CHAPTER 3:

CHARACTERISATION AND KINETICS OF PHOSLOCK®

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Published in Harmful Algae

Volume 7 Issue 4, June 2008. pp 545-550

1. Introduction

Lanthanum is a rare earth element (REE) that is relatively abundant in the earth's crust compared to other REEs. Lanthanum compounds have been used in water treatment processes, as they are cheaper than those derived from other rare earth elements and the point of zero charge of lanthanum oxides is higher than that of other well-known adsorbants (Woo Shin *et al*., 2005). Examples include use of lanthanum salts for precipitative removal of Arsenic (As) ions (Tokunaga *et al*., 1997; Tokunaga *et al*., 1999), and the use of lanthanum oxide and lanthanum impregnated alumina for adsorptive As removal (Wasay *et al*., 1996), and lanthanum impregnated silica gel for removal of As, fluoride and phosphates (Wasay *et al*., 1996). According to Douglas *et al*. (2000), lanthanum was highly efficient at removing phosphorus with a molar ratio of 1:1 (Equation 1), compared with sodium aluminate ($NaAlO_2$), which is relatively inefficient with a molar ratio of 7:1 needed to achieve a similar phosphorus uptake.

$$La^{3+} + PO_4^{3-} \rightarrow LaPO_4 \qquad (1)$$

Lanthanum is toxic, depending on its concentration and application rate. It can react with cell components such as nucleoproteins, amino acids, enzymes, phospholipids and intermediary metabolites. This is because lanthanum has many physical and chemical characteristics in common with calcium. Its action is mainly mediated by the replacement or displacement of calcium in different cell functions and its high affinity for the phosphate groups of biological molecules, resulting in toxicity or impaired function. Lanthanum is considered only slightly toxic to mammals. It is, however, highly toxic to species of *Daphnia* in both acute and chronic tests (Barry & Meehan, 2000). The potential toxicity of lanthanum ions has been overcome by incorporating it into the structure of high exchange capacity minerals, such as bentonite by taking advantage of the cation exchange capacity of clay minerals. This exchange capacity is a result of a charge imbalance on the surface of the clay platelets, which is balanced by surface adsorbed cations. These cations are exchangeable in aqueous solutions. As the rare earth element is locked into the clay structure, it can either react with the phosphate anion in the water body or stay within the clay structure under a wide range of physiochemical conditions (Douglas *et al*., 2000). Rare earth-anion products are stable, due to their low solubility (Firsching, 1992). Phoslock® forms a highly stable mineral

known as rhabdophane ($LaPO_4.nH_2O$) in the presence of oxyanions such as orthophosphates (Douglas *et al*., 2000).

In low ionic strength water, the lanthanum remains strongly bound to the clay silicate plates, but under conditions of high ionic strength (saline water) there is a possibility of re-exchange of the bound La^{3+} for ambient Na^{+} or Ca^{2+} ions. This is not a possibility in fresh water, but may present a problem in estuaries. Any lanthanum released under these conditions is not expected to remain free, but to become strongly associated with natural humic material in the water and sediments through interaction with carboxylate groups in humic and fulvic acids (Geng *et al*., 1998; Dupre *et al*., 1999). Specific formulations of Phoslock® are used under estuarine/saline conditions to minimize lanthanum release.

Metal salts, such as ferric salts and alum, can effectively precipitate phosphorus, but these have certain disadvantages. They are generally difficult to handle because of their acidity. Furthermore, the iron- or the aluminium- phosphorus complex is stable only under oxic conditions, which means that phosphorus may be released from the anoxic sediments of eutrophic waters (Chorus & Mur, 1999). Hydrogen ions are liberated when alum is added to water bodies, especially lakes with a low or moderate alkalinity, leading to a sharp decrease in pH. This may consequently lead to the formation of toxic species of aluminium such as Al^{3+} and $Al(OH)^{2+}$ (Cooke *et al*., 1993). An increase in the pH of a water body above pH 8 may result in re-release of the phosphorus from the aluminium flocs (Lewandowski *et al*., 2003).

As the lanthanum exchange process is carried out in solution, Phoslock® was originally prepared as a slurry. However, the disadvantages of the transport of the excess water and the presence of excess residual lanthanum ions from the manufacturing process led to the formation of the granular form of Phoslock®. One of the essential features of this granular Phoslock® is that it should disperse into fine particles in water that have a similar particle size distribution to that of the parent slurry. This is necessary to ensure that the maximum number of lanthanum sites are exposed to the phosphate ions.

In this study, the effects of various solution conditions on the kinetics and phosphorus adsorption capacity of Phoslock® was evaluated, as well as the effect of different

Phoslock® dosages. The effect of initial pH and phosphorus concentration was assessed in synthetic solutions, and algae-containing effluent lake water was used to analyse the performance of Phoslock® under algal bloom conditions. In this instance, the stability of the adsorbed phosphate under anoxic conditions was also examined and higher Phoslock® dosages were applied to lake water with a pH above 9 to examine the possibility of achieving a greater phosphorus removal.

2. Materials and methods

2.1. Column tests

20L perspex columns 1m long with an 8cm radius were used to evaluate Phoslock® performance under different conditions. The columns were housed in a wooden cabinet, each column surrounded by three daylight-emitting spectrum tubes and an IKA RW overhead stirrer. The columns had five taps at regular intervals along their length to facilitate sampling from different depths.

2.1.1. The effect of pH on Phoslock® performance

To evaluate the effect of different pH values on the performance of Phoslock®, synthetic solutions were prepared using reverse osmosis (RO) water. KH_2PO_4 salt (ChemSupply) was used to make a 25mg.l^{-1} phosphorus stock solution, and 800ml of this stock solution was added to 19.2L reverse osmosis water in the 20L columns to give a 1mg.l^{-1} phosphorus concentration in the columns. The conductivity of the solutions was adjusted to 0.3mS by the addition of 3.5g NaCl. The solutions were mixed overnight with the overhead stirring apparatus (IKA RW 20.n), set at the lowest speed (~200 rpm). Prior to starting the experiment the next day, the pH of the columns was adjusted to 5, 7, 8 and 9 respectively using 0.1M solutions of HCl and NaOH. An initial sample of the column test solution was taken prior to addition of Phoslock® by dispensing a quantity from a tap midway down the column into a 50ml Nalgene tube. 10ml was drawn up with a syringe and filtered through a 0.22µm filter disk (Millex-gp) into a 10ml plastic sample tube. Initial measurements of pH, conductivity (TPS Aqua-CP 1.1) and temperature were also made at this stage. pH, conductivity and temperature readings were also taken at various intervals throughout the experiment. A 230:1 ratio

of Phoslock® to phosphorus was used in all the columns. 4.5g of Phoslock® granules were measured into a 50ml Nalgene tube and RO water was added to the 15ml mark on tube, which was then vortexed for 1min to hydrate the Phoslock® granules. This slurry was then added to the columns, rinsing out remaining mixture from Nalgene tube with ≤5ml RO water from a squeeze bottle. An electronic timer was started immediately after the addition of the Phoslock® and samples were taken from the middle tap for turbidity, filterable reactive phosphorus (FRP) and particle size analysis at designated time intervals within a 6h period. Samples for turbidity were dispensed directly into the turbidimeter tube, and readings were performed on the Hach 2100A Turbidimeter, calibrated to the 100 standard range. Particle sizing was performed on the pH 5 and pH 9 solutions. 50ml was dispensed into a Nalgene tube from which 10ml was drawn up with a syringe and filtered through a 0.22µm filter disk into 10ml flat-bottomed tubes for FRP reading. Particle sizing was performed on the Malvern Mastersizer. Samples were diluted with a defined volume of tap water where necessary, and were analysed using the following particle size parameters; stirring speed 3, 3000 sweeps, low gain, and 100mm or 300mm lens depending on size of particles observed. To determine the FRP concentration of each filtered sample, 5ml was pipetted into glass test tubes. 5 drops of PO_4-1 reagent, followed by one scoop of PO_4-2 reagents from the phosphate test kit Spectroquant 0.01-5mg/l Phosphate Test Kit (Merck, catalogue #1.14848.0001), were then added to the samples, which were vortexed until the crystals were fully dissolved. Samples were then left to stand for 5 minutes before measuring absorbance with the Jasco V550 UV/Vis Spectrophotometer at 710nm. The absorbance readings were divided by the calibration coefficient 0.5061 to calculate the FRP concentration.

2.1.2. Lake water with algal bloom

Two columns were filled with environmental water samples, in this case collected from the effluent-fed lake at the University of Queensland, St Lucia Campus (Figure 1). The columns were left overnight, and a 12h day/night light schedule was applied using fluorescent bulbs under timer control (on: 6am, off: 6pm) to enhance algal growth. FRP concentration of lake water was determined prior to addition of Phoslock® (0 hour time measurement). Initial measurements at time 0 hrs were taken for pH, conductivity and temperature (TPS Aqua-CP 1.1) and turbidity (Hach Turbidimeter). A representative sample was also collected for analysis of the following parameters; Alkalinity (A),

Hardness (H), Lanthanum and Sodium (La/Na), Metals (M), and Chlorophyll a (Chl). Chlorophyll a analysis was performed using the methanol extraction method (Lorenzen, 1967; Golterman & Clymo, 1970; Holm-hansen, 1978) using the following equation:

$$\text{Chl a } (\mu g.l^{-1}) = (Abs_{665nm} - Abs_{750nm}) \times A \times Vm/V \times L \quad (2)$$

Where:
A = absorbance coefficient of Chl a in methanol (12.63)
Vm = volume of methanol used (mL)
V = volume of water filtered (L)
L = path length of cuvette (cm)
In all cases 100ml of water was filtered, 10ml of methanol was used for extraction and a cuvette with a path length of 1cm was used.

Other samples were sent away to be analysed by the Queensland Health Scientific services. Samples for alkalinity and hardness were preserved by refrigeration at 4°C, and filtered samples for lanthanum/sodium and metals were preserved with two-three drops of 1M HNO_3.

