



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: [www.elsevier.com/locate/clay](http://www.elsevier.com/locate/clay)

## A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters

F. Haghseresht<sup>a,\*</sup>, Shaobin Wang<sup>b,\*</sup>, D.D. Do<sup>c</sup>

<sup>a</sup> ARC Centre for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD, 4072, Australia

<sup>b</sup> Department of Chemical Engineering, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

<sup>c</sup> Division of Chemical Engineering, The University of Queensland, Brisbane, QLD, 4072, Australia

### ARTICLE INFO

#### Article history:

Received 25 June 2009

Received in revised form 23 September 2009

Accepted 24 September 2009

Available online xxx

#### Keywords:

Phosphate adsorption

Modified bentonite

Lanthanum

Chemisorption

### ABSTRACT

Phoslock<sup>®</sup>, a lanthanum-modified bentonite, has been investigated for phosphate uptake from synthetic and real wastewaters in laboratory and field. In laboratory tests, equilibrium and kinetics were studied at various temperatures, ionic strength, and pHs. The investigation indicated that phosphate adsorption occurs through a chemisorption process. The activation energy of the adsorption process was calculated based on pseudo-second order rate constant. The maximum adsorption capacity of Phoslock was unaffected at pH 5–7, but decreased at higher pHs. The monovalent phosphate anion, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, had the greatest affinity for the adsorbent surface. Furthermore, it was also shown that the activation energy was lower at a higher solution pH attributed to the loss of adsorption sites at the higher pHs while it remained unaffected by the ionic strength of the solution. A field test also demonstrated that the Phoslock works well for phosphate uptake in polluted waters.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

During the last several centuries, the rapid increase in anthropogenic activity has accelerated the eutrophication process significantly, markedly altering the geochemical cycles of carbon, nitrogen and phosphorous. In fact, a recent publication has shown that at least 40% of the lakes and the reservoirs in many regions of the world are considered to have eutrophication problems (Farmer, 2004). Of the key nutrients, it is the excess of bioavailable phosphorous which is understood to lead to eutrophication of water bodies, resulting in increased aquatic plant and algal growth.

In recent decades, research has considered a number of different solid adsorbents for their use in reducing phosphorous levels entering the water ways. Some of the adsorbents investigated have included clay minerals like bentonite and its pillared forms, iron oxide, red mud, fly ash, and carbonates (de-Bashan and Bashan, 2004; Huang et al., 2008; Wang et al., 2008). While they may have various beneficial applications, the use of each has similar disadvantages (Douglas et al., 2004). For example, the performance of iron oxide and red mud in reducing phosphorous concentrations is strongly affected by the solution pH. This has also been demonstrated by other authors (Tanada et al., 2003; Zeng et al., 2004). In addition, the stoichiometry of the reacting species with the phosphate anion is greater than 1:1 in most cases. The key disadvantage of these adsorbents, however, is

that the adsorbed phosphate can be re-released when the key solution chemical properties, such as pH and redox conditions, are changed.

In the 1970s, Melnyk et al. (1974) and Recht et al. (1970) reported that phosphate precipitation by lanthanum was more effective over a wider pH range (4.5–8.5) than either Fe(III) or aluminium salts. In addition, the molar ratio of lanthanum to phosphate is 1:1, as shown in Eq. (1).



The lanthanum–phosphate complex is also known to be highly insoluble and able to form when present in low concentrations and at low pH values. The extent of the insolubility of lanthanum–phosphate complexes were studied by Firsching et al. (Firsching and Brune, 1991; Firsching and Kell, 1993). The authors reported its solubility product,  $K_{sp}$ , in aqueous solution to be  $-24.76$ , and in seawater  $-27.92$ , making it the least soluble among the rare-earth-phosphate complexes. In addition, the authors noted that the solubility of the lanthanum–phosphate complex decreased with an increase in temperature, reporting a  $K_{sp}$  value of  $-26.49$  at 70 °C in aqueous solutions (Firsching and Brune, 1991), further indicating the strength of the lanthanum–phosphate bond. Using GEOCHEM-PC, Diatloff et al. (1993) indicated that the lanthanum–phosphate complex can be formed in solutions with a pH as low as 4.0. Their work demonstrated that this reaction can occur at pH 4, with the lanthanum and phosphate species concentrations as low as 0.695 and 0.15 mg/L, respectively.

However, the research on the use of lanthanum in phosphate reduction also revealed that depending on the concentration and

\* Corresponding authors. Tel.: +61 7 3346 3960; fax: +61 7 3346 3973.

E-mail addresses: [f.haghseresht@uq.edu.au](mailto:f.haghseresht@uq.edu.au) (F. Haghseresht), [shaobin.wang@curtin.edu.au](mailto:shaobin.wang@curtin.edu.au) (S. Wang).

application rates, this element can be toxic to some aquatic life (Douglas et al., 2004). This disadvantage can be overcome by incorporating lanthanum into clay minerals with high cation exchange capacities and a new lanthanum-modified bentonite (Phoslock) was developed in the 1990s by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia. It was evaluated in a field trial (Robb et al., 2003).

