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Modeling phosphate adsorption of semi-intensive shrimp pond sediment

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Abstract. Models to simulate phosphate adsorption could be useful for predicting water quality and for controlling eutrophication of ponds and lagoons. The different models of phosphate adsorption of aquaculture pond sediment were investigated, including kinetic adsorption models and adsorption isotherm models. Five sediment samples were collected from 5 different semi-intensive shrimp ponds and analyzed physical and chemical properties. We measured the P adsorption under different conditions of pH and PO_4-P concentration (pH 5, 7, and 8.5; 0.5–5 mg L^{-1}) in batch tests at a sediment-to-solution ratio of 1:10 and then the experimental data was simulated by using several adsorption models . Results showed that P adsorption was not greatly affected by pH ($p>0.05$). This is probably attributed to the high proportion of sand in sediment (>60%), which would have a low specific surface area and less reactive adsorption sites. The adsorption of P with initial concentrations of 0.5 and 5 mg L^{-1} increased within the first 10 and 30 minutes of incubation, respectively. The Langmuir model satisfactorily described the properties of P adsorption isotherms of aquaculture pond sediment. According to the Langmuir model the maximum adsorption capacity (Γ_{max}) was 0.275 ± 0.011 mg g^{-1}.

Keywords: Adsorption, Aquaculture, Langmuir model, Phosphate, Sediment.

1. Introduction

There are many researchers who have documented on the environmental impacts of aquaculture in the world. The results of these researchers had a common conclusion that the increase and development of shrimp farming has generated considerable concern about the effects of aquaculture pond effluents on the nearby aquatic ecosystems. It is noted that effluents from aquaculture farms discharge directly to the lagoon without treatment. The risk of eutrophication in Tam Giang lagoon has been warned by several researchers in recently years [1, 2]. It is suspected that effluents from the hundreds of hectare shrimp ponds at its surroundings are the main reason.

Phosphorus (P) is an essential element for the growth of organisms in aquaculture pond ecosystems, especially for algae development.

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Algae or phytoplankton are the population of microscopic single and multiple-celled aquatic plants that live in pond water. The phytoplankton, which produce dissolved oxygen in the water body, is an essential food source for many aquatic organisms. Phosphorus enters in the aquaculture pond by the fate of application of fertilization, animal feeding, and water intake [3]. However, excessive supply of phosphorus into pond water causes pond eutrophication, resulting in the algae bloom and depletion of pond-dissolved oxygen. As a consequence, pond productivity is reduced. Practically, only 35.5% and 6.1% total nitrogen and phosphorus inputs were recovered from shrimp harvested [4] in semi-intensive shrimp systems. Technique of semi-intensive shrimp culture is regarded as being more ecological method of aquaculture. There are several aquatic animals are stocked in a pond in which Black tiger shrimp (*Penaeus monodon)* is still the main target production (Table 1).

The phosphate ion (PO_4^{3-}) is a highly particle-reactive anion and thus the sorption properties of sediment are crucial for P-retention capacity [5]. The phosphorus form in aquatic ecosystem is under complex control of many factors that depends on the change of environmental conditions.

According to earlier studies, the availability of phosphorus is dependent on the sorption characteristics of the underlying sediments and the phosphorus can be released or accumulated from sediments under certain environments [5-8] but these researches mainly focused on lake sediment. Very few data have been reported for phosphate adsorption onto aquaculture pond sediment where derives P inputs from feeding and fertilization. Therefore, phosphorus absorption and release from aquaculture pond sediments have not been interpreted yet. An experiment was designed with the hypothesis that the availability of phosphate concentration in aquaculture pond sediment at different pH levels can be simulated and predicted by using several adsorption models.

2. Materials and methods

2.1. Sediment sampling and analytical methods

The area of the present study simulated is at 16^0 27' 8'' N and 107^0 36'57'' W, located at Tam Giang lagoon, and adjacent to Thuan An sea inlet and Huong River estuary. Sediment samples of five semi-intensive shrimp ponds were collected in September, 2011 (Figure 1). One sample was taken from each pond at the middle by using a 5-cm core sampler to take layer of 0-10 cm from pond bottom interface. Semi-intensive shrimp culture system in Tam Giang Lagoon was summarized in Table 1.