A 230:1 treatment ratio (Phoslock®: phosphorus) was added to one column. The second column was left untreated to act as a control. Samples taken for turbidity, FRP and particle size analysis at designated time intervals within a 6h period, in the same manner as for the pH column tests. The same size parameters were also applied to the particle sizing. Following the initial 6h of sampling, columns were monitored over a three-day period for changes in FRP, pH, temperature, DO and chlorophyll a. At 72h post Phoslock® addition, the column volume was increased with an additional 1L of lake water from the initial water sample. Bentonite was added to both columns at $0.5g.l^{-1}$ to flocculate the algae that remained on the surface. Fluorescent light schedule was suspended, and the columns were covered to prevent light penetration and further algal growth. Columns were monitored for a further three days following addition of bentonite, for changes in pH and FRP. At 72h post bentonite addition (6 days after initial Phoslock® treatment), Phoslock® was added to the treated column using a sediment-capping regime of $250g.m^{-2}$. Further monitoring of columns for pH, FRP, and DO continued for 5 days, and on the fifth day the columns were covered with parafilm

to accelerate the development of anoxic conditions (DO <1mg.l^{-1}). An anoxic state was achieved on the sixth day, allowing for assessment of whether the phosphorus remained bound to Phoslock® under anoxic conditions.

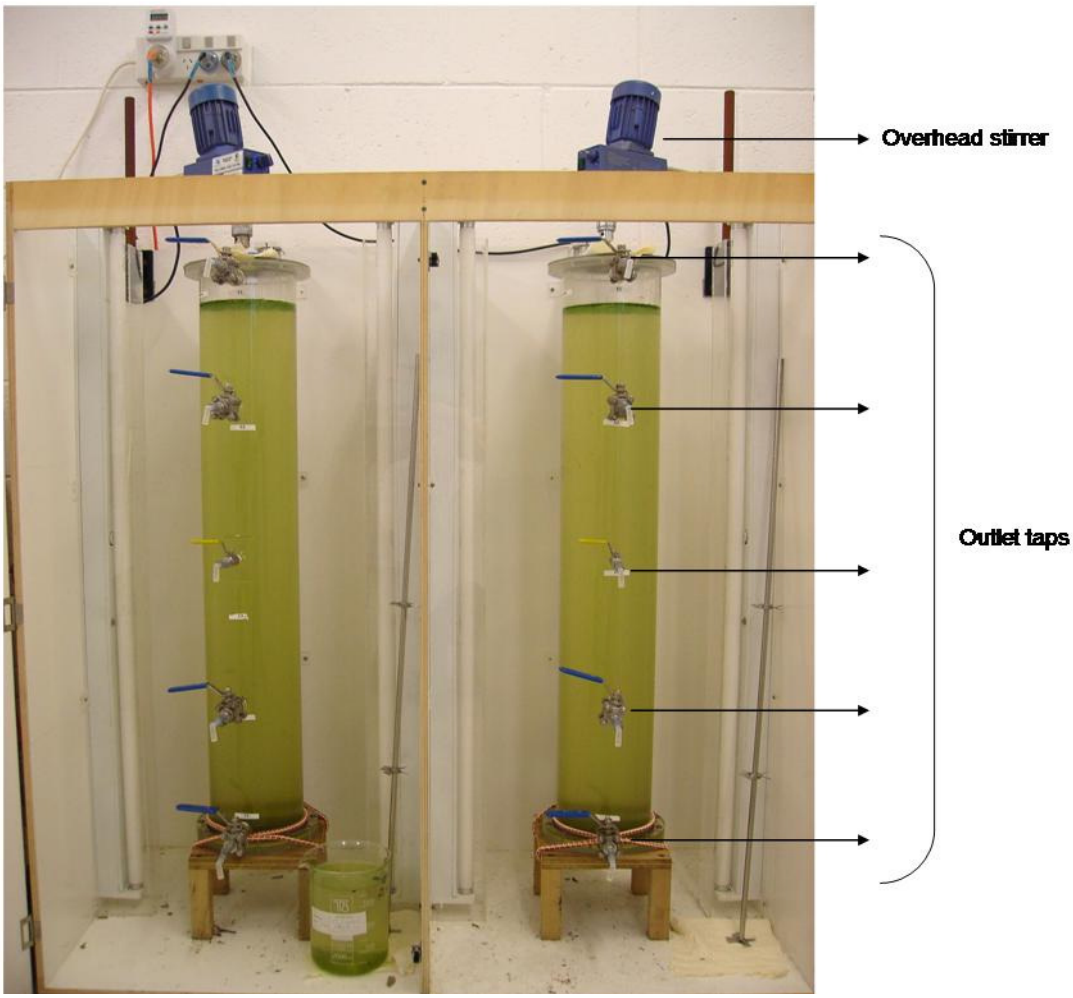

Figure 1: Columns filled with effluent lake water

2.1.3. Lake water with algal bloom treated at high dose ratios

Two further column tests were performed using the effluent lake water at pH 9, but with higher Phoslock® dosages of 340:1 and 450:1 (Phoslock® to phosphorus) respectively. The tests were performed in the same manner as the first effluent water column, except that particle sizing was not performed, and only conductivity, pH, temperature, DO, turbidity and FRP measurements were taken. Control columns were set up and monitored at the same time as the treated columns.

2.2. Beaker tests

2.2.1. Effect of initial phosphorus concentration

In order to determine the effect of different initial FRP concentrations on the adsorption capacity of Phoslock® when applied at a 230:1 dosage, solutions were prepared in 2L beakers using reverse osmosis water. KH_2PO_4 salt was added to make solutions with concentrations of 0.5mg.l^{-1}, 1mg.l^{-1}, 2mg.l^{-1} and 4mg.l^{-1} phosphorus. The pH of each solution was adjusted to 7, and the conductivity of the solutions was adjusted to 0.3mS by the addition of NaCl. The beakers were stirred continuously on a magnetic stirrer throughout the duration of the experiment to ensure maximum contact of the phosphorus with the Phoslock® particles. Phoslock® was hydrated into a slurry form in the same manner as the column experiments, and was added to the beakers. Filtered samples were taken at designated time intervals over a 3h period, and the FRP concentration determined. pH levels and conductivity were monitored throughout the test period.

2.2.2. Lake water

A beaker test was also performed on a water sample from the effluent-fed lake at the University of Queensland. A Phoslock® dosage of 230:1 was used, in order to investigate the effect of continuous stirring on the adsorption capacity of Phoslock® when compared to the non-stirring conditions of the columns. Once again, filtered samples were taken over a 3h time period to determine the FRP concentration, and measurements were taken for pH and conductivity.

3. Results

3.1. Pseudo-second order model for determining phosphorus adsorption kinetics

The sorption kinetics of Phoslock® may be described by a pseudo-second order (Ho & Chiang, 2001). The differential equation is the following:

$$dq_t/dt = k(q_e-q_t)^2 \qquad (2)$$

Where qt is the amount of phosphorus sorbed at time t ($mg.g^{-1}$), and qe is the amount of phosphorus sorbed at equilibrium ($mg.g^{-1}$).
Integrating Eq. (2) for the boundary condition t = 0 to t = t and qt = 0 to qt = qt, gives:

$$1/ (q^e-q^t) = 1/q^e + kt \qquad (3)$$

which is the integrated rate law for a pseudo second order reaction. k is the equilibrium rate constant of pseudo-second order ($g.mg^{-1}.min^{-1}$). Equation (3) can be rearranged to obtain a linear form:

$$t/q_t = 1/kq_e^2 + 1/q_e .t \qquad (4)$$

The straight-line plots of t/qt against time have been tested to obtain rate parameters. The value of k, q_e and the correlation coefficients, R^2 of phosphorus concentration under different conditions were calculated from these plots.

3.2. Column tests

3.2.1. The effect of pH on Phoslock® performance

The effect of pH on the phosphate uptake of Phoslock® is shown in Figure 2. Linear plots of t/q_t against t in Figure 3 shows the applicability of the pseudo-second order equation for the system with initial pH ranging from 5 to 9. Values of k and q_e calculated from equation (4) and the correlation correlation coefficient (R^2) calculated from Figure 3 are listed in Table 1. It is clear that the kinetics of phosphorus adsorption onto Phoslock® followed the pseudo-second order model with correlation coefficients higher than 0.999 for all the systems. The equilibrium adsorption capacity of Phoslock® (q_e) decreased from 4.38$mg.g^{-1}$ to 3.19$mg.g^{-1}$ as the initial pH of the solution increased from 5 to 9. However, the adsorption capacity of Phoslock® remained similar within the range of pH 5 to 7 (Figure 3). The conductivity of the solution was not affected by the addition of Phoslock® and remained at 0.3$mS.cm^{-1}$ throughout the 6h test period.

The turbidity of the solutions decreased after the addition of Phoslock®, with all four solutions having a final turbidity of 5NTU or lower after 6h (Figure 4). However, the turbidity showed a more rapid decrease at the higher initial pH values of 8 and 9 than at pH 5 and 7.

Figures 5 and 6 present the particle size distribution (D) of the pH 5 and pH 9 solutions expressed as a volume diameter (µm). The values D[v, 0.1], D[v, 0.5] and D[v, 0.9] refer to particle diameters below which 10%, 50% and 90% of the particle volume is contained, respectively. In the pH 5 column, the values obtained for D[v, 0.1] decreased from 2.37µm to 2.11µm, the D[v, 0.5] value decreased from 8.02µm to 6.3µm and the diameter for D[v, 0.9] decreased from 23.44µm to 17.68µm over the 6h study period. In the pH 9 column, the D[v, 0.1] value decreased from 2.6µm to 1.81µm, the D[v, 0.5] value decreased from 12.16µm to 6.25µm and the diameter for D[v, 0.9] decreased from 46.15µm to 33.04µm. There was a similar decrease in the D[v, 0.1] value in both columns, but the values for D[v, 0.5] and D[v, 0.9] were higher in the pH 9 column, and decreased by greater amounts.