As in most adsorption processes in the aqueous phase, any changes in the solution chemistry can lead to changes in other equilibria in the adsorption system. This includes changes in the chemistry of active sites that are responsible for the phosphate adsorption (the lanthanum ions), the net charge on the material surface and the nature of the phosphate species. For example, with an increase in pH, it is not only the phosphate anions which lose hydrogen ions, the lanthanum ions are also hydroxylated simultaneously as well. Since the development of Phoslock, few investigations have been found in open publications. This work was therefore performed to gain insights into the phosphate uptake by Phoslock, by studying its physicochemical properties, adsorption kinetics and equilibrium behaviour. The purpose of this research was twofold: firstly, to investigate the effectiveness of Phoslock in reducing phosphorous concentrations, and, secondly, to gain an insight into the adsorption mechanism of this lanthanum-modified bentonite product. This paper will describe the equilibrium and kinetic studies which contributed to our understanding of the properties of the new adsorbent. Importantly, the effect of pH on the adsorption process of phosphate by Phoslock was explored, and the key physical and chemical characteristics of the product are described.

## 2. Methods

### 2.1. Adsorbent and characterisation

Lanthanum-modified bentonite was provided by Phoslock Water Solutions Pty Ltd (PWS), which was prepared by an ion exchange process using bentonite and lanthanum solution. The ion exchanged bentonite was then mixed with precipitated silica for granulation. All characterisation and laboratory and field experiments were performed using the adsorbent as received. The elemental composition of the adsorbent was determined by X-ray fluorescence spectroscopy. The moisture content of the modified bentonite was obtained by drying a 10–15 g sample at 110 °C overnight. After drying the sample was then placed in a desiccator for a final mass measurement.

The pore volume and BET specific surface area of Phoslock were determined using the N<sub>2</sub> adsorption/desorption isotherms at –196 °C, using a NOVA 2000 (Quantochrome Corporation). The sample was degassed at 160 °C for 5 h. The BET specific surface area was obtained by applying the BET equation. The total pore volume of the sample was obtained from the adsorption amount at P/P<sub>0</sub> = 0.98.

The pH of the dispersed adsorbent was obtained by adding 2 g of Phoslock to 100 mL of reverse osmosis (RO) treated water. After mixing the dispersion for 15–20 min, its pH was then measured using a TPS meter.

In order to measure the particle size distribution of the dispersed Phoslock, a sample was vortexed for 1 min in 20 mL of reverse osmosis treated water. A sub-sample of the dispersion was then used for particle size distribution measurement with a Malvern Particle Sizer.

### 2.2. Equilibrium studies

The adsorption isotherms were obtained by adding different amounts of the modified bentonite (0.01–1 g) to 200 mL of 10 mg P/L solution (using A.R. Grade KH<sub>2</sub>PO<sub>4</sub>). All samples were placed in a Julabo SW22 shaking water bath at the desired temperature for 5 h. Following this period, some samples were removed from each bottle and filtered through a 0.22 μm syringe filter (Millipore) and frozen

until their soluble phosphate concentration was analysed in accordance to the American Public Health Association Standard (APHA, 1985).

The effect of pH on adsorption behaviour was obtained by adjusting the pH of initial phosphate solution to desired pH, using either 0.1 M NaOH or 0.1 M HCl solution.

### 2.3. Kinetic studies

The modified bentonite (0.92 g) was added to 4 L of RO water, containing 1 mg P/L (using A.R. Grade KH<sub>2</sub>PO<sub>4</sub>), at a set temperature and mixed at 300 rpm, using an IKA overhead mixer. The rate of phosphate uptake was then measured by taking 10 mL samples at various time intervals for three hours. During the first 30 min the rate of phosphate uptake was at its highest. The rate of uptake was determined at 10, 23 and 40 °C using untreated RO water and RO water that was adjusted to pH 7 and conductivity of 0.3 mS/cm. The conductivity of the water was adjusted by NaCl.

Three polluted water samples obtained from different sources were also tested for kinetic studies of phosphate removal. These samples were mixed with modified bentonite at a solid/liquid ratio of 0.25 at total volume of 20 L.

### 2.4. Field trial

A nursery dam with the initial water chemical characteristics (Table 1) was treated with the required amount of Phoslock. The required amount of Phoslock was found to be 4 metric tons. Such a large quantity was a result of the high pH of the water (9.0) and its large initial phosphate concentration (0.98 mg/L). However, in most field applications, even though the pH may be high, the typical initial filterable reactive phosphorous (FRP) concentrations were much lower. In order to examine the effect of Phoslock treatment on the reduction of FRP, the inflows into the dam were diverted away for a period of three days, and then reconnected again.

## 3. Results and discussion

### 3.1. Physicochemical properties of the lanthanum-modified bentonite

The BET specific surface area and total pore volume of Phoslock are presented in Table 2. The N<sub>2</sub> adsorption/desorption isotherm showed a mesoporous pattern. The BJH pore size distribution plot, using the desorption branch, demonstrated that the majority of the pores have a diameter of approximately 40 Å (Fig. 1). This indicates that water should be able to diffuse into the structure of the material reasonably well. This fact, together with its relatively small particle size (Table 2), assists in maximising the exposure of the adsorption sites, the exchanged lanthanum ions, to the phosphate anions.

The elemental composition of modified bentonite (Table 2) demonstrated large quantities of Si and Al, as expected. The modified bentonite contains approximately 49 mg of lanthanum per gram of Phoslock. Considering the 1:1 molar ratio of La and P, the theoretical adsorption capacity of Phoslock is approximately 10.6 mg of phosphorus per gram of the adsorbent. This indicates that, if all adsorption sites are available for the adsorption process, the adsorption capacity of the product cannot be greater than 10.6 mg P/g.