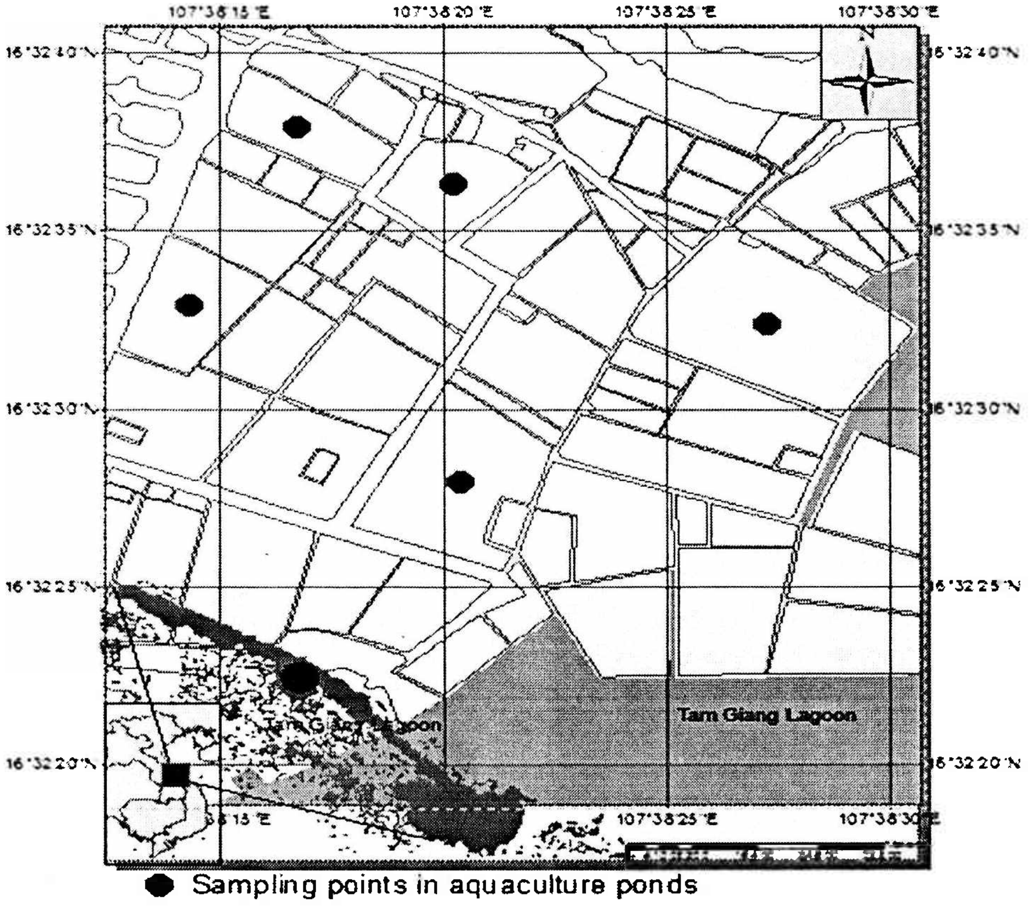

Figure 1. Map of area study.

Table 1. Technical practices applied for semi-intensive shrimp culture at sampling ponds

Pond No.	Area (m^2)	Depth (m)	Stocking density (unit/m)			Cultural duration (months)	Shrimp feed used (kg/ha/cycle)	Fertilizer (kg/ha/cycle) (10:5:5)	Production (kg/ha/cycle)
			Shrimp	Fish	Crab				
1	2,500	1.0	7	0.00	0.04	4.5	420	50	690
2	3,500	1.1	9	0.15	0.04	4.5	560	60	720
3	5,000	0.9	7	0.15	0.00	4.5	700	70	560
4	4,000	1.0	8	0.01	0.03	4.5	580	60	600
5	4,500	0.8	6	0.01	0.02	4.5	550	50	580
Mean	**3,900**	**0.96**	**7.4**	**0.06**	**0.03**	**4.5**	**562**	**58**	**630**

Source: Farmer interview and farm records

Pond sediment samples were dried up at natural condition and determined total carbon (TC); total nitrogen (TN), and C: N ratio, and ground sediment was analyzed by C: N Coder. To examine total phosphorus (TP), dried sediment was treated with H_2SO_4 1 mol L^{-1} and then combusted at 300 ^{0}C before being analyzed by the QuAAutro2 – HR analyzer. Sediment particle-size was determined by using International Soil Science Society (ISSS) standard in which the four size classes were clay (0.0002 mm to 0.002 mm); silt (0.002 mm to 0.02 mm); sand (0.02 mm to 0.2 mm) and coarse sand (0.2 mm to 2 mm) in diameter.

