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Reusing spent polyaluminum chloride sludge as adsorbent for phosphate removal from secondary wastewater effluent

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ABSTRACT

This study explored the reuse potential of spent polyaluminum chloride (PAC) sludge as an adsorbent for removing phosphate from secondary wastewater effluent. The adsorption isotherm and kinetics were examined in batch experiments. The effect of temperature, pH, and foreign anions on phosphate adsorption was also investigated. Additionally, continuous column adsorption was employed to evaluate the applicability of the bed-depth-service-time (BDST) model. Experimental results reveal that the adsorption of phosphate onto PAC sludge was rapid in the preliminary 30 min and the adsorption behavior followed a pseudo-second-order model. Langmuir isotherm correlated the experimental data better than Freundlich isotherm and the maximum value of adsorbed phosphate (q_m) was 2.21 mg P/g SS. Besides, the phosphate adsorption was favored at higher temperature and lower pH and was hardly interfered by the competing anions. Furthermore, the process of phosphate adsorption was spontaneous and endothermic in terms of the thermodynamic parameters, ΔH^0, ΔS^0, and ΔG^0. Finally, the BDST model was appropriate to describe the adsorption of phosphate by PAC sludge in the column mode and could be successfully used in predicting the breakthrough and exhaustion time.

Keywords: PAC sludge; Phosphate; Adsorption isotherm; Adsorption kinetics; Breakthrough time

1. Introduction

Phosphorus, an essential factor causing eutrophication in water bodies, is mostly present in the form of phosphate in typical municipal wastewater. Various techniques based on physical, chemical, and biological processes are extensively applied for phosphate removal in wastewater treatment facilities. Among these techniques, physical methods, such as electrodial-

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ysis, membrane filtration, and reverse osmosis, are relatively expensive due to their high operational and maintenance cost [1]; whereas, biological processes exhibit a highly variable performance due to their operational difficulties [2]. Chemical treatments are the most effective and well-established methods up to date [3].

However, the conventional chemical techniques, e.g. phosphate precipitation with calcium, aluminum or iron salts, are affected by wastewater pH, dosing points, chemical dosage, and agitation energy. Besides, it consumes plentiful chemicals and accordingly produces more chemical sludge than other techniques do. Therefore, the alternative methods utilizing industrial wastes or inorganic materials as absorbents have been widely investigated to reduce operation cost for phosphorous removal. Successful results have been obtained, such as, with synthesized goethite, commercial alumina, commercial hydrotalcite [4], activated alumina [5], fly ash [6], calcined alunite [7], iron oxide tailings [8], metal-loaded orange waste [9], and active red mud [10].

Polyaluminum chloride (PAC) is a commonly used coagulant for removing turbidity in water purification plants of Taiwan. The spent PAC sludge, an inescapable by-product of the coagulation process, has long been treated as a waste for landfill. Although the spent alum sludge was previously verified to be capable of adsorbing phosphate, most of the reported studies were carried out on synthetic wastewater [11–14]. The phosphate removal from real wastewater has only been investigated by Hung and Chiswell [15]. However, their study focused more on examining the phosphate adsorption ability of alum sludge in a small-scale continuous flow system, rather than exploring the basic adsorption characteristics of sludge, such as the adsorption isotherms and kinetics, and the effect of temperature, pH, and competing anions on phosphate adsorption. This study, therefore, conducted a comprehensive experiment to investigate the adsorption characteristics of phosphate on spent PAC sludge in real secondary effluent to evaluate the applicability of the bed-depth-service-time (BDST) model for continuous column adsorption.

2. Materials and methods

2.1. Preparation of test materials

The PAC sludge used in this study was obtained from the sedimentation tank of Feng-Yuan Water Purification Plant, Taiwan. The sampled sludge was freezing dried, ground, and then stored in a dried cabinet for further experiments. The tested wastewater was sampled from the secondary effluent of the Wastewater Treatment Plant of Yunlin University of Science & Technology, Taiwan. The secondary effluent sample was then stored at 25℃ in the laboratory. Its initial phosphate concentration was 1.27 mg P/L and pH was 7.7.

Phosphate (PO_4^{3-}) stock solution (1,000 mg/L) was prepared by dissolving 1 g of potassium dihydrogen phosphate (KH_2PO_4) in 1 L of deionized water. The working phosphate concentration of the secondary effluent was adjusted to 4.0 mg P/L by using the phosphate stock solution so as to conduct the following experiments: kinetics and isotherm tests, temperature effect tests, and column adsorption tests.

