentration of phosphate in soil solution.

The purpose to study effect of heating on phosphate adsorption by soils it because soils can be exposed to extreme heating during burning activities, either via forest fires or agricultural practices. This will have an impact on soil properties (Jiang *et al,* 2004, Santa *et al.*, 2006) and consequently on phosphate adsorption characteristics.

## 1.2 Objectives

The objectives of this study are:

(1) To determine the effect of initial phosphate concentration on phosphate adsorption by soil.

(2) To determine the effect of heating temperature on phosphate adsorption by soil.

## 1.3 Scope of Study

In this study, soil sample obtained within the university campus was sieved to obtain particles size of < 2 mm and was subjected to different heating temperature before its respective adsorption ability for phosphate was tested. The residual phosphate concentration in solution was determined colorimetrically.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Phosphorus in Soil and Water

Phosphorus (P) is the tenth most abundant element, with an average concentration of 0.1 % in the earth's crust, 0.07 % in the continental sediments, 0.10 % in igneus rock and about 0.12% in marine sediments (Nriagu and Moore, 1984).

### 2.1.1 Forms of phosphorus in soil

Phosphorus in soil comprises of organic-P and inorganic-P. Organic-P is abundant in soils and is an important source of phosphorus for plants in both natural and managed environments (Turner *et al.*, 2004). Organic-P is present as a constituent of organic compounds. Exampes of organic phosphate are phosphate esters, inositol phosphate and myoinositol hexaphosphate (Turner *et al.*, 2004).

In soil, the amount inorganic-P is less that the organic-P (Cornforth, 1998). The main forms of inorganic-P in acid soil are Al-P and Fe-P while in calcareous soil is Ca-P. The phosphorus in soil solution is mainly inorganic phosphate which exists in three orthophosphate ion forms, namely $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$. $H_2PO_4^-$ and $HPO_4^{2-}$ are the dominant type of phosphorus in the soil solution (Cornforth, 1998).

### 2.1.2 Phosphate in water

Phosphorus exist in water as inorganic phosphorus and mainly as orthophosphates. The speciation of orthophosphate ions in solution is pH dependent as shown in (Figure 2.1) and can be explained by the following reactions (Roques, 1996):

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad {}_pK_1 \approx 2.16$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad {}_pK_2 \approx 7.16$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad {}_pK_3 \approx 12.$$

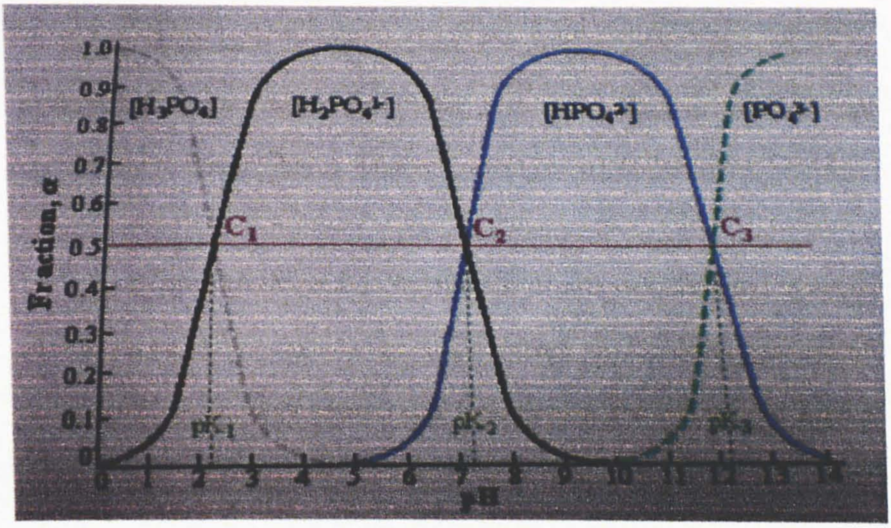

**Fig. 2.1** Type of phosphate ions in solution at different pH level.

### 2.1.3 Equilibria of phosphorus in soil

The equilibrium between orthophosphate ions in the soil solution and in the soil components is controlled by mobilization and immobilization processes shown by (Fig 2.2). The reactions involved are desorption, dissolution, precipitation and adsorption.