**Table 1**  
Key chemical properties of the wastewater in nursery dam.

Volume of the dam (Mega litre)	Total P (mg/L)	Initial FRP (mg/L)	Alkalinity (mg CaCO <sub>3</sub> /L)	Hardness (mg CaCO <sub>3</sub> /L)	pH
10	1.1	0.98	59	95	9.1 ± 0.1

**Table 2**  
Physical properties of the lanthanum-modified bentonite.

Property	Concentration (%)
Chemical composition	
SiO <sub>2</sub>	61.36
Al <sub>2</sub> O <sub>3</sub>	14.73
MgO	2.76
Fe <sub>2</sub> O <sub>3</sub>	3.64
CaO	1.79
La <sub>2</sub> O <sub>3</sub>	0.058
Specific surface area (m <sup>2</sup> /g)	39.3
Total pore volume (cm <sup>3</sup> /g)	0.171
Average particle size (μm)	22
Moisture content (%)	7–9
pH	7–7.5
Bulk Density (kg/m <sup>3</sup> )	910–960

### 3.2. Equilibrium studies

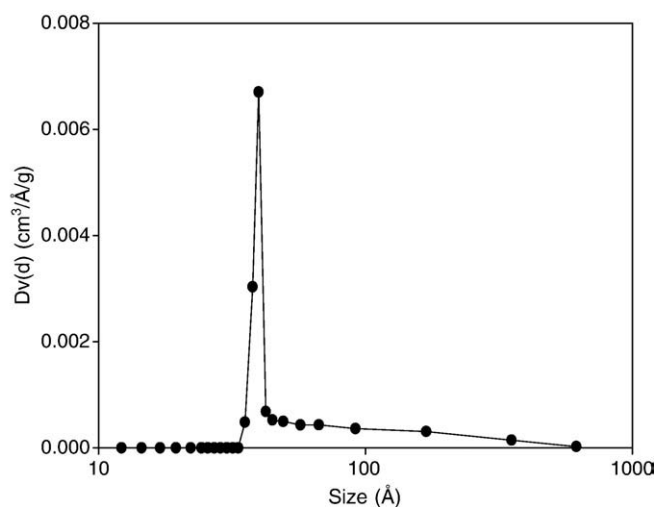
#### 3.2.1. Adsorption isotherms

Preliminary studies showed that the unmodified bentonite, used to manufacture Phoslock, adsorbed negligible amount of phosphate (<0.5 mg P/g). Two sets of adsorption isotherms of phosphate onto the lanthanum-modified bentonite at 23 °C, together with the corresponding isotherms at various temperatures are shown in Fig. 2a and b, respectively. While Fig. 2a illustrates the reproducibility of the experimental technique, both figures show that all isotherms exhibited a rapid rise in the adsorption capacity with an increase in the equilibrium solution concentration, followed by a plateau at equilibrium, demonstrating typical Langmuir isotherm characteristics. Fig. 2b also shows that the maximum adsorption capacity of the modified bentonite was increased at higher temperatures.

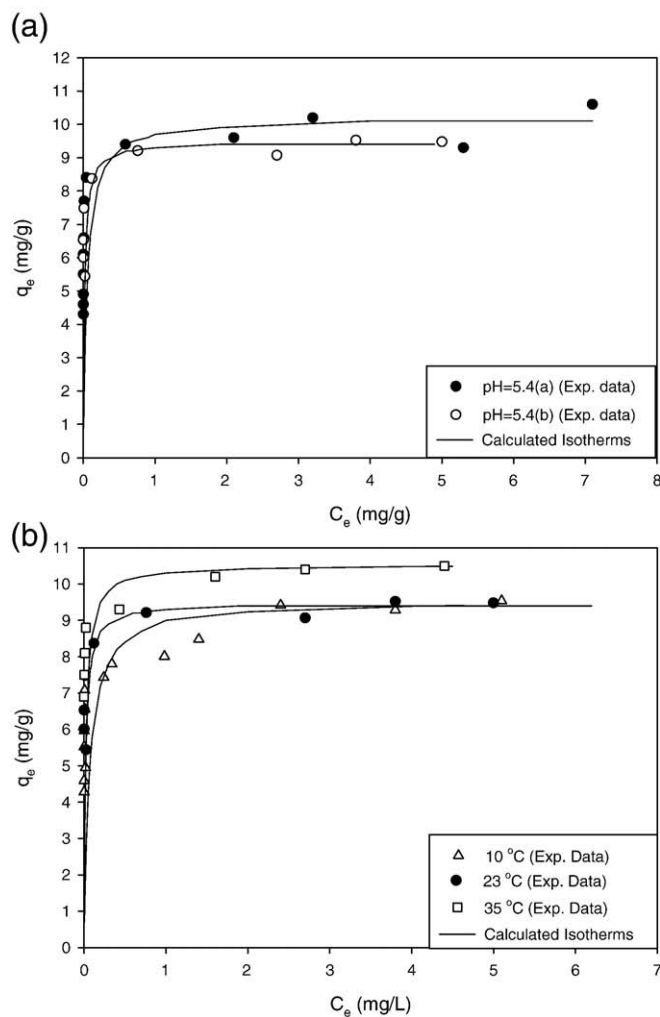
The increase in the maximum adsorption capacity of the modified bentonite, with an increase in the solution temperature, together with the shape of the isotherms described earlier, indicates that the adsorption of phosphate by the lanthanum-modified bentonite most likely occurs through chemical rather than physical interactions. In order to gain a better understanding of the adsorption mechanism, all isotherms were fitted by the Langmuir equation (Eq. (2)).