To prevent any interference by existing anions in real wastewater, the tests of competing anions and pH effects were performed by utilizing the test solution prepared by deionized water. The same phosphate stock solution was diluted to attain a 15 mg P/L of the working phosphate solution.

2.2. Kinetics and isotherm tests

A series of batch tests were conducted by varying the dosage of PAC sludge in the range of 0.4–4 g (corresponding to 0.8–8 g/L) so as to evaluate the kinetics and isotherm behaviors of phosphate adsorption. Different amounts of sludge were added to 500 mL of working secondary effluent in Erlenmeyer flasks. The flasks were covered and immediately placed on an orbital shaker, and then the flasks were shaken for 48 h at 200 rpm. A 20 mL solution was sampled with a pipettor at different time intervals of adsorption. The sampled solution was filtered through a 0.45 μm filter membrane, and the PO_4^{3-} of the filtrate was analyzed by using a spectrophotometer according to the ascorbic acid method described in Standard Methods (APHA, 1992).

2.3. Effect of temperature

The adsorption experiments were performed at different temperatures (15, 25, and 35℃) and various sludge dosages (0.2–2 g). Using the same method operated in the isotherm test, different dosages of sludge were added to 250 mL of working secondary effluent in Erlenmeyer flasks. The flasks were covered and immediately placed in the temperature shaker incubator which was controlled at different temperatures. Then, the flasks were shaken at 200 rpm for 24 h. At the end of shaking, the suspension was filtered and the PO_4^{3-} of the filtrate was analyzed.

2.4. Effect of pH

The effect of pH on phosphate adsorption was examined by varying pH from 4 to 9. One gram of

PAC sludge was added to 250 mL of the working phosphate solution in an Erlenmeyer flask. The pH of the phosphate solution was adjusted by using 0.1 M H_2SO_4 and 0.01 M NaOH so as to obtain the required pH value. The flask was then shaken for 24 h at 200 rpm. Then the mixed liquor was filtered and the phosphate in the solution was analyzed.

2.5. Effect of competing anions

The competitive effect of anion on PO_4^{3-} adsorption by PAC sludge was examined by adding 1.0 g sludge to the Erlenmeyer flask containing 250 mL of working phosphate solution, which was comprised of an equal concentration (15 mg/L) of PO_4^{3-} and competing anions (SO_4^{2-}, Cl^-, HCO_3^-, NO_3^-, or BO_3^-). The flasks were then shaken at 200 rpm for 24 h. The solution in the flask was subsequently filtered for phosphate concentration analysis.

2.6. Column adsorption test

The schematic diagram of the fixed-bed column experiment is illustrated in Fig. 1. Three fixed-bed columns were vertically constructed in series. The fixed-bed columns were made of Perspex tubes with 3 cm internal diameter and 30 cm height. Each column used in the experiments was packed with 10 cm PAC sludge. The filter membranes and glass beads were placed at the top and bottom of the sludge to prevent any loss of sludge. The influent feed was pumped upward through the column at a constant flow rate of 9 mL/min. The effluent solutions sampled from each column were analyzed by using a spectrophotometer to determine their phosphate concentrations. The column experiments were continued until a constant concentration of effluent phosphate was obtained.

3. Results and discussion

3.1. Adsorption kinetics

The phosphate adsorbed by PAC sludge, as is shown in Fig. 2, increased obviously during the first 6 h and remained constant after a contact time of about 24 h (i.e. the equilibrium time). More than 90% of phosphate was adsorbed within 6 h; phosphate removal was improved less than 10% during the remaining 18 h. Furthermore, the adsorption capacity (q_e) decreased from 2.61 to 0.53 mg/g when the sludge dosage was increased from 0.4 to 4 g. Raising sludge dosages obviously increased the availability of sorption sites, thus the phosphate uptaken by unit weight of sludge, as indicated above, decreased with increment in sludge dosages.