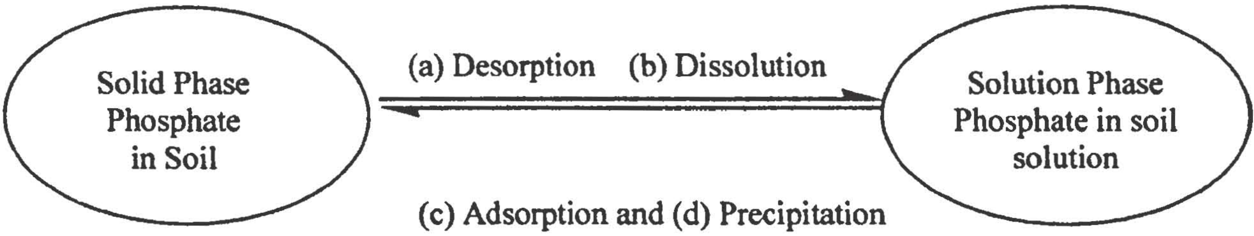

**Fig. 2.2** Schematic diagram of phosphate equilibrium in soil environment.

*a. Desorption*

Desorption is a reverse reaction of adsorption in which the adsorbed substances are released from the surface. If the bonding strength is weak, then the adsorbed substances can be readily desorbed. By contrast, it would be hard to desorb if the bonding is strong.

*b. Dissolution*

Dissolution is a process of dissolving phosphate minerals in soils. The solubility of the mineral is dependent on the type of mineral.

*c. Adsorption*

Adsorption is a process in which the phosphate ions are removed from soil solution by interacting with the surfaces of soil components.

*d. Precipitation*

Precipitation is a process in which phosphate in solution is transformed into insoluble phosphate following interaction with ions present in soil solution.

### 2.1.4 Significance of phosphorus in soil and water

Phosphorus (P) is an essential nutrient element for plant growth and all forms of life (Hu *et al.*, 2001). So, phosphorus availability is a critical factor in determining autotrophic production in the ecosystem (Nriagu and Moore, 1984). Despite the total-P in soil can be high, plant available phosphorus can be relatively low in acid and calcareous soils. This is because phosphate can be strongly fixed or adsorbed while the solubility of phosphorus minerals is low. Therefore phosphorus availability in soils is normally improved by using phosphate fertilizer (Cornforth, 1998). However, excessive applications of the phosphate fertilizers can result in the release of phosphate into rivers or lakes through surface runoff. When rivers or lakes contain high level of phosphate, eutrophication may occur. Eutrophication is a phenomenon where the algae bloom at the surface of the water until covering the entire water surface. As a result, it will affect the ecosystem of the river or lake by blocking the light from penetrating into the water. Without light, aquatic plants cannot undergo photosynthesis and will die and decay, thus increasing the biological oxygen demand, (BOD) (Dorte *et al*, 2007).

## 2.2 Phosphate Adsorption by Soil and Soil Components

### 2.2.1 Basic concept of adsorption

Adsorption is the net accumulation of matter at the interface between a solid phase and an aqueous solution phase or a gas phase (Sposito, 1989). The matter that accumulates at the interface is known as adsorbate while the solid phase on which it accumulates is the adsorbent (Sposito, 1989). Adsorption can be classified in two types, physisorption and chemisorption. In physisorption, the adsorbate interacts with adsorbent in a weak and general way. It could be as simple as van der waals, dispersion interaction that keeps a molecule on a surface or it could be a dipole interaction (Ball, 2003). As a result, the physisorption is a reversible reaction. For chemisorption, the strength of bond between adsorbate and adsorbent is high enough to be considered as covalent bond (Ball, 2003).