Table 1: Kinetic parameters for phosphorus adsorption onto Phoslock® at different initial pH values

pH	k ($g.mg^{-1}min^{-1}$)	q_e ($mg.g^{-1}$)	R^2
5	0.046	4.37	0.9999
7	0.031	4.36	1
8	0.036	3.38	1
9	0.038	3.19	1

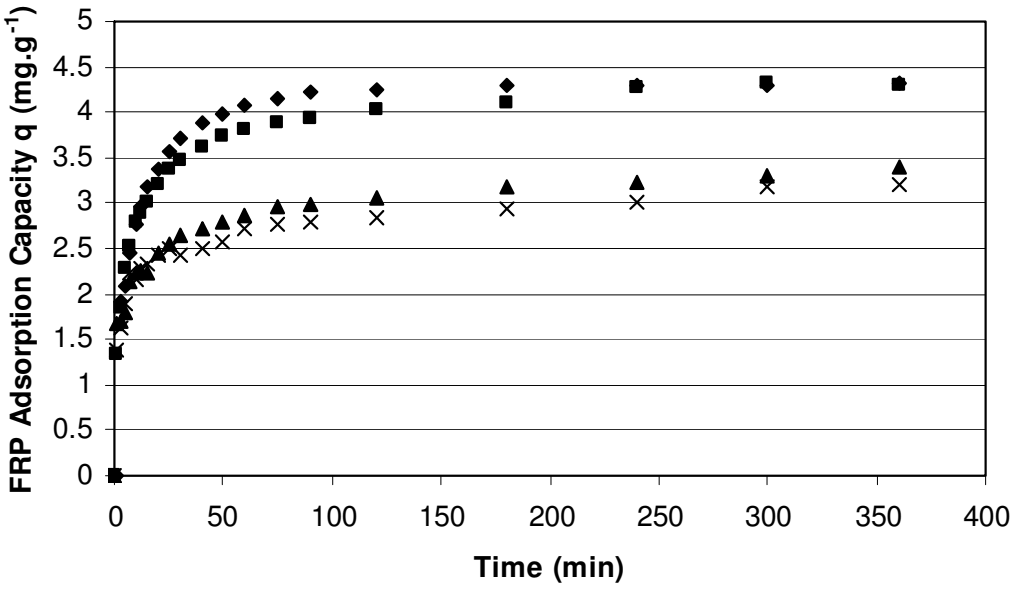

Figure 2: FRP adsorption capacity of Phoslock® versus time at various initial pH values (♦) pH 5 (■) pH 7 (▲) pH 8 (x) pH 9

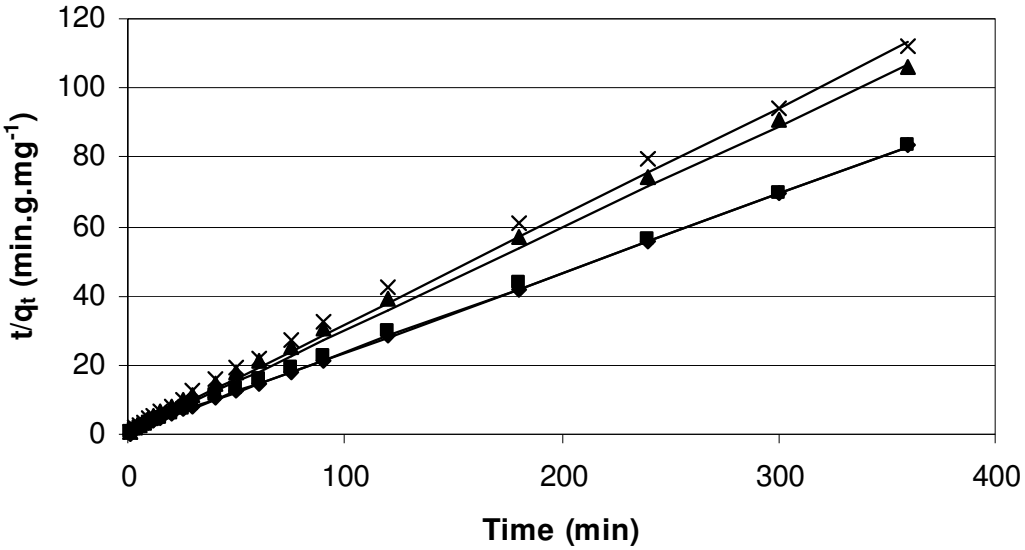

Figure 3: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® at various initial pH values. (♦) pH 5 (■) pH 7 (▲) pH 8 (x) pH 9. Conditions: Initial FRP = 1mg.l^{-1}, Initial conductivity = 0.3mS

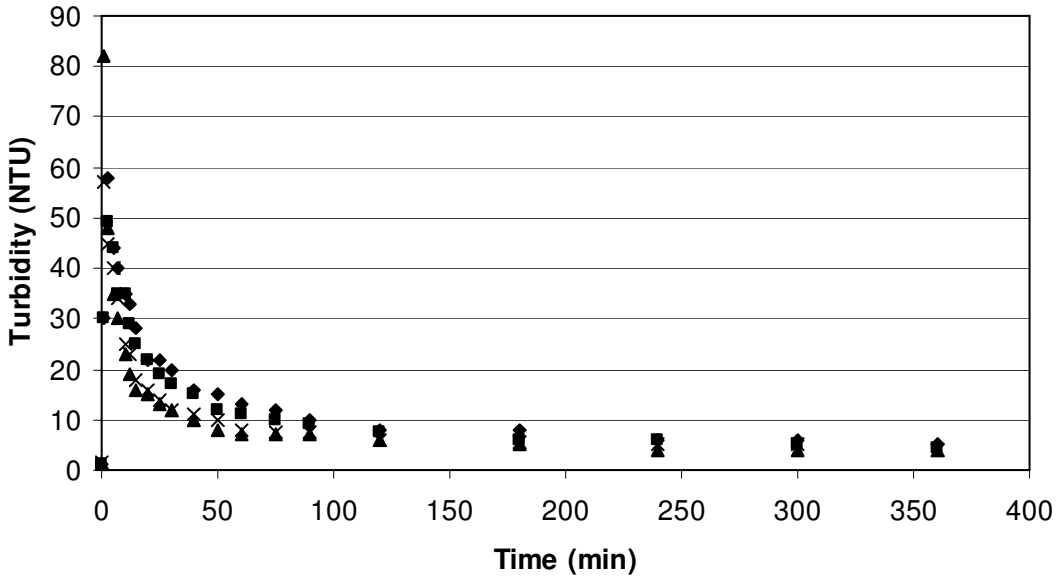

Figure 4: Turbidity of column solutions over time at various initial pH values. (♦) pH 5 (■) pH 7 (▲) pH 8 (x) pH 9

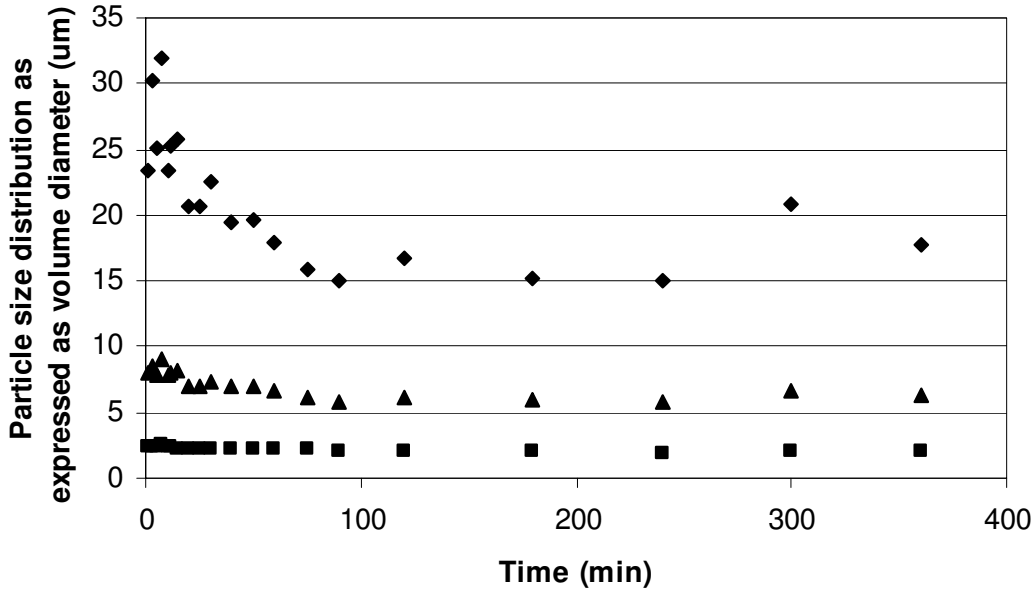

Figure 5: Particle size distribution of the Phoslock® grains in the pH 5 column expressed as volume diameter at each time interval over the 6h period of study. (■) D[v, 0.1], (▲) D[v, 0.5] and (♦) D[v, 0.9]

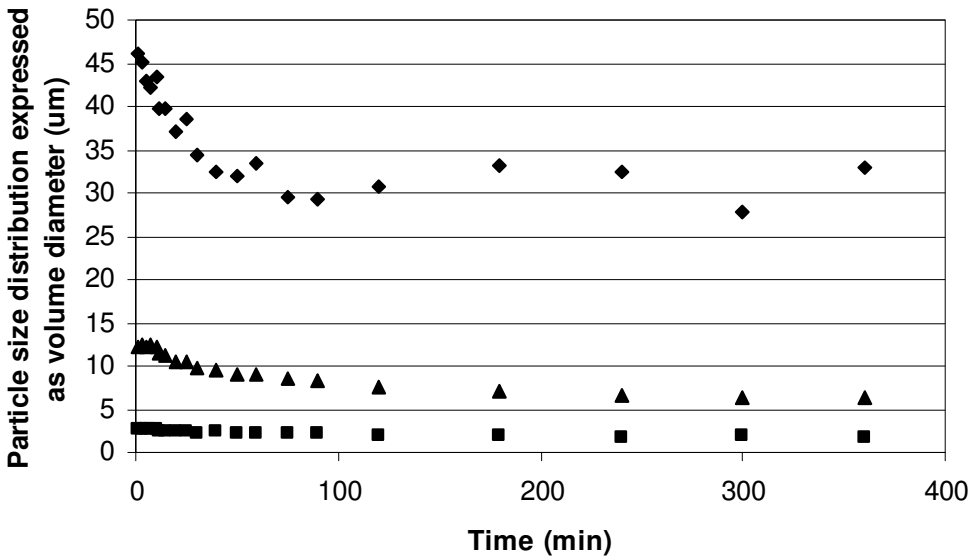

Figure 6: Particle size distribution of the Phoslock® grains in the pH 5 column expressed as volume diameter at each time interval over the 6h period of study. (■) D[v, 0.1], (▲) D[v, 0.5] and (♦) D[v, 0.9]

3.2.2. Lake water with algal bloom

The initial FRP concentration of the lake water at the start of the experiment was 0.82mg.l^{-1}, the initial pH 8.45, DO 12.5mg.l^{-1} and the conductivity 0.4mS/cm. The initial chlorophyll a concentration was 11.7µg.l^{-1}. Following the addition of a 230:1 dosage of Phoslock®, the FRP concentration decreased to 0.4mg.l^{-1} after 6h (Figure 7). The FRP concentration in the control column fluctuated over the 6h period but remained above 0.75mg.l^{-1}. The conductivity remained unchanged at 0.4mS/cm.