Pseudo-first and pseudo-second-order models were used to fit the phosphate adsorption kinetic data so as to examine the reaction rate of phosphate adsorption onto PAC sludge. The two models can be rearranged as follows [7]:

Pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}$$

Pseudo-second-order model: $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

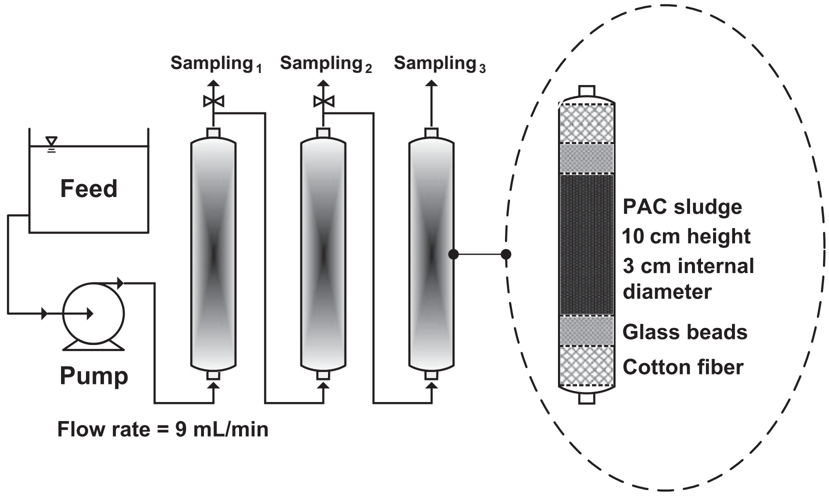

Fig. 1. Schematic diagram of a continuous fixed-bed column experiment.

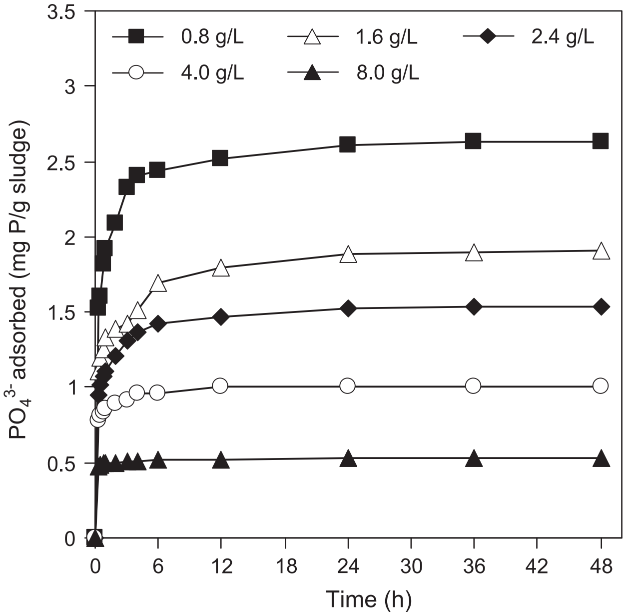

Fig. 2. Kinetic data of phosphate adsorption onto different doses of PAC (0.8–8.0 g/L).

where q_e is the amount of phosphate adsorbed at equilibrium (mg/g); q_t is the amount of phosphate sorbed at time t (mg/g); k_1 is the rate constant of pseudo-first-order sorption (1/h); and k_2 is the rate constant of pseudo-second-order sorption (g/mg/h).

The results of fitting kinetic data to the two models are presented in Table 1 accompanied with the comparison of the experimental and calculated q_e. The observed q_e values from experimental data, as shown in Table 1, did not correspond well with q_e values calculated from the first-order model. While q_e values calculated from the second-order model were satisfactorily close to the experimental q_e values. The regression coefficient (R^2) was further used to evaluate the data fitness of the two models. The R^2s of the pseudo-second-order model (0.9997–1.0) were much higher than those of the pseudo-first-order model (0.7153–0.9502), indicating that the entire experimental kinetic data were superiorly described by the pseudo-second-order model. The above-mentioned comparisons apparently suggest that the adsorption of phosphate onto PAC sludge obeyed a pseudo-second-order kinetic model. Similar results of previous studies [7,16,17] also reported the same pseudo-second-order kinetic model in the phosphate adsorption process. The k_2 of the equilibrium rate constant was found in this study to be 45.45 g/mg/h when the sludge dosage was 0.8 g/L. This k_2 value of PAC sludge was lower than those of calcined alunite (85.06 g/mg/h) [7] and ion-exchange fiber (597.31 g/mg/h) [16], but was almost equal to that of Fe(III)/Cr(III) hydroxide (53.4 g/mg/h) [17].