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{QK} \quad (2)$$

Where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium solution concentration (mg/L),  $Q$  is the maximum



**Fig. 1.** Pore size distribution of Phoslock.



**Fig. 2.** Experimental and calculated isotherms at different temperatures. (a) Repeat tests at 23 °C, (b) various temperatures.

adsorption capacity (mg/g) and  $K$  is the Langmuir constant, related to the adsorption energy.

The corresponding isotherm parameters were obtained by plotting  $C_e/q_e$  vs.  $C_e$  (Airoldi and Goncalves, 1987; Goncalves and Airoldi, 1989; Arakaki et al., 2002, 2004) (Table 3). As illustrated in Fig. 2a and b, the maximum adsorption capacity of Phoslock was reached when the equilibrium solution concentration was well below 1 mg/L. This means that most of the equilibrium solution concentrations were quite low ( $\ll 0.1$  mg/L). As a result of scattering low  $C_e$  data, the Langmuir equation was best used to provide an indication of the equilibrium adsorption capacities, rather than the prediction of  $q_e$ , when it is less than the equilibrium value, even though the  $R^2$  values are high.

**Table 3**  
Parameters of the linear Langmuir equation for the isotherms at various temperatures.

Temperature (°C)	Langmuir isotherm parameters			Percentage of the theoretical uptake
	$Q$ (mg/g)	$b$ (L/mg)	$R^2$	
10	9.54	15.4	0.9984	91 ± 1
23 (first run)	10.19	18.9	0.994	97 ± 1
23 (second run)	9.47	53	0.9995	90 ± 1
35	10.54	45.2	0.9998	<99

**Table 4**  
Adsorption capacity of phosphate on some adsorbents.

Adsorbent	Temperature (°C)	P adsorption (mg/g)	Reference
Red mud	25	0.58–0.80	Huang et al. (2008)
Bauxsol	23	6.5 – 14.9	Akhurst et al. (2006)
MgMn-layered double hydroxides	–	7.3	Chitrakar et al. (2005)
Palygorskites	25	3.73–8.31	Ye et al. (2006)
Lithium intercalated gibbsite	25	93	Wang et al. (2007)
Mesoporous ZrO <sub>2</sub>	25	29.7	Liu et al. (2008)
Tamarind nut shell activated carbon	14	2–18	Bhargava and Sheldarkar (1993)
Phoslock	10–35	9.5–10.5	This work

Table 3 also shows the experimental maximum adsorption capacity values,  $Q$ , in terms of the theoretical adsorption capacity, calculated using the lanthanum content of the modified bentonite (Table 1), assuming a La:P stoichiometry of 1:1. The experimental  $Q$  values are very close to the calculated values. This further indicates the 1:1 stoichiometry of lanthanum and phosphate. Table 4 presents a comparison of adsorption capacity of Phoslock with other various adsorbents for phosphate adsorption. Phoslock exhibits higher adsorption than some minerals, but less than mesoporous ZrO<sub>2</sub>.

The thermodynamic parameters of phosphate adsorption on Phoslock can be calculated using the following equation.

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

Where  $K$  is the constant in the Langmuir isotherm,  $\Delta H^\circ$  and  $\Delta S^\circ$  are enthalpy of adsorption and entropy. Using the results in Table 3,  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained as 31.6 kJ/mol and 135 J/K• mol, respectively.

### 3.2.2. Effect of pH

The equilibrium adsorption capacity of Phoslock changed very little within the pH range of 5–7 (Fig. 3) and decreased in solutions with higher pH values. At pH=9,  $Q$  was reduced by 29%, compared with the value at pH 5.

Phosphate acid undergoes dissociation at different pHs, yielding different species (Eqs. (4)–(6)). The dissociation constants for each reaction, together with the initial total phosphate concentration could

then be used to determine the concentration of the different phosphate species.



$$\text{pK}_{a1} = 2.16$$



$$\text{pK}_{a2} = 7.20$$



$$\text{pK}_{a3} = 10.3$$

Since the main phosphate species present when  $7.2 < \text{solution pH} < 10.2$  are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ , the variation of the equilibrium adsorption capacity,  $Q$ , with the concentration of these species could be calculated using Eq. (7)

$$\text{pH} - \text{pK}_a = \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (7)$$

where  $\text{A}^-$  and  $\text{HA}$  are  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ , respectively.

$Q$  increased when the concentration of the  $\text{H}_2\text{PO}_4^-$  species was increased (Fig. 4). This indicates that the lanthanum ions had a greater affinity for the monovalent dihydrogen phosphate. This finding can also be explained in terms of the hydroxylation of the lanthanum ions. The hydroxylation process occurs in three steps with the  $\text{La}(\text{OH})_3$  being the only insoluble species, formed at  $\text{pH} = 7.58$  (Suzuki et al., 1989). This means when pH is in the range of 5–7, the most likely form of lanthanum is  $\text{La}(\text{OH})_2^+$  species, which would have the stoichiometric ratio of 1:1 with the  $\text{H}_2\text{PO}_4^-$  species. This does not mean that the  $\text{HPO}_4^{2-}$  species is not adsorbed; it simply infers that the monovalent ion can react with the active sites of Phoslock more readily.