Linear plots of t/q_t against t in Figure 8 show the applicability of the pseudo-second order equation for the system. Values of k and q_e calculated from equation (4) and the correlation correlation coefficient (R^2) were calculated and are listed in Table 2. The equilibrium adsorption capacity of Phoslock® (q_e) in the effluent lake water was 2.38mg.g^{-1}, which was less than that observed in the synthetic water columns at either pH 8 or pH 9.

The chlorophyll a concentrations in the treated and control columns at various time intervals is shown in Table 3. Although the initial values differed in the two columns before the addition of Phoslock®, the chlorophyll a concentration in the control column

increased more than the treated column in the first 6h. This may be attributed to the higher turbidity in the treated column, which may have prevented algal growth by blocking the light. After 24 and 72h, the chlorophyll a concentration decreased by similar amounts in both columns, so it is unlikely that Phoslock® was responsible for this decrease.

The initial lanthanum concentration of the lake water was less than 0.003mg.l^{-1}, and increased to 0.023mg.l^{-1} 15min after the addition of Phoslock® (Table 4). After 24h, the lanthanum concentration had stabilized at 0.025mg.l^{-1}. The sodium concentration remained constant after treatment (Table 4), and the conductivity remained at 0.4mS. The alkalinity and hardness of the water was measured before treatment, and the concentration of various metals was measured before treatment and 24h after treatment (Table 5). The metal concentrations were not affected by the addition of Phoslock®.

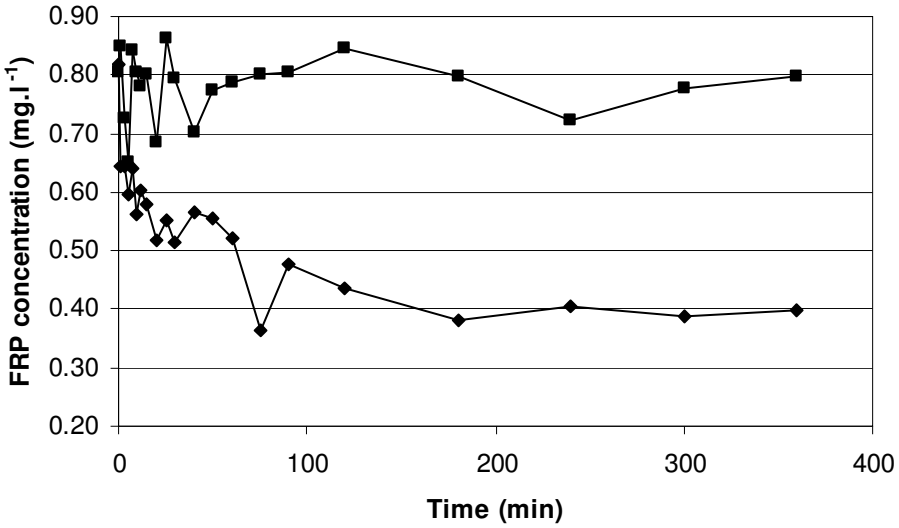

Figure 7: Comparison of the FRP concentration in the Phoslock® treated and control columns for the first 6h following the 230:1 dosage (♦) Treated (■) Control

Table 2: Kinetic parameters for phosphorus adsorption onto Phoslock® in effluent lake water following a 230:1 treatment and a subsequent sediment capping treatment of 250g.m^{-2}

Dosage	k (g.mg^{-1}min^{-1})	q_e (mg.g^{-1})	R^2
230:1	0.029	2.38	1
250g.m^{-2}	0.446	0.47	1

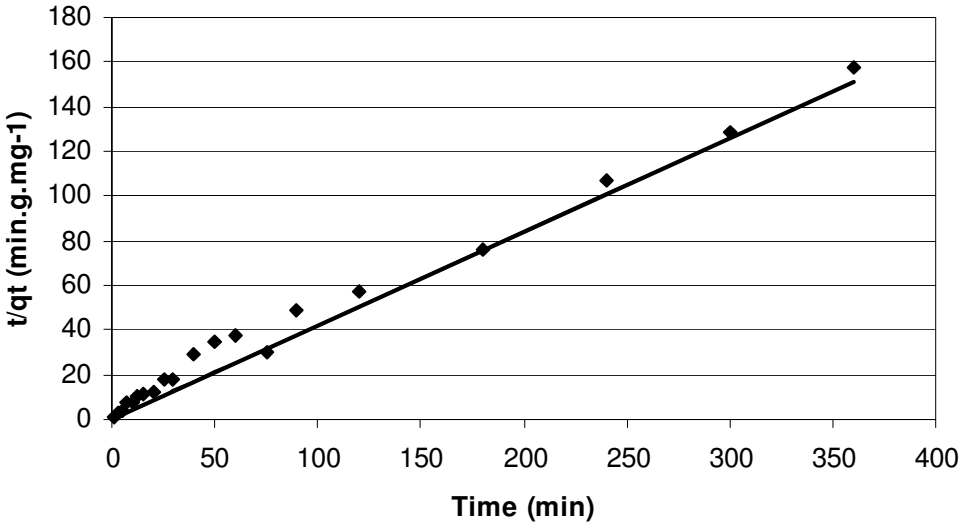

Figure 8: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® in effluent lake water. Conditions: Phoslock® dosage 230:1, initial FRP concentration = 0.82mg.l^{-1}, initial pH = 8.45, water temperature = 25.5°C, conductivity = 0.4mS

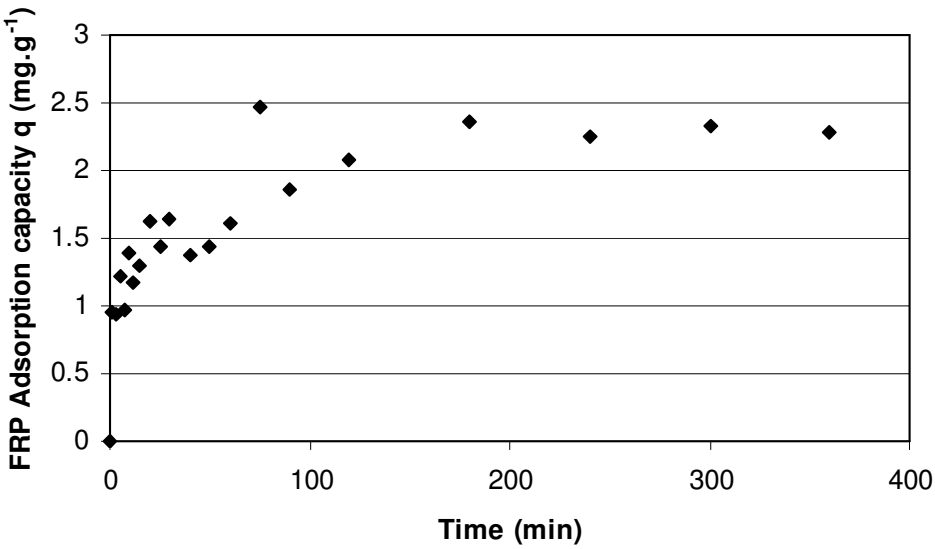

Figure 9: FRP adsorption capacity of Phoslock® versus time in effluent lake water following a 230:1 dosage

Table 3: Chlorophyll a concentrations (µg.l^{-1}) in the 230:1 treated and control columns at various time intervals after treatment

Time (h)	Treated	Control
0	11.7	17.1
6	10.21	22.56
24	13.3	18.7
72	7.53	11.35

Table 4: Lanthanum and sodium concentrations in the effluent lake water prior to Phoslock® treatment and at various times after treatment

Time (h)	La (mg.l^{-1})	Na (mg.l^{-1})
0	<0.003	61
0.25	0.023	62
1	0.024	62
2	0.022	62
24	0.025	62

72h after the 230:1 Phoslock® treatment, the lights were turned off and bentonite added to flocculate some of the algae on the surface. By this stage the FRP concentration of the treated column had decreased to 0.07mg.l^{-1}, and the control column had decreased to 0.24mg.l^{-1}, most likely as a result of algal uptake during growth. The pH of the treated column had increased to 10.07, and the control column to 10.17. A further 72h after adding the bentonite, the FRP concentration had increased to 0.13mg.l^{-1} in the middle of the treated column and 0.3mg.l^{-1} at the bottom of the column, and the pH had decreased to 8.55 at the top and 8.74 at the bottom. The FRP concentration of the control column also increased to 0.16mg.l^{-1} in the middle and 0.6mg.l^{-1} at the bottom, and the pH decreased to 9.09 at the top and 9.04 at the bottom. The increase in FRP was most likely due to the breakdown of dead algal cells and subsequent release of phosphorus into solution. The DO of the treated column was 9.1mg.l^{-1} at the top and 13.3mg.l^{-1} at the bottom, and that of the control column was 11.7mg.l^{-1} at the top and 11.4mg.l^{-1} at the bottom. At this point a sediment capping treatment of Phoslock® was applied.

Table 5: Concentrations of various metals ($mg.l^{-1}$) in the effluent lake water both prior to Phoslock® treatment and 24h after treatment, as well as the alkalinity and hardness of the water prior to treatment

	0h	24h
Alkalinity	112	
Hardness	98	
Calcium	21.8	
Magnesium	10.6	
Aluminium	<0.04	<0.04
Arsenic	<0.04	<0.04
Boron	0.43	0.4
Barium	0.024	0.02
Beryllium	<0.0002	<0.0002
Cadmium	<0.004	<0.004
Cobalt	<0.005	<0.005
Chromium	<0.004	<0.004
Copper	<0.03	<0.03
Iron	0.025	0.017
Manganese	0.002	0.002
Molybdenum	0.012	0.012
Mercury	<0.010	<0.010
Nickel	<0.005	<0.005
Lead	<0.01	<0.01
Selenium	<0.04	<0.04
Sodium	62	62
Vanadium	<0.003	<0.003
Zinc	<0.004	<0.004

Values of k and q_e calculated from equation (4) and the correlation correlation coefficient (R^2) calculated from Figure 10 for the sediment capping treatments are listed in Table 2. The equilibrium adsorption capacity of Phoslock® (q_e) in the effluent lake water was $0.47mg.g^{-1}$ (Figure 11).