3.2. Adsorption isotherm

The Freundlich and Langmuir equations are the most frequently used models for describing adsorption isotherms of experimental data. These two models are expressed as follows:

$$\text{Freundlich equation: } q_e = KC_e^{\frac{1}{n}} \tag{3}$$

$$\text{Langmuir equation: } q_e = \frac{bq_m C_e}{1 + bC_e} \tag{4}$$

where q_e is the amount of phosphate adsorbed at equilibrium (mg/g); q_m is the maximum amount of adsorbed phosphate (mg/g); C_e is the equilibrium phosphate concentration in solution (mg/L); K and n are the Freundlich constants; and b is the Langmuir constant.

Fig. 3 compares the fitting results of experimental data between the Freundlich and the Langmuir models. The experimental results of phosphate adsorption on PAC sludge, as shown in Fig. 3, could be well explained by both the Langmuir and the Freundlich models; whereas, the Langmuir isotherm better fit the

Table 1
Comparisons of pseudo-first- and pseudo-second-order models for phosphate adsorption

Dosage (g/L)	q_e (exp) (mg P/g)	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mg P/g)	k_1 (1/h)	R^2	q_e (mg P/g)	k_2 (g/mg/h)	R^2
0.8	2.61	0.957	0.179	0.8796	2.651	45.45	0.9999
1.6	1.88	0.884	0.135	0.9502	1.930	10.99	0.9997
2.4	1.53	0.729	0.140	0.9132	1.549	8.55	0.9999
4.0	1.01	0.510	0.205	0.8298	1.014	5.18	1.0
8.0	0.53	0.304	0.160	0.7153	0.534	1.20	1.0

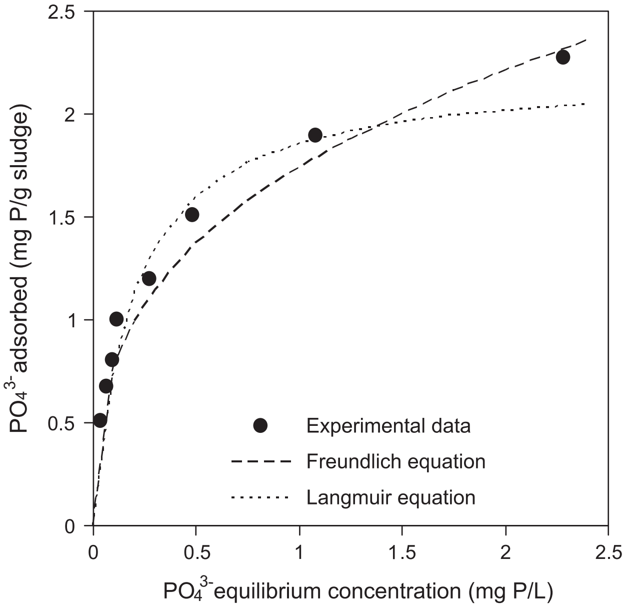

Fig. 3. Phosphate adsorption isotherm for PAC sludge.

experimental data than did the Freundlich isotherm. The estimated Freundlich and Langmuir constants, K, n, b, q_m, are shown in Table 2. The value of K generally represents the adsorption capacity and the value of n means beneficial adsorption if n was between 1 and 10. The values of the Freundlich model constants K and n are 1.74 and 2.88, respectively, implying the reaction of phosphate and PAC sludge was a favorable adsorption.

The estimated maximum value of adsorbed phosphate (i.e. the Langmuir constant q_m) was 2.21 mg P/g, as shown in Table 2. Compared with other reported adsorbents for phosphate removal, such as fly ash (14.0 mg P/g) [6], iron oxide tailing (5.64 mg P/g) [8], and dewatered alum sludge (3.5 mg P/g) [12], the adsorption capacity of PAC sludge was seemingly lower. However, this adsorption capacity was still higher than the spent alum sludge (0.30–0.33 mg P/g) [15] and blast furnace slag (0.65 mg P/g) [18].