### 2.2.2 Previous studies on phosphate adsorption

Numerous studies have been carried out on phosphate adsorption by soil and other soil components. Some of the studies are listed in the (Table 2.1):

**Table 2.1** Type of adsorbents and the variables studied in previous studies on phosphate adsorption..

| Reference | Types of Soil/ Soil Component | Variables Studied. |
|---|---|---|
| Hu *et al.* (2001) | Acidic soil | Concentration of organic acid and pH. |
| Rhoton and Bigham (2004) | Ferrihydrite-Amended Soils | Initial phosphate concentration, pH and adsorbent dosage. |
| Luengo *et al.* (2007) | Goethite, FeO(OH) | Initial concentration of oxoanions, pH & temperature |
| Ozacar (2006) | Alunite or alumstone | Adsorbent's particle size, pH, temperature & initial phosphate concentration. |
| Chen *et al.* (1971) | Aluminum Oxide and kaolinite (clay mineral) | Temperature & adsorbent dosage. |
| Karaca *et al.* (2004) | Dolomite | pH, temperature, stirring speed & initial phosphate concentration. |
| Karageorgiou *et al.* (2006) | Calcite or limestone | pH, contact time & orthophosphate/solid ratio. |
| Zeng *et al.* (2004) | Iron oxide tailing | pH & temperature |
| Li *et al.* (2006) | raw and activated red mud and fly ash | Heat, pH & contact time. |
| Pradaz *et al.* (1992) | Soil | pH, organic matter content & free iron oxide content. |
| Borggaard *et al.* (2005) | Aluminium and iron oxide. | Dosage of humic acid. |

### 2.2.3 Kinetics of phosphate adsorption

Adsorption is a time-dependent process and can be generally described by using pseudo first order kinetic model and pseudo second order kinetic model or intraparticle diffusion model.

*(a) Pseudo First Order Kinetic*

The pseudo first order equation can be expressed as follows (Ozacar, 2006):

$$\log (q_e - q_t) = \log q_e - K_1 t/2.303$$

where,

$q_e$ = amount adsorbed at equilibrium.

$q_t$ = amount adsorbed at a time, t.

$K_1$ = rate constant of Pseudo first order.

A linear graph of $\log (q_e - q_t)$ vs t implies that the adsorption is conforms to the pseudo first order kinetics.

*(b) Pseudo Second Order Equation*

The pseudo second order equation can be expressed as follow (Karaca *et al.*, 2007).

$$t/q_t = 1/K_2 q_e^2 + 1/q_e t$$

where,

$q_e$ = amount adsorbed at equilibrium.

$q_t$ = amount adsorbed at a time, t.

$K_2$ = rate constant of Pseudo second order.

A linear graph of $t/q_t$ vs t implied that the adsorption is conforms to the pseudo second order kinetic and therby indicates a chemisorption process.

*(c) Interparticle Diffusion Equation*

The interparticle diffusion equation can be expressed as follows (Fierro, 2007):

$$qt = k_{id}. t^{1/2} + C$$

where,

$qt$ = the amount of phosphate adsorbed at time t.

$k_{id}$ = the intraparticle diffusion rate constant.

C = a constant related to the thickness of the boundary layer.

A linear plot of qt versus $t^{1/2}$ implies that the sorption process is controlled by intra-particle diffusion and the transport of phosphate into the pores of adsorbent is the rate limiting step.

Depending on the type of adsorbent, phosphate adsorption conform to pseudo-first model, pseudo-second model and/or intraparticle diffusion kinetic model (Table 2.2).

**Table 2.2** Examples of previous study on phosphate adsorption kinetics on various adsorbent.

| Adsorbents | Kinetic models | | | Reference |
|---|---|---|---|---|
| | Pseudo first order | Pseudo second order | Intraparticle diffusion | |
| Goethite, FeO(OH) | | | √ | Luengo *et al.* (2006) |
| Aluminum hydroxide | √ | | | Guan *et al.* (2006) |
| Alunite or alumstone | | √ | | Ozacar (2006) |
| Aluminum Oxide and kaolinite (clay mineral) | √ | | | Chen *et al.* (1971) |
| Iron oxide tailing | - | - | - | Zeng *et al.* (2004) |
| Blast furnace slags | | √ | √ | Kostura *et al.* (2005) |
| aluminum oxide hydroxide | √ | | | Tanada *et al.* (2002) |

* √= conform to

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