The FRP concentration in the control column remained constant for the 3h period after the sediment capping treatment, whereas the FRP concentration in the treated column decreased by 86% to $0.02mg.l^{-1}$ (Figure 12), indicating that Phoslock® was responsible for the decrease in FRP concentration.

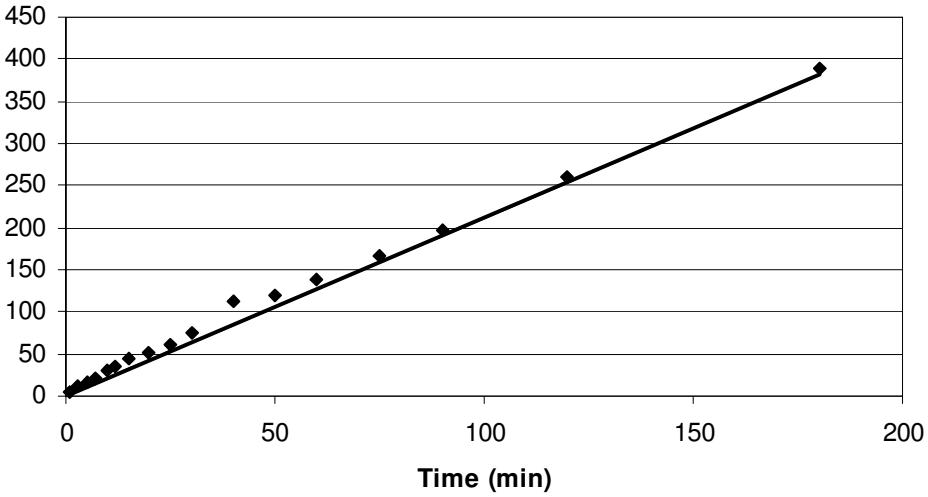

Figure 10: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® in effluent lake water. Conditions: Phoslock® dosage = 250g.m^{-2}, initial FRP concentration = 0.14mg.l^{-1}, initial pH at top of column = 8.55, initial pH at bottom of column = 8.74, initial DO top = 9.1mg.l^{-1}, initial DO bottom = 13.3mg.l^{-1}

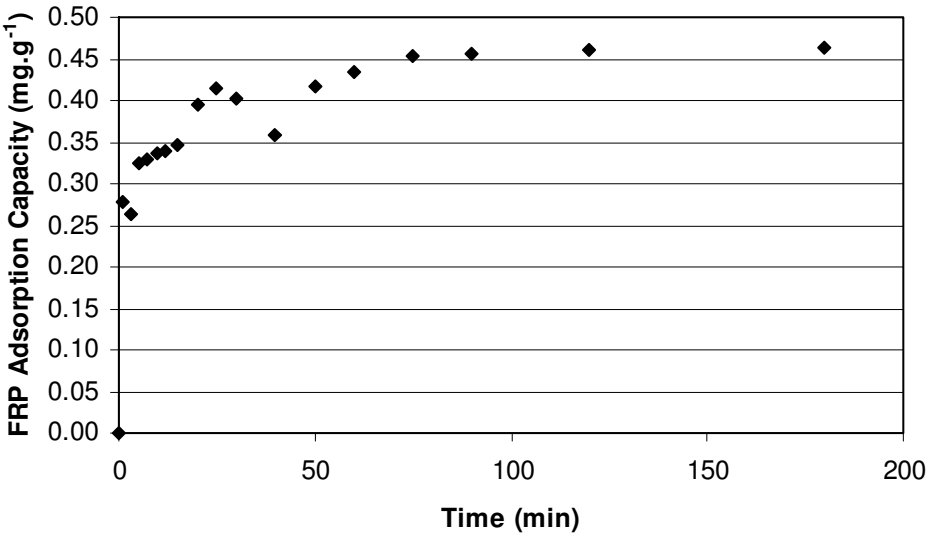

Figure 11: FRP adsorption capacity of Phoslock® versus time in effluent lake water following a sediment capping dosage of 250g.m^{-2} (6d after 230:1 dosage)

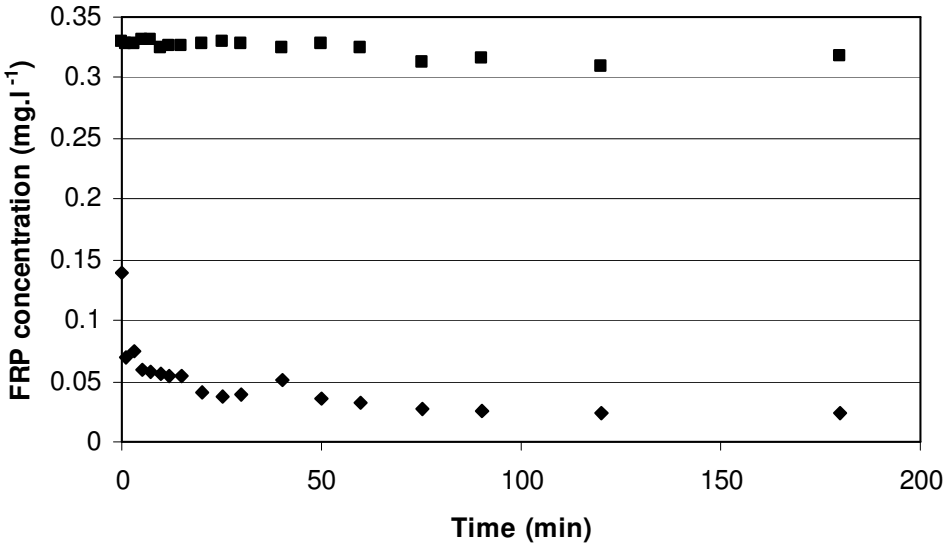

Figure 12: Comparison of the FRP concentration in the Phoslock® treated and control columns for the first 3h following the sediment capping treatment. (♦) Treated (■) Control

The pH of both columns continued to decrease after the sediment capping treatment, especially after the columns were covered with parafilm 5d after treatment. The pH of the water at the bottom of the treated column decreased from 9.02 to 7.12, and that of the control column decreased from 9.12 to 7.61 (Figure 13). Similarly, there was a decrease in the DO concentration of both columns (Figure 14). The control column reached an anoxic state (DO <1mg.l^{-1}) after 4 days, and the treated column only after covering with parafilm. After 6 days the DO concentrations at the bottom of the treated and control columns were 0.45mg.l^{-1} and 0.3mg.l^{-1} respectively. The FRP concentration of the control column increased over the 6d period, from 0.39mg.l^{-1} to 0.731mg.l^{-1}. However, the FRP concentration of the treated column remained below 0.1mg.l^{-1} (Figure 15).

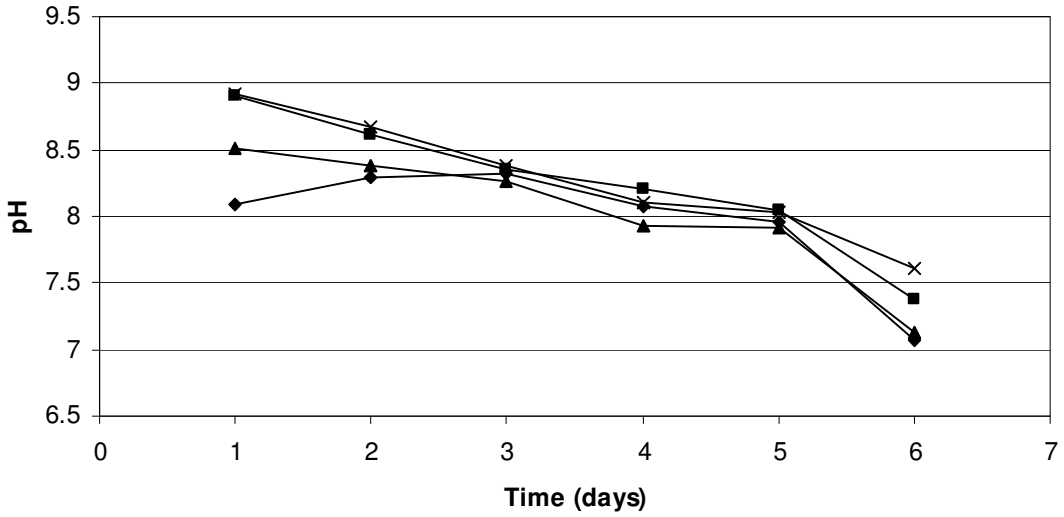

Figure 13: Change in pH at the top and bottom of the treated and control columns for 6 days following the sediment capping treatment. (♦) Treated top (■) Control top (▲) Treated bottom (x) Control bottom

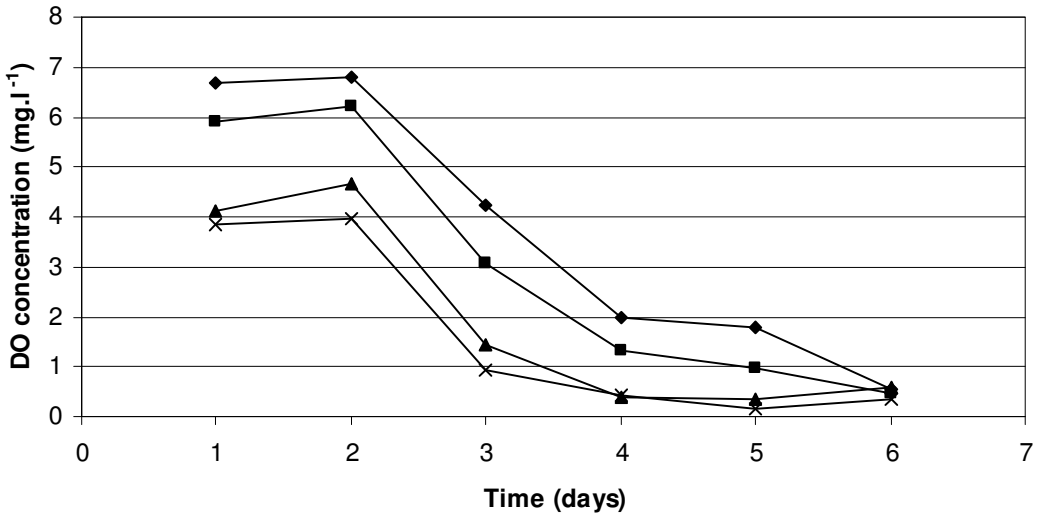

Figure 14: Dissolved oxygen concentration at the top and bottom of the control and treated columns for 6 days following the sediment capping treatment. (♦) Treated top (■) Treated bottom (▲) Control top (x) Control bottom