The Langmuir constant b, representing affinity of the adsorbent and adsorbate, can be employed to calculate the dimensionless separation factor (r) by the equation: $r = 1/(1 + bC_0)$, in which C_0 is the initial phosphate concentration, and an r value between 0 and 1 is indicative of favorable adsorption [8]. The calculated value of r in this study was 0.044, indicating again that the adsorption of phosphate on to PAC sludge was favorable. Furthermore, the experimental data of phosphate adsorption on PAC sludge apparently matched well with both the Freundlich and the Langmuir models, as shown in Table 2 by comparing the regression coefficient (R^2) and the standard error (SE) of the two models. Still, the Langmuir model provided a better fit than the Freundlich model in this study. This result suggests that the adsorbed phosphate on the surface of the sludge particle was possibly a monolayer saturation.

Table 2
Freundlich and Langmuir constants

Freundlich	K	n	R^2	SE
	1.74	2.88	0.9651	0.546
Langmuir	b	q_m	R^2	SE
	5.27	2.21	0.9955	0.383

3.3. Effect of temperature

The effect of temperature and the phosphate adsorption by PAC sludge was carried out at 15, 25, and 35℃. The phosphate removal was followed in experimental results to follow the order of 35℃ > 25℃ > 15℃; that is, phosphate adsorption on the sludge surface was favored at higher temperatures. This phenomenon implies that the adsorption process is a natural endothermic reaction. Similar findings were reported for the adsorption of phosphate on Fe(III)/Cr(III) hydroxide [17] and blast furnace slag [19].

The Langmuir constant b can be used to evaluate the standard Gibbs free energy change (ΔG^0) by using the Eq. (5) [20]:

$$\Delta G^0 = -RT \ln b \tag{5}$$

where R is the gas constant (8.314 J/mol/K) and T is the absolute temperature (K). Besides, standard enthalpy and entropy change (ΔH^0 and ΔS^0) are correlated with the Langmuir constant b according to the following Eq. (6) [20]:

$$\ln b = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{6}$$

The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the linear plot of $\ln b$ vs. $1/T$, as shown in Fig. 4. The values of thermodynamic parameters, ΔG^0, ΔH^0, and ΔS^0 are summarized in Table 3. The negative values of ΔG^0 decreased along with the increase of temperature, indicating that the spontaneous nature of adsorption was favored at higher temperatures. The positive value of ΔH^0 reflected that the adsorption reaction of PO_4^{3-} on PAC sludge was endothermic. This is also why rising the temperature of solution can increase the adsorption

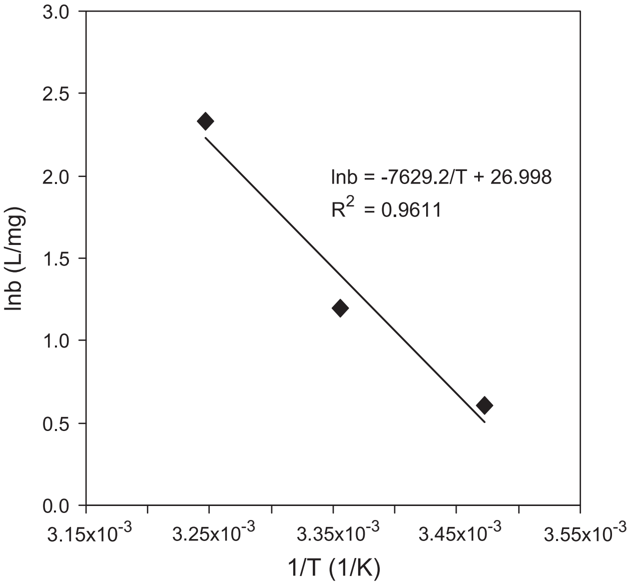

Fig. 4. Plot of $\ln b$ vs. $1/T$.

Table 3
Thermodynamic parameters for phosphate adsorption on PAC sludge

ΔG^0 (kJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol/K)
288 K	298 K	308 K		
−1.08	−3.33	−4.44	63.43	0.224

capacity of PAC sludge. The positive value of ΔS^0 demonstrates the increasing randomness at the solid/solution interface during the adsorption of PO_4^{3-} onto PAC sludge [17,20].

3.4. Effect of pH

The influence of pH to phosphate adsorption by PAC sludge is shown in Fig. 5. As is indicated in this figure, the pH obviously had a significant effect on the adsorption capacity of PAC sludge. Increasing pH from 4 to 9 remarkably decreased the phosphate adsorption capacity from 3.7 to 1.4 mg/g. The ligand exchange between phosphate and hydroxyl ions is broadly recognized to be the most important mechanism of phosphate adsorption onto a hydroxylated mineral surface [12,17,21]. Lower pH values therefore facilitated the release of hydroxyl ions and, subsequently, improved the adsorption capability of PAC sludge. The maximum phosphate removal, as shown in Fig. 5, was obtained at pH 4. Besides, hydroxyl ions in solution competed with phosphate for active sites on the PAC sludge. Higher pH thus hindered the adsorption of phosphate onto PAC sludge. The result that a lower pH is favorable to phosphate adsorption was also reported by Tanada et al. [22], Chubar et al. [23], and Liu et al. [24].