The above-mentioned explanation could apply within the pH of 5–7 and even up to pH 8. However, as lanthanum was mainly in its insoluble form of  $\text{La}(\text{OH})_3$  at the higher pHs, there may have been other mechanisms involved. In studying reduction of arsenic by lanthanum compounds, another oxyanion that can be removed by the modified bentonite, other authors (Tokunaga et al., 1997) suggested that, at the higher pHs, reaction of  $\text{La}(\text{OH})_3$  with the  $\text{ASO}_4^{3-}$  involved exchange of hydroxyl ions with the oxyanions. This could explain the unusually high Langmuir constant,  $b$ , when  $\text{pH} = 9$ .

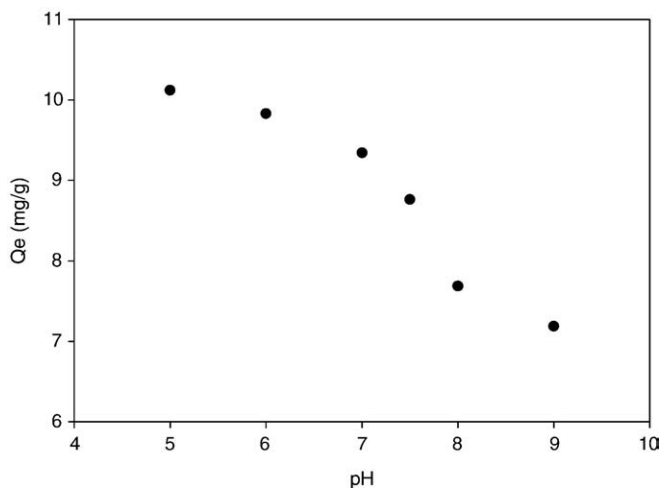


Fig. 3. Effect of pH on phosphate adsorption on Phoslock.

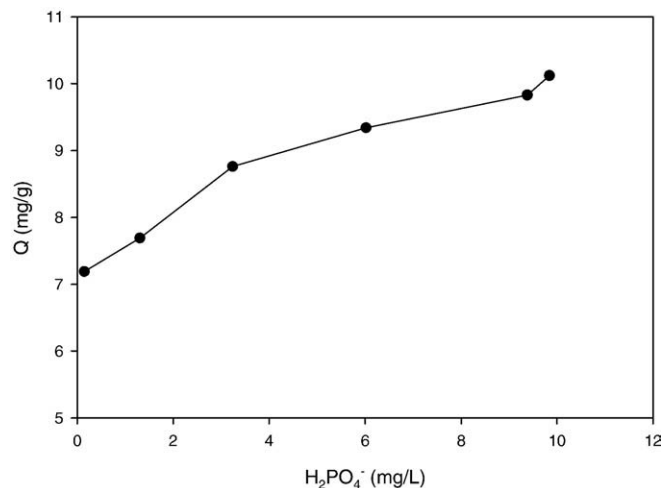
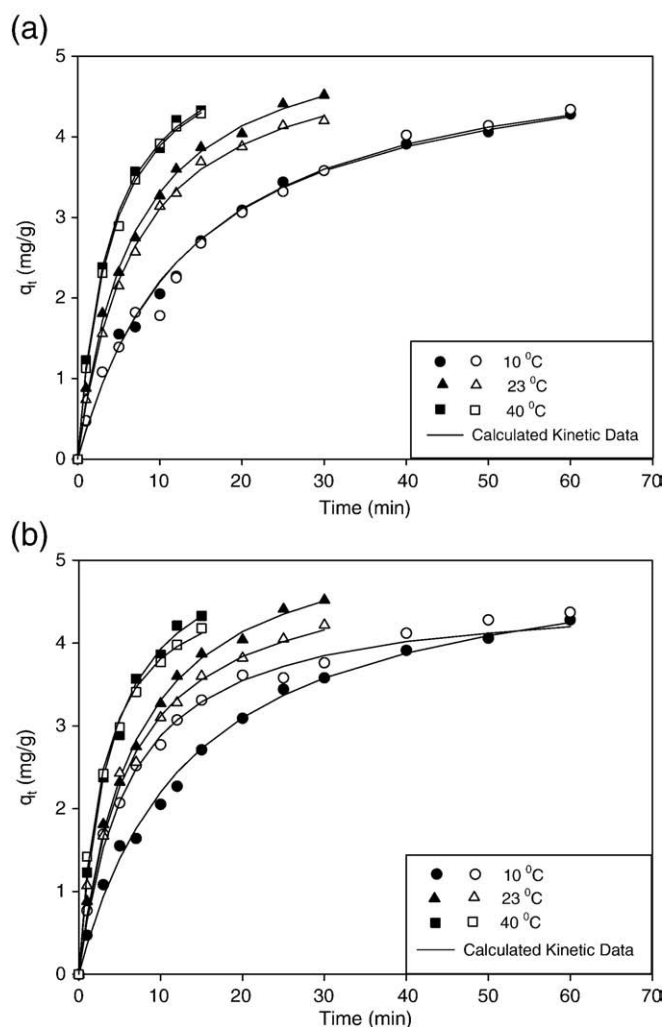


Fig. 4. Variation of  $Q$  with the initial  $\text{H}_2\text{PO}_4^-$  concentration.