Sdiment samples were treated with hydrogen peroxide to destroy the organic matter and also with sodium hexametaphosphate to disperse the clay particles.

The sieve-pipette method was used for determination of the proportion of clay, silt and sand in the sediment samples. Sediment density was assumed at 2.60 g cm^{-3} [9].

Mineral composition of sediments was analyzed by Energy Dispersive X-ray Fluorescence Spectrometer.

3.2. Experiment of phosphate adsorption kinetic models

To measure the phosphate adsorption kinetics, two experiments were performed with an amount of 0.3 g dried sediment loading into a series of 50 ml centrifuge tubes, with 30 ml of phosphate solution, which contained 0.5 mg L^{-1} and 5 mg L^{-1} of P (anhydrous KH_2PO_4).

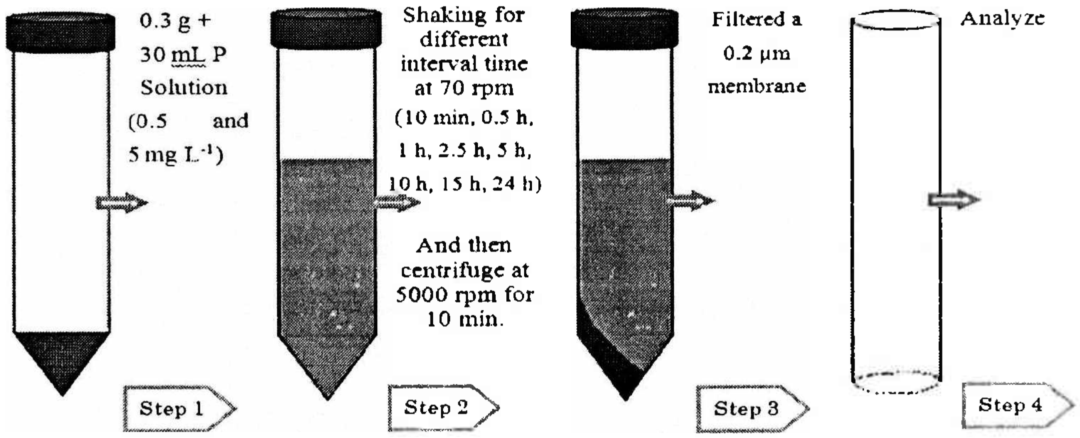

Figure 2. Experiment of phosphate adsorption kinetic measurement.

To determine phosphate released from sediments and adsorbed by plastic centrifuge tubes, P solution was not added to two sediment centrifuge tubes, while two centrifuge tubes stored only P solution without sediments, respectively. The centrifuge tubes were capped and incubated at 25 ± 1 ^0C in a shaker at 70 rpm for various time intervals between 0 and 24 h of adsorption (10 min, 0.5 h, 1 h, 2.5 h, 5 h, 10 h, 15 h, 24 h). The sampled solutions were immediately centrifuged at 5000 rpm for 10 min to accumulate suspended solid substances and then filtered through a 0.2-µm plastic membrane filter [6, 8]. The phosphate concentration (PO_4^{3-}) was measured by the QuAAtro – 2HR analyzer. The experiment was conducted in duplicates. Power function and Simple Elovich models are used to simulate phosphate adsorption kinetics:

Power function model: $\Gamma = at^b$ (1)

Simple Elovich model: $\Gamma = c + d \ln t$ (2)

Where: Γ is the amount of PO_4^{3-} adsorbed (mg g^{-1}), t is the adsorption time (h), *a*, *b*, *c and d* are constants,