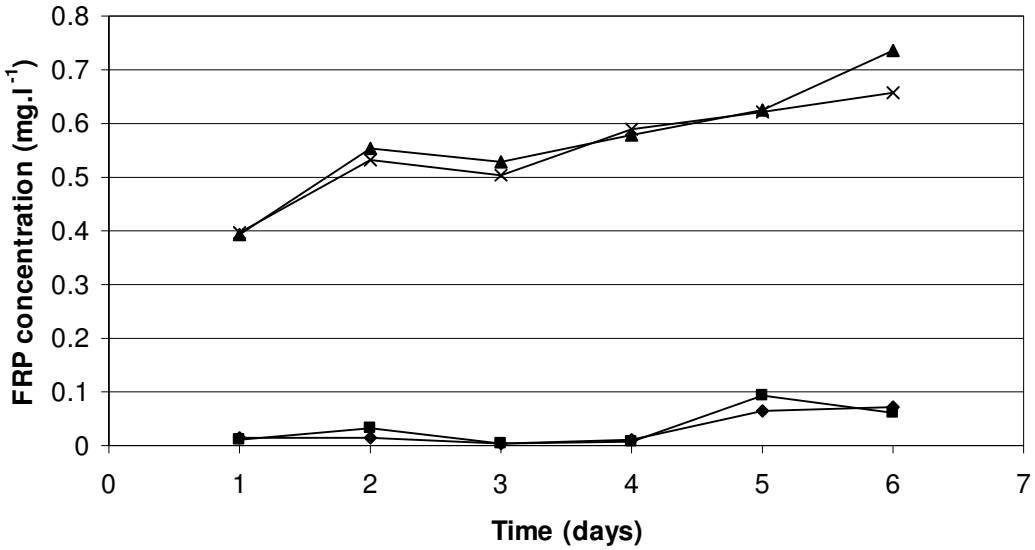

Figure 15: FRP concentrations in the middle and bottom of the treated and control columns for 6 days following the sediment capping treatment. (♦) Treated middle (■) Treated bottom (▲) Control middle (x) Control bottom

3.2.3. Lake water with algal bloom treated at high dose ratios

The initial FRP concentration of the effluent lake water for both the 340:1 treatment and the 450:1 treatment was 0.5mg.l^{-1}; the pH was 9.22 in the 340:1 treatment and 9.04 in the 450:1 treatment. Both had similar initial conductivity (0.4mS/cm) and DO (12.9mg.l^{-1}) concentrations. Linear plots of t/q_t against t in Figure 16 show the applicability of the pseudo-second order equation for the system. Values of k and q_e calculated from equation (4) and the correlation coefficient (R^2) were calculated and are listed in Table 6. The equilibrium adsorption capacity of Phoslock® (q_e) in the effluent lake water treated at a 340:1 ratio of Phoslock® to phosphorus was 1.43mg.g^{-1}, and that of the 450:1 treatment was lower, at 1.34mg.g^{-1} (Figure 17), which is close to the adsorption capacity of the 340:1 treatment. In the 340:1 treated column there was a decrease in FRP concentration from 0.57mg.l^{-1} to 0.32mg.l^{-1} and the FRP concentration of the control column decreased from 0.56mg.l^{-1} to 0.5mg.l^{-1} (Figure 18). In the 450:1 treatment, the FRP concentration decreased from 0.52mg.l^{-1} to 0.2mg.l^{-1}, and decreased in the control from 0.52mg.l^{-1} to 0.4mg.l^{-1} (Figure 19).

Table 6: Kinetic parameters for phosphorus adsorption onto Phoslock® in effluent lake water following treatment dosages of 340:1 and 450:1

Dosage	k ($g.mg^{-1}min^{-1}$)	q_e ($mg.g^{-1}$)	R^2
340:1	0.032	1.43	1
450:1	0.06	1.34	1

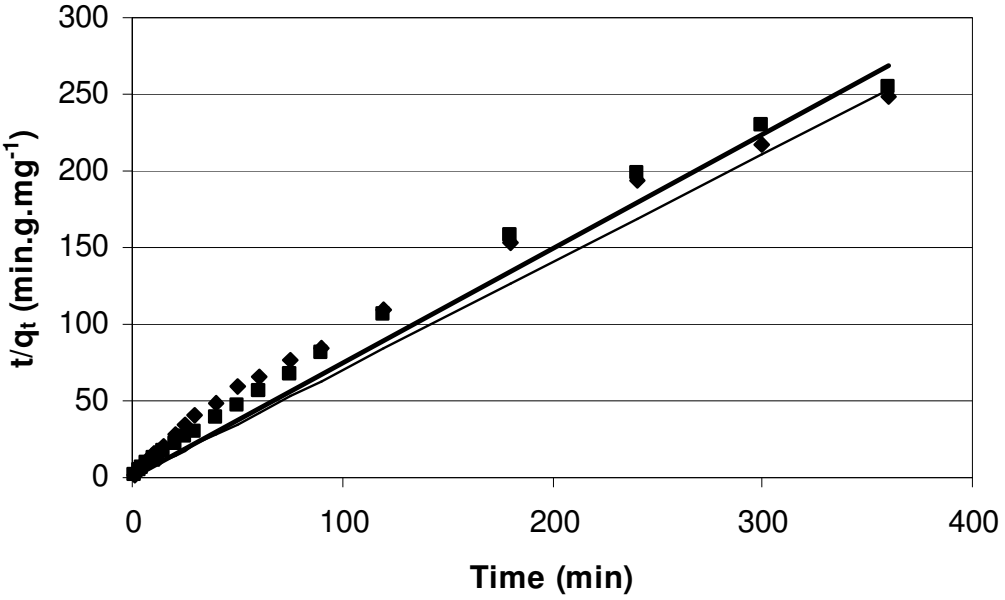

Figure 16: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® in effluent lake water above pH 9.

(♦) 340:1 Phoslock® dosage, (—) Linear trendline for 340:1 dosage. Conditions: initial FRP concentration = 0.5mg.l^{-1}, initial pH = 9.22, Conductivity = 0.4mS, DO = 12.2.mg.l^{-1}, Temperature = 24°C.

(■) 450:1 Phoslock® dosage, (▬) Linear trendline for 450:1 dosage. Conditions: initial FRP conc. = 0.5mg.l^{-1}, initial pH = 9.04, Conductivity = 0.4mS, DO = 12.9mg.l^{-1}, Temperature = 24°C

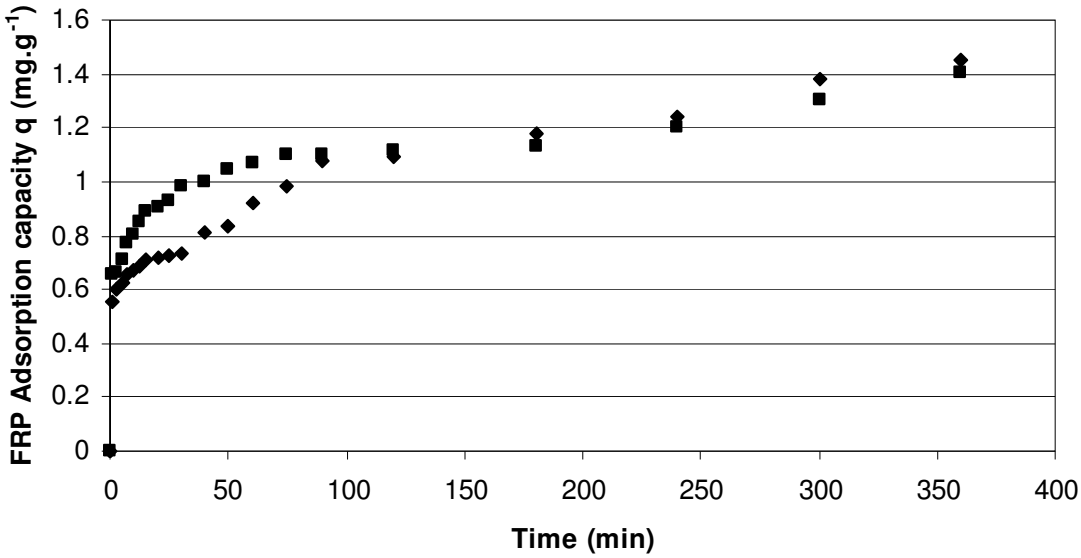

Figure 17: FRP adsorption capacity of Phoslock® versus time in effluent lake water following a (♦) 340:1 Phoslock® dosage, and (■) 450:1 Phoslock® dosage

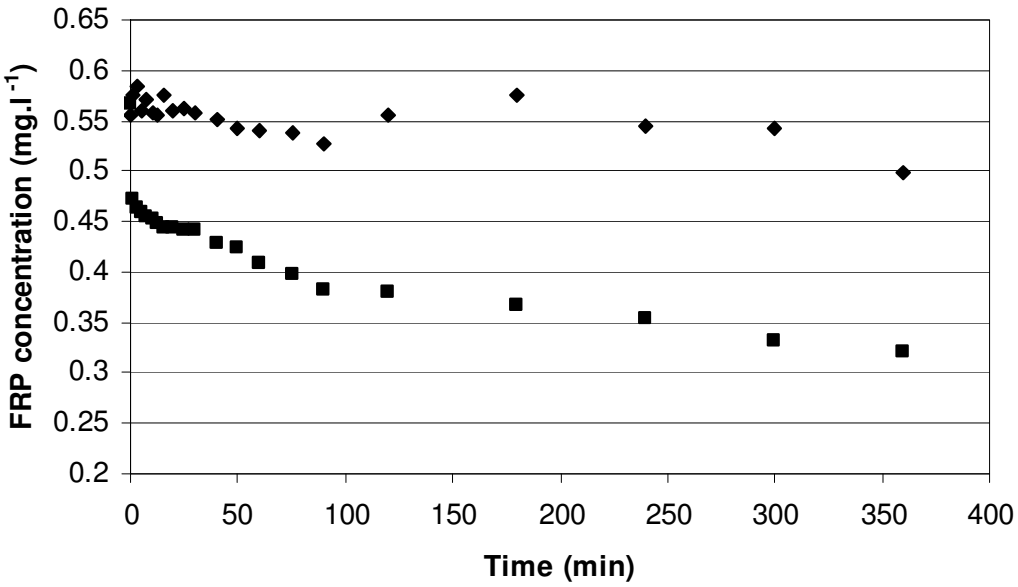

Figure 18: Comparison of the FRP concentration in the Phoslock® treated and control columns for the 6h following the 340:1 treatment (♦) Control (■) Treated