**Fig. 5.** Phosphate adsorption kinetics at 10, 23 and 40 °C. (a) 0.175 mg/L NaCl (full symbols) and unaltered RO water (empty symbols), (b) pH 5 (full symbols) and 7 (empty symbols).

### 3.3. Kinetics of phosphate adsorption

The adsorption process was close to the equilibrium uptake in less than 60 min for all cases (Fig. 5a, b). The adsorption rate increased at higher temperatures. The ionic strength did not significantly affect the rate of phosphate uptake while the solution pH affected the adsorption rates. At 23 °C, lower pH would favour the uptake of phosphate while at 10 and 40 °C the uptake rate of phosphate seemed to be lower at pH 5.

The kinetic data were fitted by the pseudo-second rate equation (Eq. (8)) as modified by Ho et al. (Ho and Chiang, 2001; Ho, 2004). This equation was widely used to describe other adsorption processes,

including that of phosphate onto blast furnace slags (Kostura et al., 2005) and calcined alunite (Ozacar, 2003). Slopes of the  $t/q_t$  vs.  $t$  plots were then used to obtain the rate constant,  $k$ , and the equilibrium adsorption capacity  $Q_e$ . The correlation coefficients, shown in Table 5, together with the calculated kinetic data (Fig. 5), indicated that Eq. (8) fitted the experimental data.

$$\frac{t}{q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \quad (8)$$

Where,  $t$  is time (min),  $Q_e$  and  $q_t$  are the adsorption capacity of Phoslock at equilibrium and at time  $t$ , respectively,  $k$  is the rate constant (g/mg min).

As a part of the kinetic data analysis, it is essential to assess whether the observed data were affected by the diffusion of the phosphate ions into the pore structure of the adsorbent. The adsorbent had a relatively small particle size (22  $\mu\text{m}$ ) and a mesoporous structure. In addition, the  $\text{N}_2$  adsorption data showed that the average pore size of Phoslock was approximately 40 Å, with a considerable pore volume having a pore size of >100 Å. Considering these properties, together with the reported ionic radius of the phosphate anions being approximately 0.64 Å (Soliscorrea and Gomezlara, 1987), it is unlikely that the observed rates are diffusion-limited.

Therefore, the kinetic parameters,  $k$  and  $Q_e$  (Table 5), can be examined to obtain further insight into the adsorption mechanism and process. The adsorption capacity,  $Q_e$ , was increased slightly with an increase in temperature, regardless of the ionic strength or the solution pH. While the rate constant,  $k$ , was increased with an increase in temperature, it was unaffected by the ionic strength of the solution. The rate constant,  $k$ , at pH=7 was higher than the corresponding value at pH=5.4. As at pH 7 there was approximately a 30% reduction in concentration of the  $\text{H}_2\text{PO}_4^-$  species, it infers that the ratio of the active sites, the lanthanum ions, to the number of dihydrogen phosphate ions was therefore higher than when pH=5.4. This would consequently translate into a higher rate constant.

Using the well known Arrhenius Eq. (9), the activation energy,  $E_a$ , of the phosphate adsorption onto Phoslock at the two pH values and ionic strengths were calculated from the slope of the  $\ln(k)$  vs.  $1/T$  plots.

$$\ln(k) = \ln(k_0) - \frac{E_a}{RT} \quad (9)$$

Where  $E_a$  is the activation energy in kJ/mol,  $R$  is the gas constant 8.314 J/K·mol,  $T$  is the temperature in K, and  $k_0$  is the pre-exponential factor.

At pH=5.4 and NaCl concentrations of 0 and 0.175 g/L the  $E_a$  values were 28.2 and 27 kJ/mol, respectively. This shows that the adsorption process was independent of the ionic strength of the solution. In addition, these values were much higher than the corresponding value for other adsorbents. For example, in examining the adsorption of phosphate onto dolomite, the authors reported an  $E_a$  value of 5.44 kJ/mol, which was shown to occur through physical interactions (Karaca et al., 2004, 2006). This further indicates that the

**Table 5**  
Kinetic parameters,  $Q_e$  (mg/g) and  $k$  (g/mg min) of the pseudo-second rate equation at different pH values and temperatures.

Temperature (°C)	pH=5.4			pH=7					
	[NaCl]=0			[NaCl]=0.175 g/L (Conductivity=0.3 mS/cm)					
	$Q_e$	$k$	$R^2$	$Q_e$	$k$	$R^2$			
10	5.25	0.014	0.9894	5.21	0.014	0.9863	4.63	0.036	0.9961
23	5.22	0.028	0.9974	5.50	0.028	0.9970	4.99	0.033	0.9979
40	5.47	0.045	0.9971	5.43	0.049	0.9918	4.94	0.068	0.9995

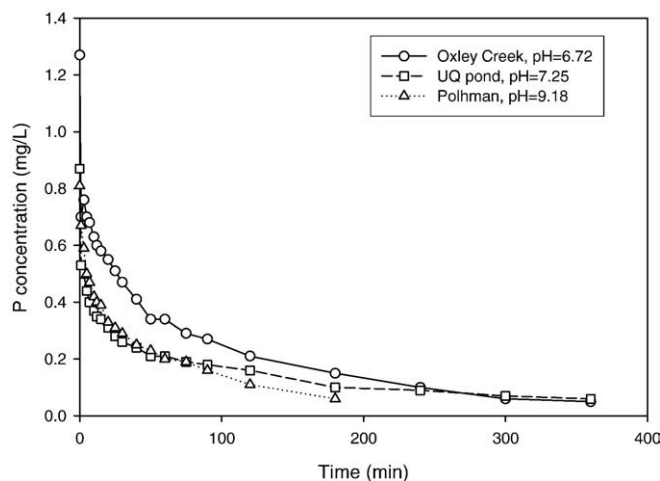


Fig. 6. Removal efficiency of Phoslock in real wastewater collected from different sources.

adsorption of phosphate onto Phoslock is a chemical rather than a physical process.