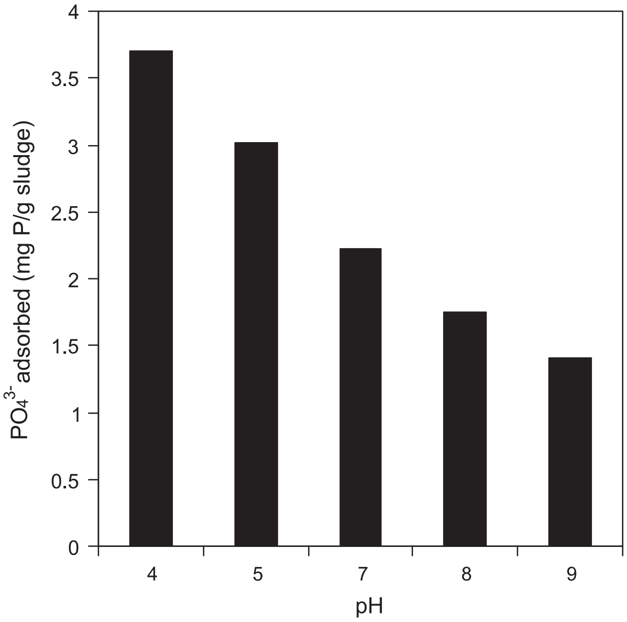

Fig. 5. Effect of pH on phosphate adsorption by PAC sludge.

3.5. Effect of competing anions

Typical municipal wastewater contains various anions. In order to assess their possible interference in the phosphate removal process by PAC sludge, the experiments were performed with solutions containing equal concentrations of various anions to that of phosphates. Experimental results, as are reported in Table 4, revealed that the anions of SO_4^{2-}, Cl^-, HCO_3^-, NO_3^-, and BO_3^- evidently exhibited no harmful effects on the phosphate adsorption process. Phosphate

Table 4
Effect of competing anions on adsorption of PO_4^{3-}

Species	PO_4^{3-} removal percent (%)
PO_4^{3-}	33.5
$PO_4^{3-} + SO_4^{2-}$	33.5
$PO_4^{3-} + Cl^-$	33.8
$PO_4^{3-} + HCO_3^-$	33.5
$PO_4^{3-} + NO_3^-$	34.6
$PO_4^{3-} + BO_3^-$	34.3

removal remained at a constant efficiency of 34% in all cases, meaning that these ions hardly interfered with the adsorption of phosphate on PAC sludge. This result indicates that PAC sludge could selectively adsorb phosphate ions and is suitable for removing phosphate in real wastewater.

3.6. Column adsorption

The breakthrough curves for phosphate adsorption onto PAC sludge at different bed depths (10, 20, and 30 cm) are depicted in Fig. 6. They are done by plotting C_t/C_0 (the ratio of effluent and influent phosphate concentrations) vs. time. The resulting curves obviously follow the typical S-shape profile of column adsorption, as are indicated in Fig. 6. When bed depth expanded, the breakthrough curves shifted from the left to the right and the slope of the curves tilted downward gradually, implying that more PO_4^{3-} ions were removed. The breakthrough time therefore occurred later when bed depth was increased.

The BDST model is generally employed to describe the relationship between the service time and the packed-bed depth of the column. The model is represented as follows [25,26]:

$$t = \frac{N_0 Z}{C_0 F} - \frac{1}{K_a C_0} \ln\left[\frac{C_0}{C_t} - 1\right] \tag{7}$$

where t is the service time (min); N_0 is the adsorptive capacity (mg/L); F is the volume flow rate (mL/cm^2/min); Z is the bed depth (cm); and K_a is the rate constant (L/mg/min).