3.3. Experiment of phosphate adsorption models with different pH levels

To develop the simulation of phosphate adsorption, loading 0.3 g dried sediments into a series of 50 ml centrifuge tubes with 30 ml of phosphate solution, which were in concentrations of 0.5; 1; 2; and 5 mg L^{-1} of P (anhydrous KH_2PO_4). pH value of solutions at 5, 7 or 8.5 were adjusted by adding HCl or $NaHCO_3$ into the solution before experimented. The centrifuge tubes were capped and placed at 25 ± 1^0C in a shaker at 70 rpm for 48 h to ensure approximate equilibrium (kinetic measurement experiment). The sampled solutions were immediately centrifuged at 5000 rpm for 10 min and filtered through a 0.2-µm membrane filter. The phosphate concentration (PO_4^{3-}) was measured by the QuAAtro – 2HR analyzer.

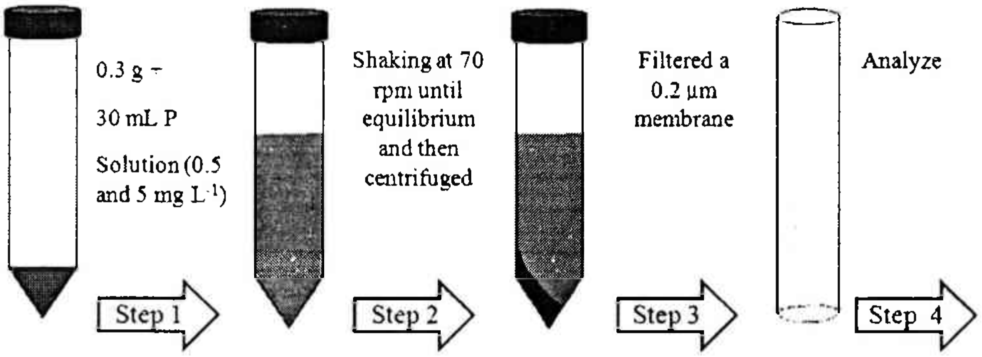

Figure 3. Experiment of phosphate adsorption isotherms at different pH levels.

The experiments were conducted in duplicates. The three following models are used to describe phosphate adsorption isotherms:

Linear model: $\Gamma = KC + b$ (3)

Freundlich model: $\Gamma = KC^n$ (4)

can be linearized as $\text{Log}\,\Gamma = \text{Log}\,K + n\,\text{Log}\,C$

Langmuir model:

Langmuir model: $\Gamma = \dfrac{\Gamma_{max} KC}{1 + KC}$ (5)

can be linearized [10]: $\dfrac{C}{\Gamma} = \dfrac{C}{\Gamma_{max}} + \dfrac{1}{K\Gamma_{max}}$

The amount of phosphate adsorbed by adsorbent:

$\Gamma = (C_b\text{-}C\text{-}C_b)V$ (mg g^{-1})

Where Γ is the amount of phosphate adsorption; Γ_{max} is the maximum adsorption capacity (mg g^{-1}); c_0 and c are the initial concentration of solution and the adsorption equilibrium concentration (mg L^{-1}); c_b is concentration of blank control (including phosphate concentration released from sediments and adsorbed by plastic centrifuge tubes); m is the weight of absorbent (g); V is the volume of solution (L); K is the adsorption coefficient; a and b are the constants.

2.3. Data analysis

Data was analyzed in three replicates. Means and standard deviations were calculated and expressed as "mean (±SD)." Significant variations in the amount of phosphate adsorbed at different pH levels was tested by using one way ANOVA analysis of variance by using Software SPSS version 15.0 with significant value at 5% level of confidence.

3. Results

3.1. Sediment properties

Physicochemical properties of sediment were summarized in Table 9. Because of applied shrimp feed and fertilizer (Table 1), lime, concentration of TC, TN, TP and mineral compositions were at a relatively high level. The presence of other components in sediment depend on what kind of soil the pond is located in and how long and how the pond has been accumulation with time, because of loading of suspended solids by water exchange and flood, especially high densities of phytoplankton. The grain sizes of sediment samples was quite different from propotion, while sand was the major component in sediment (> 60 %), the proportion of clay fractions was very low (only 18.49%). According to Wang et al., 2006, particle size fractions had different effects on the exchange of phosphate between overlaying water and sediment.