On the other hand, determination of  $E_a$  for  $\text{pH}=7$  was calculated to be 17 kJ/mol. As at the higher pH, there were a greater number of active sites available for  $\text{H}_2\text{PO}_4^-$  ions, a lower  $E_a$  is therefore expected.

Fig. 6 shows the variation of phosphate concentration of three polluted water samples at varying time. Phosphate concentration decreased faster in the first 10 min and would decrease to very low level after 200 min. For the three samples, removal efficiency was achieved around 97% at varying phosphate concentrations and pHs, suggesting its good performance for remediation of environmental waters.

### 3.4. Field test

Fig. 7 presents the variation of total phosphorus (TP) and FRP during the field test. As shown, TP and FRP concentrations decreased after applying Phoslock and continued to decline in the next three days to the value of 0.16 and 0.017 mg/L, respectively. The TP and FRP removal was achieved at 85% and 98%, respectively. When wastewater inflow started again, TP and FRP gradually increased. After 30 days, TP and FRP levels would only reach 0.7 mg/L and 0.6 mg/L, which suggested that remaining Phoslock still played role for phosphorus adsorption.

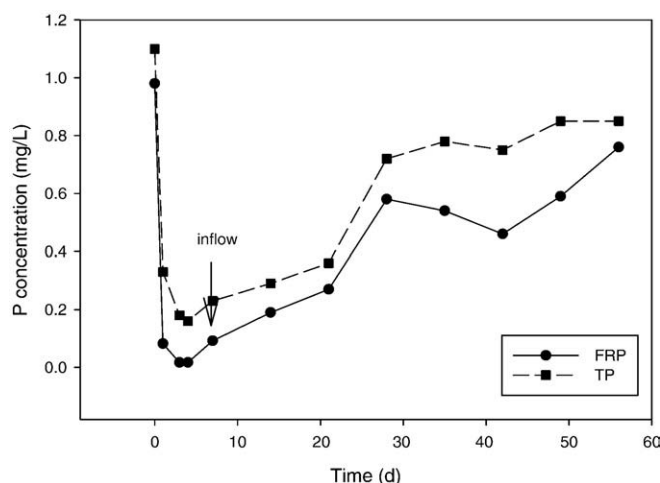


Fig. 7. Variation of P content of the nursery dam after applying Phoslock.

## 4. Conclusions

The equilibrium, kinetics and field test of phosphate uptake by Phoslock, a lanthanum-modified bentonite, showed that the Phoslock is a highly effective adsorbent. Solution pH and adsorption temperature influenced adsorption capacity. When the solution pH was increased, especially at  $\text{pH}>7$ , the amount of phosphate adsorbed decreased. This was attributable to the loss of the active sites, the lanthanum ions, through their hydroxylation and, as well, to a decrease in the concentration of  $\text{H}_2\text{PO}_4^-$  ion. It was demonstrated that the monovalent dihydrogen phosphate ion had the greatest affinity for the clay mineral surface. The study of the kinetics of the phosphate adsorption showed the chemical nature of the adsorption process. The calculated activation energy,  $E_a$ , of the adsorption process was higher than for typical physical adsorption processes. Field tests demonstrated that the Phoslock could achieve 98% removal of phosphate from real wastewater.