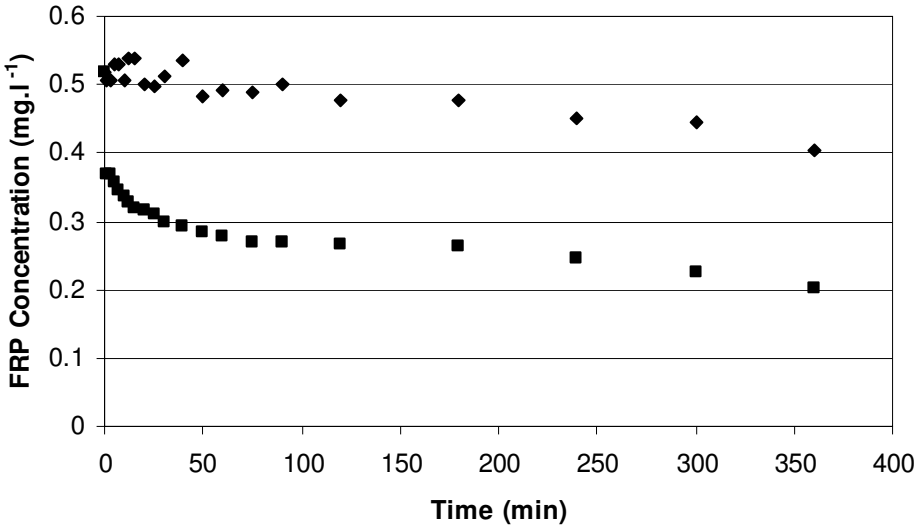

Figure 19: Comparison of the FRP concentration in the Phoslock® treated and control columns for the 6h following the 450:1 treatment

3.3. Beaker tests

3.3.1. Effect of initial phosphorus concentration

Values of k and q_e calculated from equation (4) and the correlation correlation coefficient (R^2) calculated from Figure 20 are listed in Table 4. With increasing FRP concentration, the rate constant (k) decreased and the adsorption capacity of Phoslock® increased (Figure 21). When the beaker experiment at 1mg.l^{-1} was compared with the results from the synthetic solution column experiment at pH 7 and an FRP concentration of 1mg.l^{-1} (Table 1), the adsorption capacity of 4.37mg.g^{-1} was slightly higher in the column than in the beaker (4.26mg.g^{-1}), but the rate constant was higher in the beaker.

Table 4: Kinetic parameters for phosphorus adsorption onto Phoslock® at different initial FRP concentrations

FRP concentration (mg.l^{-1})	k (g.mg^{-1}min^{-1})	q_e (mg.g^{-1})	R^2
0.5	0.72	2.23	0.9982
1	0.11	4.26	0.9979
2	0.01	8.01	0.9991
4	0.02	8.01	0.9972

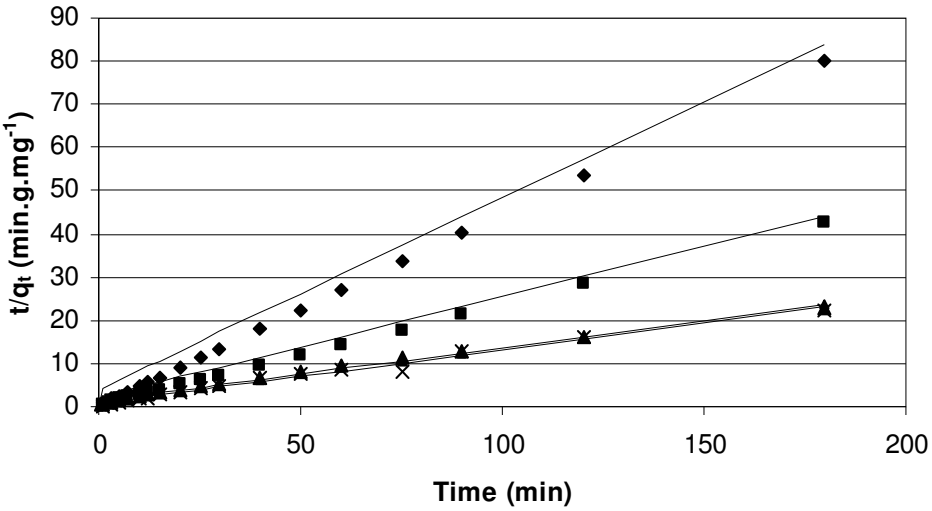

Figure 20: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® at different initial phosphorus concentrations (♦) 0.5mg.l^{-1} (■) 1mg.l^{-1} (▲) 2mg.l^{-1} (x) 4mg.l^{-1} Conditions: continuous stirring, pH = 7, conductivity = 0.3mS

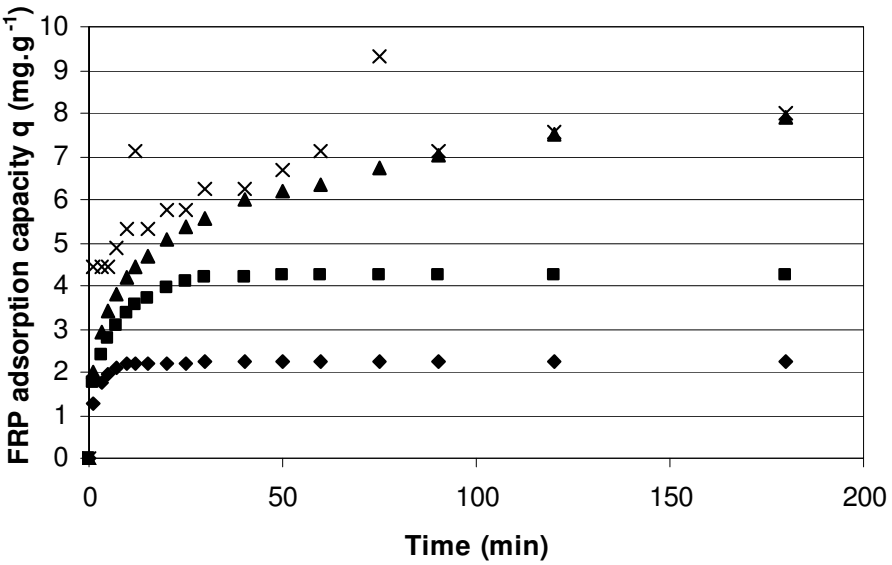

Figure 21: FRP adsorption capacity of Phoslock® versus time at different initial phosphorus concentrations (♦) 0.5mg.l^{-1} (■) 1 mg.l^{-1} (▲) 2 mg.l^{-1} (x) 4 mg.l^{-1}

3.3.2. Lake water

The pH of the effluent lake water was 7.02, and the initial FRP concentration was 0.9mg.l^{-1}. The kinetic parameters for phosphorus adsorption onto Phoslock® in effluent lake water under conditions of continuous stirring following a Phoslock® dose of 230:1 (Figure 22) are shown in Table 5. The effect of humic acids in the effluent lake water is

obvious when the adsorption capacity of 3.84mg.g^{-1} is compared to the synthetic solution beaker experiment at 1mg.l^{-1} FRP and pH 7, which had an adsorption capacity of 4.31mg.g^{-1} (Figure 23). The rate constant in the effluent lake beaker test was higher than that of the synthetic water. The FRP concentration decreased in the treated beaker by 94% from 0.9mg.l^{-1} to 0.05mg.l^{-1}, over the 3h test period, and that of the control beaker stayed constant (Figure 24). The reduction in phosphorus can therefore be attributed to Phoslock® and not algal uptake.

Table 5: Kinetic parameters for phosphorus adsorption onto Phoslock® in effluent lake water under conditions of continuous stirring following a Phoslock® dose of 230:1

Dosage	k (g.mg^{-1}min^{-1})	q_e (mg.g^{-1})	R^2
230:1	0.037	3.84	0.9999

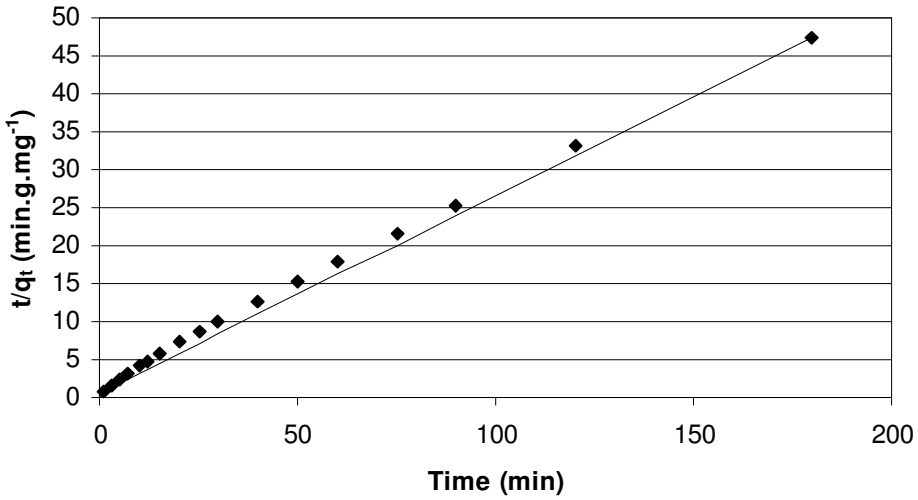

Figure 22: Pseudo-second order kinetics of phosphorus adsorption onto Phoslock® in effluent lake water. Conditions: Continuous stirring, initial FRP concentration = 0.9mg.l^{-1}, Phoslock® dosage = 230:1, pH = 7.02, conductivity = 0.2mS