Table 2. Soil particle-size and physicochemical properties of sediment

Items	**Mean ± SD**
TC (mg g^{-1})	14.7 ± 1.4
C: N	9.7 ± 1.0
TN (mg g^{-1})	1.5 ± 0.3
TP (mg g^{-1})	0.3 ± 0.0
Al (%)	17.9 ± 1.4
Si (%)	59.7 ± 0.7
K (%)	2.8 ± 0.3
S (%)	0.5 ± 0.2
Ca (%)	0.4 ± 0.2
Cl (%)	0.4 ± 0.3
Fe (%)	5.8 ± 0.1
Ti (%)	0.7 ± 0.1
Cu (ppm)	21.3 ± 15
Zn (ppm)	128.5 ± 7.3
Sr (ppm)	83.1 ± 32.0
pH	6.8 ± 0.4
EC (dS m^{-1})	5.2 ± 0.4
Particle-size (mm)	
Clay (%)	18.5 ± 9.6
Silt (%)	16.3 ± 6.3
Sand (%)	65.2 ± 6.6

X-ray analysis indicates that mineralogy of present study is agreement with Smith, 1996 [11], who reported that the quartz content was dominant in sediment samples collected prawn farms and mangrove habitats.

3.2. Modeling phosphate adsorption kinetics

The results of phosphate adsorption kinetic models and estimation of parameters with different initial concentrations at 25 ± 1 ^{0}C are shown in Table 3 and Figure 4.

It can be seen that the majority of phosphate adsorption on the adsorbents occurred quickly at 10 minutes (51.5%), and then adsorption increased gradually until 24 h for an initial concentration of 0.5 mg L^{-1} P. Similarly, phosphate kinetic adsorption increased dramatically at the first 0.5 h and then rose slightly and reached concentration equilibrium at 2.5 h for a concentration of 5 mg L^{-1} P.

Table 3. Estimated kinetic model parameters for phosphate adsorption of sediment

Concentration of initial P	Power function model	R^2	Simple Elovich model	R^2
0.5 mg L^{-1}	$\Gamma = 0.037 * t^{0.1043}$	0.774	$\Gamma = 0.001 * \ln t + 0.038$	0.410
5 mg L^{-1}	$\Gamma = 0.159 * t^{0.1686}$	0.796	$\Gamma = 0.005 * \ln t + 0.161$	0.643

The Γ-adsorbed phosphate (mg /g) at time t (h), Initial phosphate was added at 0,5 mg L-1 and 5 mg/L, Kinetic model parameters were estimated without using the origin ($\Gamma = 0$; $t = 0$)

Based on R^2, the Power function model (R^2 = 0.774 to 0.796) was more adequate than Simple Elovich model (R^2 = 0.410 to 0.686). Higher applicability of the Power function model to properly describe the phosphate adsorption kinetics was reported by several researchers [6, 8].