## References

- Airoldi, C., Goncalves, A.S., 1987. Immobilized 3-aminopyridine on silica – adsorption of some metal(II) chlorides in non-aqueous solutions. *Colloids and Surfaces* 28, 199–208.
- Akhurst, D.J., Jones, G.B., Clark, M., McConchie, D., 2006. Phosphate removal from aqueous solutions using neutralised bauxite refinery residues (Bauxsol<sup>TM</sup>). *Environmental Chemistry* 3, 65–74.
- American public Health Association (APHA), 1985. *Standard Methods for the Examination of Water and Wastewater*.
- Arakaki, L.N.H., de Sousa, A.N., Espinola, J.G.P., Oliveira, S.F., Airoldi, C., 2002. Chemisorption and thermodynamic data of the interaction between a chelate free acidic center with basic groups attached to grafted silicas. *Journal of Colloid and Interface Science* 249, 290–294.
- Arakaki, L.N.H., Espinola, J.G.P., da Fonseca, M.G., de Oliveira, S.F., de Sousa, A.N., Arakaki, T., Airoldi, C., 2004. Thioglycolic acid grafted onto silica gel and its properties in relation to extracting cations from ethanolic solution determined by calorimetric technique. *Journal of Colloid and Interface Science* 273, 211–217.
- Bhargava, D.S., Sheldarkar, S.B., 1993. Use of TNSAC in phosphate adsorption studies and relationships. Effects of adsorption operating variables and related relationships. *Water Research* 27, 313–324.
- Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2005. Adsorption of phosphate from seawater on calcined MgMn-layered double hydroxides. *Journal of Colloid and Interface Science* 290, 45–51.
- de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Research* 38, 4222–4246.
- Diatloff, E., Asher, C.J., Smith, F.W., 1993. Use of geochem-pc to predict rare-earth element (REE) species in nutrient solutions. *Plant and Soil* 156, 251–254.
- Douglas, G.B., Robb, M.S., Coad, D.N., Ford, P.W., 2004. A review of solid phase adsorbents for the removal of phosphorus from natural and wastewaters. In: Valsami-Jones, E. (Ed.), *Phosphorus in Environmental Technology: Principles and Applications*. WA, pp. 291–320.
- Farmer, A.M., 2004. Phosphate solution: A global view of the problem. In: Valsami-Jones, E. (Ed.), *Phosphorus in Environmental Technology: Principles and Applications*. IWA, pp. 174–191.
- Firsching, F.H., Brune, S.N., 1991. Solubility products of the trivalent rare-earth phosphates. *Journal of Chemical and Engineering Data* 36, 93–95.
- Firsching, F.H., Kell, J.C., 1993. The solubility of the rare-earth-metal phosphates in seawater. *Journal of Chemical and Engineering Data* 38, 132–133.
- Goncalves, A.S., Airoldi, C., 1989. Some features of 2-aminopyridine and 4-aminopyridine anchored on silica-gel – properties and chemisorption of metal(II) chlorides in non-aqueous solutions. *Polyhedron* 8, 2901–2906.
- Ho, Y.S., 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59, 171–177.
- Ho, Y.S., Chiang, C.C., 2001. Sorption studies of acid dye by mixed sorbents. *Adsorption-Journal of the International Adsorption Society* 7, 139–147.
- Huang, W.W., Wang, S.B., Zhu, Z.H., Li, L., Yao, X.D., Rudolph, V., Haghseresht, F., 2008. Phosphate removal from wastewater using red mud. *Journal of Hazardous Materials* 158, 35–42.
- Karaca, S., Gurses, A., Ejder, M., Acikyildiz, M., 2004. Kinetic modeling of liquid-phase adsorption of phosphate on dolomite. *Journal of Colloid and Interface Science* 277, 257–263.
- Karaca, S., Gurses, A., Ejder, M., Acikyildiz, M., 2006. Adsorptive removal of phosphate from aqueous solutions using raw and calcined dolomite. *Journal of Hazardous Materials* 128, 273–279.
- Kostura, B., Kulveitova, H., Lesko, J., 2005. Blast furnace slags as sorbents of phosphate from water solutions. *Water Research* 39, 1795–1802.
- Liu, H., Sun, X., Yin, C., Hu, C., 2008. Removal of phosphate by mesoporous  $\text{ZrO}_2$ . *Journal of Hazardous Materials* 151, 616–622.
- Melnyk, P.B., Norman, J.D., Wasserlauf, M., 1974. Lanthanum precipitation. Alternative method for removing phosphates from waste water. In: Haschke, J.M., Eick, H.A.

- (Eds.), Proc. Rare Earth Res. Conf., 11th. NTIS, Springfield, Cleveland, OH, USA, pp. 4–13.
- Ozacar, M., 2003. Equilibrium and kinetic modelling of adsorption of phosphorus on calcined alunite. *Adsorption-Journal of the International Adsorption Society* 9, 125–132.
- Recht, H.L., Ghassemi, M., Kleber, E.V., 1970. Precipitation of phosphates from water and waste water using lanthanum salts. *Proceedings of the 5th International Water Pollution Research*. Pergamon, pp. 1–17.
- Robb, M., Greenop, B., Goss, Z., Douglas, G., Adeney, J., 2003. Application of Phoslock (TM), an innovative phosphorus binding clay, to two Western Australian waterways: preliminary findings. *Hydrobiologia* 494, 237–243.
- Soliscorrea, H., Gomezlara, J., 1987. Approximation of spherical polyatomic thermochemical radii of general formula  $mxnz$ . *Journal of Chemical Education* 64, 942–943.
- Suzuki, Y., Saitoh, H., Kamata, Y., Aihara, Y., Tateyama, Y., 1989. Precipitation incidence of the lanthanoid(III) hydroxides: II Precipitation from chloride and perchlorate solutions. *Journal of the Less-Common Metals* 149, 179–184.
- Tanada, S., Kabayama, M., Kawasaki, N., Sakiyama, T., Nakamura, T., Araki, M., Tamura, T., 2003. Removal of phosphate by aluminum oxide hydroxide. *Journal of Colloid and Interface Science* 257, 135–140.
- Tokunaga, S., Wasay, S.A., Park, S.W., 1997. Removal of arsenic(V) ion from aqueous solutions by lanthanum compounds. *Water Science and Technology* 35, 71–78.
- Wang, S.-L., Cheng, C.-Y., Tzou, Y.-M., Liaw, R.-B., Chang, T.-W., Chen, J.-H., 2007. Phosphate removal from water using lithium intercalated gibbsite. *Journal of Hazardous Materials* 147, 205–212.
- Wang, S.B., Ang, H.M., Tade, M.O., 2008. Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. *Chemosphere* 72, 1621–1635.
- Ye, H., Chen, F., Sheng, Y., Sheng, G., Fu, J., 2006. Adsorption of phosphate from aqueous solution onto modified palygorskites. *Separation and Purification Technology* 50, 283–290.
- Zeng, L., Li, X.M., Liu, J.D., 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research* 38, 1318–1326.