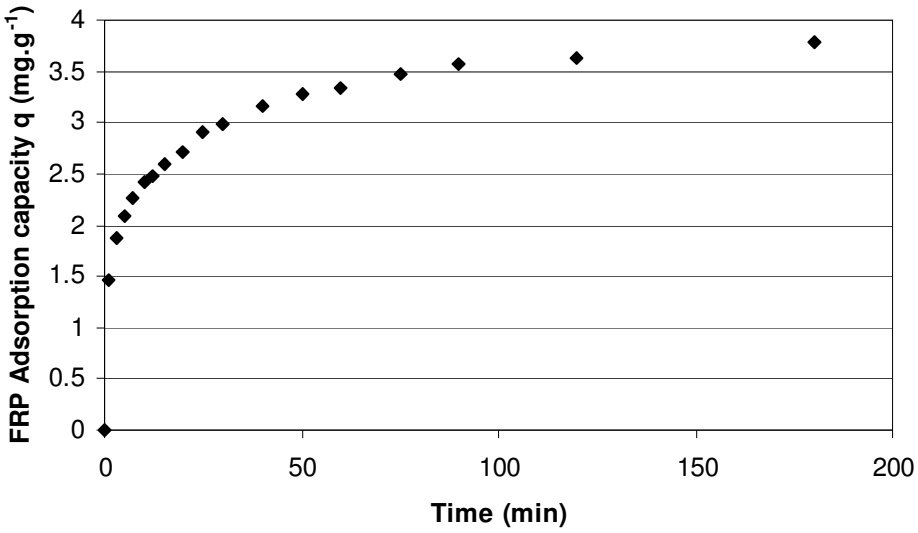

Figure 23: FRP adsorption capacity of Phoslock® versus time in effluent lake water under continuous stirring conditions

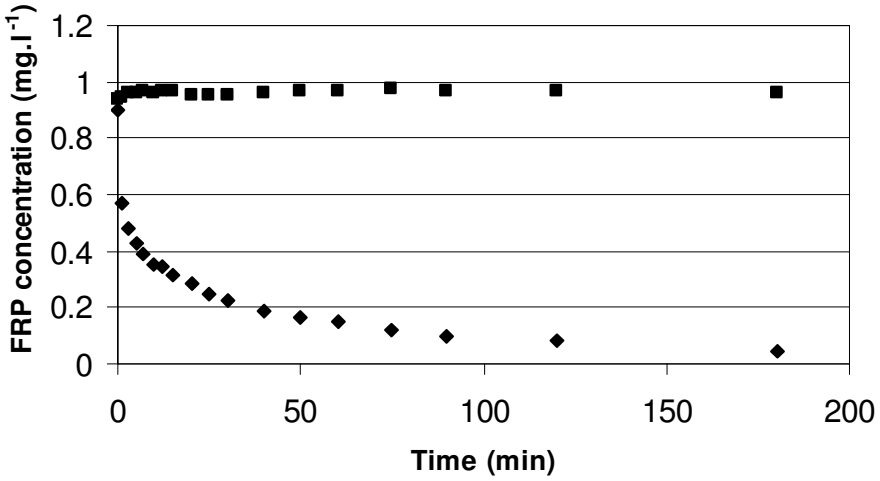

Figure 24: Comparison of the FRP concentration in the Phoslock® treated (♦) and control (■) beakers

4. Discussion

4.1. Column tests

4.1.1. The effect of pH on Phoslock® performance

The extent of phosphorus removal decreased rapidly as the pH was increased from 7 to 9. This can be attributed to the formation of the hydroxyl species of the lanthanum ions, decreasing the number of phosphorus binding sites on the Phoslock® surface. Lanthanum hydroxides begin to precipitate at pH 8.35 (Dibtseva *et al.,* 2001), so a rapid decrease in adsorption capacity is therefore expected above this pH.

The solution turbidity following the Phoslock® application decreased at a faster rate when the initial solution pH was 9, when compared to the pH 5 solution. This is supported by the particle size data. There was a similar decrease in the D[v, 0.1] value in both columns, but the values for D[v, 0.5] and D[v, 0.9] were higher in the pH 9 column, and decreased by greater amounts. The particles were therefore bigger in the pH 9 column, and settled out at a faster rate, as a result of the aggregation of the smaller particles at this pH. The faster settling time at high pH values may contribute to the reduced performance of Phoslock® due to a shorter contact time with the solution. Niriella & Carnahan (2006) reported that bentonite particles displayed a negative zeta potential (the overall charge that a particle acquires in a particular medium) at all pH values between pH 4 and pH 10, with no reverse in charge at any point. However, bentonite particles in distilled water showed an increase in zeta potential value (a larger negative) above pH 8, which could be due to charge development at the edges by direct transfer of H^+ from clay to water. If particles in a solution have a high negative or positive zeta potential then they will tend to repel each other and resist the formation of aggregates. However, if the particles have a low zeta potential (close to zero) there is nothing to prevent the particles from approaching one another and aggregating. Because one would expect the zeta potential of Phoslock® to become more negative at high pH values in the same manner as bentonite, especially because of the increase in the hydroxyl ion species of lanthanum, the increased aggregation of Phoslock® particles observed at high pH is unexpected. It may be explained by the fact that the negatively charged edges are attracted to the positively charged lanthanum ions. This would also contribute to the decrease in phosphorus adsorption capacity of Phoslock® at high pH

values. The presence of counterions in the suspension as a result of the added salt may have caused a reduction in surface charge, thereby contributing to the formation of larger aggregates and the possibility for more rapid settling. Apart from the loss of lanthanum sites to hydroxylation, another reason for the observed decrease in the adsorption capacity, q_e, could also be due to the unavailability of the lanthanum sites, caused by aggregation of the small particles. Aggregation of the smaller particles reduced the available surface area; hence less lanthanum ions per unit surface become available for reaction with the phosphate anions.

4.1.2. Lake water with algal bloom

The FRP concentration in the treated column decreased by approximately 50% from 0.82mg.l^{-1} to 0.4mg.l^{-1} after 6h, but the FRP concentration in the control column remained above 0.7mg.l^{-1}. As a result, the reduction in FRP in the treated column was attributed to Phoslock® and not to algal uptake during growth.

The equilibrium adsorption capacity of Phoslock® (q_e) in the effluent lake water was less than that observed in the synthetic water columns at either pH 8 or pH 9. This may be due to the presence of humic acids in the water, which lowered the phosphorus adsorption capacity of Phoslock®, especially at higher pH values (Douglas *et al*., 2000).

The chlorophyll a concentrations in the treated and control columns at various time intervals is shown in Table 3. Although the initial chlorophyll a values differed in the two columns before the addition of Phoslock®, that of the control column increased more than the treated column in the first 6h. This may be attributed to the higher turbidity in the treated column, which may have prevented algal growth by blocking the light. After 24 and 72h, the chlorophyll a concentration decreased by similar amounts in both columns, so it is unlikely that Phoslock® was responsible for this decrease.

In examining the stability of the adsorbed phosphorus under anoxic conditions, the FRP concentration in the control column remained constant for the 3h period, whereas the FRP concentration in the treated column decreased by 86% following the addition of a sediment capping dosage, indicating that Phoslock® was responsible for the decrease.

After the columns became anoxic, the FRP concentration of the control column increased from 0.39mg.l^{-1} to 0.731mg.l^{-1} over a 6d period, whereas the FRP concentration of the treated column remained below 0.1mg.l^{-1}, even though the system was anoxic, as indicated by the large decrease in the dissolved oxygen (DO) concentration. This demonstrated that Phoslock® was unaffected by the anoxic conditions in the column and the adsorbed phosphorus was not re-released. This is important, as the sediments of water bodies, especially those in a eutrophic state, are usually anoxic (Sweerts *et al*., 1991; Cermelj & Faganeli, 2003).

4.1.3. Lake water with algal bloom treated at high dose ratios

The rate constant (k) was higher for the 340:1 treatment than the 450:1 treatment because the ratio of available FRP to Phoslock® was higher. The equilibrium adsorption capacity of Phoslock® (q_e) in the effluent lake water treated at a 340:1 ratio of Phoslock® to phosphorus was 1.43mg.g^{-1}, and that of the 450:1 treatment was lower, at 1.34mg.g^{-1}, which is close to the adsorption capacity of the 340:1 treatment. In the 340:1 treated column there was a 44% decrease in FRP concentration from 0.57mg.l^{-1} to 0.32mg.l^{-1}. The control showed a 10.1% decrease in FRP from 0.56mg.l^{-1} to 0.5mg.l^{-1}. Therefore only about 34% of the reduction can be attributed to Phoslock® and the rest to algal uptake during growth. In the 450:1 treatment, there was a 61% decrease in FRP concentration from 0.52mg.l^{-1} to 0.2mg.l^{-1}, but there was a 23% decrease in the control from 0.52mg.l^{-1} to 0.4mg.l^{-1}. Therefore, only 38% of the decrease in the FRP concentration can be attributed to Phoslock®, which is similar to the 34% noted in the 340:1 column. The large increase in Phoslock® dosage to 450:1 therefore did not improve the phosphorus removal at this high pH (above pH 9). The dosage may need to be even higher to have an effect.

4.2. Beaker tests

4.2.1. Effect of initial phosphorus concentration

The adsorption capacity of Phoslock® increased with an increase in the FRP concentration, although the equilibrium adsorption capacity of Phoslock® at an FRP

concentration of 1mg.l^{-1} was similar to that at 2mg.l^{-1}. The removal of FRP increased rapidly at the beginning and then more slowly until equilibrium, though more steeply at higher FRP concentrations. When the beaker experiment at 1mg.l^{-1} was compared with the results from the synthetic solution column experiment at pH 7 and an FRP concentration of 1mg.l^{-1}, the adsorption capacity was slightly higher in the column than in the beaker, but the rate constant was higher in the beaker. This may be due to the effect of continuous stirring in the beaker, which allowed for maximum contact between the Phoslock® and the solution.

4.2.2. Lake water

The adsorption capacity of 3.84mg.g^{-1} in the effluent lake water was lower than that of the synthetic solution beaker experiment at 1mg.l^{-1} FRP and pH 7. This is most likely due to the presence of humic acids in the water, which reduce the adsorption capacity of Phoslock®. The FRP concentration decreased by 94% in the treated beaker over the 3h test period, but that of the control beaker stayed constant. The reduction in phosphorus can therefore be attributed to Phoslock® and not algal uptake.

5. Conclusions

- Phoslock® was the most effective at removing phosphorus from the water at pH values between 5 and 7, and the adsorption capacity decreased greatly above pH 9.
- Phoslock® did not affect the conductivity of the water.
- The settling rate of Phoslock® increased with an increase in pH.
- The adsorption capacity of Phoslock® was lower in lake water than in a synthetic water solution at the same pH, most likely due to the effect of humic acids.
- Other than lanthanum, Phoslock® does not have an effect on the concentration of metals in the solution.
- Phosphorus remains bound to Phoslock® under anoxic conditions.
- Above pH 9, the negative effects of pH cannot be overcome by increasing the Phoslock® dosage.

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