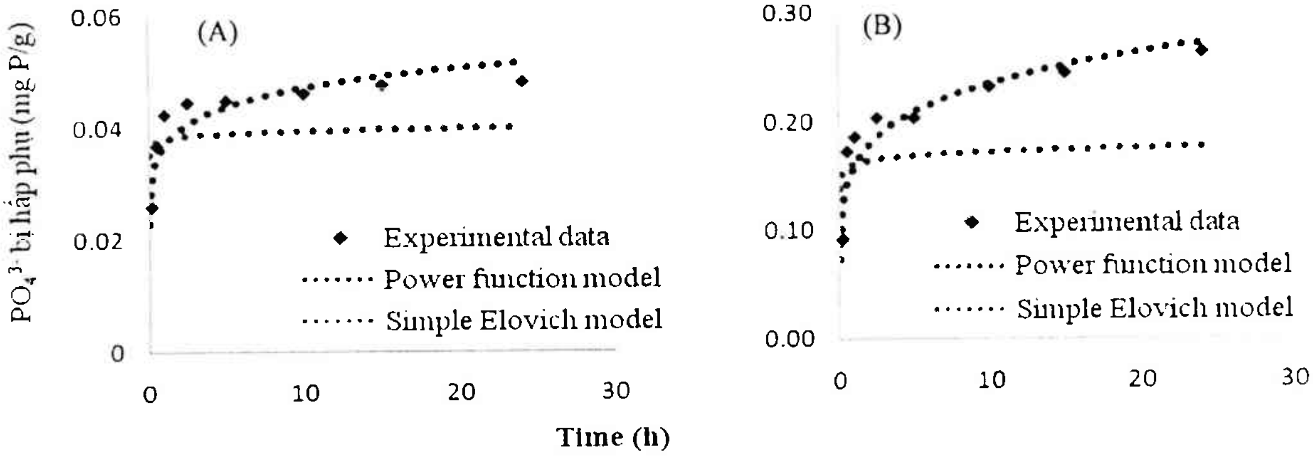

Figure 4. Different model descriptions of adsorption kinetics for phosphate on sediment *(A) and (B) are initial P concentration of 0.5 and 5 mg L^{-1}.*

3.3. Modeling phosphate adsorption isotherms at different pH levels

Estimation of phosphate adsorption data of sediments with different pH levels were summarized in Table 4 and described in Figures 5, 6 &7. Based on R^2, the Langmuir model (R^2 = 0.952 to 0.996) satisfactorily described phosphate adsorption isotherms for sediment at different pH levels.

The maximum adsorption capacity (Γ_{max}) of sediment at pH 5, pH 7, and pH 8.5 was 0.288; 0.267; 0.270 mg g $^{-1}$, respectively. Sediment can bind and release phosphorus depending on its concentration in the sediments and environmental conditions. The release of phosphate ions from the material to the solutions is very low (equivalent 0) and could be partially due to the low content of P in the adsorbent. The phosphate adsorption was not affected much by pH in this study (p>0.05). This is probably attributed to the high proportion of sand in sediment (> 60 %) which had a low specific surface area and less reactive adsorption sites. According to previous studies [8, 12], lower phosphate adsorption at high pH values resulted from an increase repulsion between the more negatively charged PO_4^{3-} species and negatively charged surface sites. The result of this study also indicated that the amount of phosphate absorbed by adsorbents was depended on the initial concentration of P added.

The pH of the aqueous solution is an important factor that affects phosphate adsorption near the sediment-water interface [8]. Modeling phosphate adsorption of sediment was presented in Figures 5, 6, &7.

Table 4. Estimated adsorption model parameters for phosphate adsorption isotherms at different pH levels

pH	Linear model	R^2	Langmuir model	R^2	Freunlich model	R^2
5	$\Gamma = 0.0879x + 0.067$	0.964	$\Gamma = \frac{0.929C}{1+3.229C}$	0.952	$\Gamma = 0.176x^{0.295}$	0.953
7	$\Gamma = 0.0761x + 0.092$	0.820	$\Gamma = \frac{3.453C}{1+12.938C}$	0.996	$\Gamma = 0.219x^{0.251}$	0.969
8.5	$\Gamma = 0.0757x + 0.074$	0.913	$\Gamma = \frac{1.106C}{1+4.093C}$	0.986	$\Gamma = 0.186x^{0.366}$	0.919

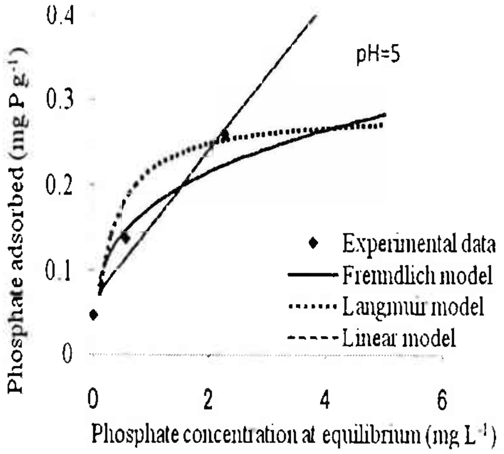

Figure 5. Modeling phosphate adsorption isotherms at pH=5.

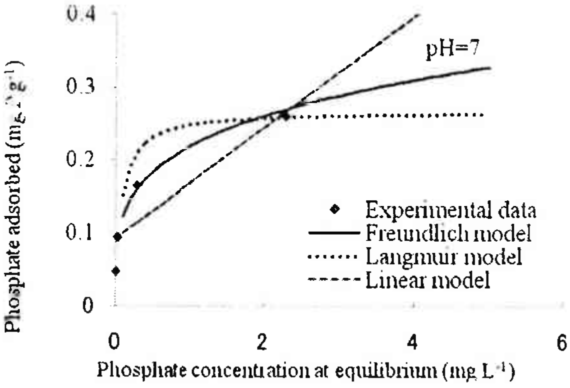

Figure 6. Modeling phosphate adsorption isotherms at pH=7.

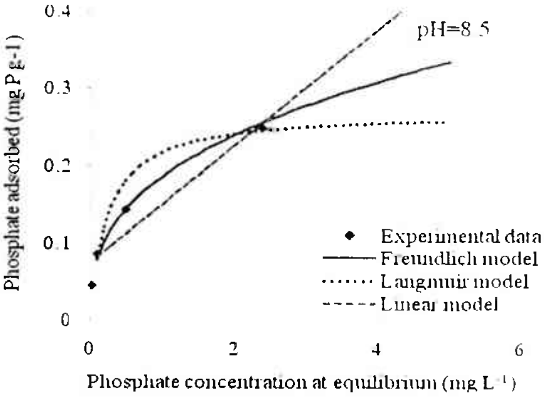

Figure 7. Modeling phosphate adsorption isotherms at pH=8.5.

4. Discussions

4.1. Modeling phosphate adsorption kinetics

The results of this study indicated that the amount of phosphate adsorption by adsorbents was dependent on concentration of P added. The sorption kinetic with an initial concentration of 0.5 and 5 mg L^{-1} P increased sharply within 10 minutes and a half-hour of incubation, respectively. This was strongly in agreement with Wang et al., 2005 who have reported that the majority of phosphate adsorption onto the lakes' sediments was completed in 0.5 h. Based on R^2, the Power function model was more satisfactory to describe phosphate sorption kinetics of aquaculture pond sediment than Simple Elovich models in the present study [6, 8].

4.2. Modeling phosphate adsorption isotherms

The present experiment was performed at 25 ± 1 ^{0}C with different pH levels and the amount of P sorption increased with equilibrium P concentration. The pH levels between 5 and 8.5 had a negligible effect on the rate of phosphate adsorption by aquaculture pond sediment. Sediment particle-sizes may be the cause of a low amount of phosphate adsorption. According to Wang et al., 2006, maximum phosphate sorption capacity, equilibrium concentration, phosphate sorption efficiency and phosphate sorption rate decreased as particle-size increased. Similarly, pond soil strongly adsorbed phosphorus, and the capacity of sediment to adsorb phosphorus increases as a function of increasing clay content [13, 14].

The data of the present study was much lower than be result of Lefrancois et al., 2010, who reported that maximum adsorption capacity was 1.32 mg P g^{-1} for aquaculture pond sediment. On the other hand, [15], reported the phosphorus adsorption maximum of sands of 0.035 to 0.079 mg g^{-1} was much lower than that of our study. This is also a clear answer for the question as to why phosphate adsorption was not greatly affected by pH variables. The sediment characteristics stored a much higher proportion of sand than that of silt and clay. This may be the result of low adsorption capacity that increased with increasing clay content.

Several previous studies demonstrated that the sorption reactions of P, caused by inorganic particles, are enhanced as a function of decreasing sediment grain size. Other negatively charged anions can also complete with the PO_4^{3-} of adsorption sites in sediment. An increase in pH can also increase the negative charge of adsorbing oxides. But sediments of this study had a low concentration of total phosphorus and high proportion of sand. As a result, changes in environmental conditions may not be important to adsorption capacity due to low specific surface area and less active adsorption sites.

The Langmuir model, which (R^2 = 0.952 to 0.996) adequately described phosphate adsorption isotherms, was strongly in agreement with [10, 15].

5. Conclusion

Models of phosphate adsorption kinetic of aquaculture pond sediments has a similar trend; that is phosphate asorption rate tends to increase sharply at first, then remains stable, and then increase slightly before reached equilibrium. The Power function model could provide satisfactory fitting for the kinetic data of adsorption of aquaculture pond sediment.

The models for simulation of phosphate adsorption behaviour into aquaculture pond sediment was relativerly satisfactory of which the Langmuir model was the best. The adsorption capacity of sediment was not greatly affected by pH levels, this attribute to be a high percentage of sand.

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