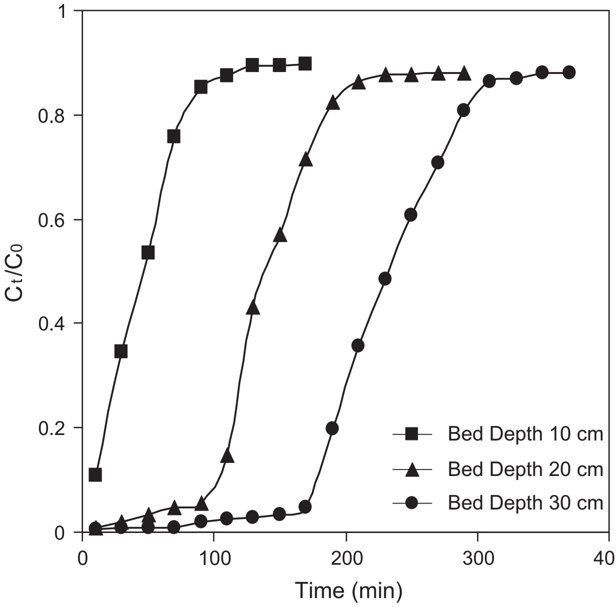

Fig. 6. Breakthrough curves for different bed depths.

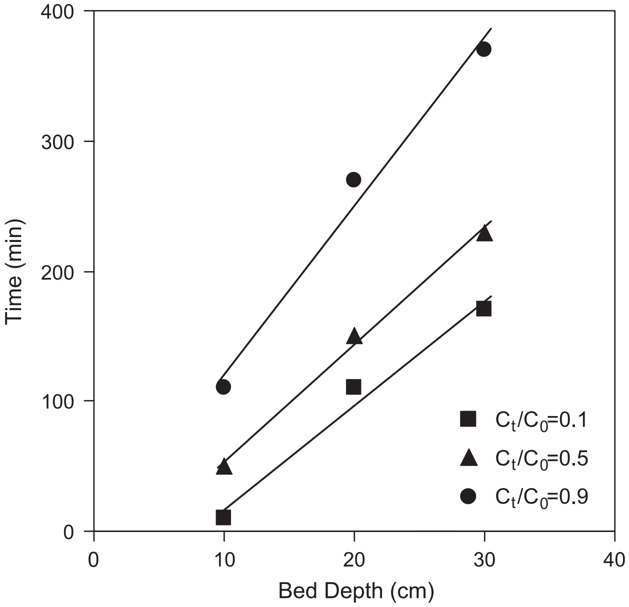

Fig. 7. Service time vs. bed depth for breakthrough at C_t/C_0 ratio 0.1, 0.5, and 0.9.

Fig. 7 depicts the relationship between service time and bed depth for breakthrough at $C_t/C_0 = 0.1$, 0.5, and 0.9. The parameters, N_0 and K_a, can therefore be calculated from the slope and intercept of the graph. The values of the parameters obtained from the graph are summarized in Table 5. As is shown in this table, increasing bed depth raised the values of adsorptive capacity (N_0) and rate constant (K_a). Increasing bed depth provided more time for the phosphate to contact with the PAC sludge and offered more available binding sites for adsorption. Consequently, higher bed depth resulted in superior phosphate uptake. Besides, the coefficients of determination (R^2) in Table 5 were all greater than 0.97, indicating that the experimental data were in good agreement with the BDST model.

Furthermore, acceptable differences were observed between the experimental and the theoretical values in the breakthrough and exhaustion times (Table 5). These results again confirmed that the BDST model was appropriate to describe the column adsorption of phosphate by PAC sludge, and could be successfully used in predicting the breakthrough and exhaustion time.

In addition, the second term of the BDST equation become zero at 50% breakthrough, i.e. $C_t/C_0 = 0.5$. In such a case, Eq. (7) may be simplified as follows:

$$t_{1/2} = \frac{N_0 Z}{C_0 F} \tag{8}$$

Table 5
The calculated constants of BDST model for the phosphate adsorption on PAC sludge at different bed depths

Bed depth (cm)	Breakthrough time[a] (cm)		Exhaustion time[b] (cm)				
	$t_{b(exp)}$	$t_{b(theo)}$	$t_{tot(exp)}$	$t_{tot(theo)}$	N_0 (mg/L)	K_a (mL/mg/min)	R^2
10	10	17	110	120	42.7	0.0080	0.9796
20	110	97	270	250	48.0	0.0130	0.9959
30	170	177	370	380	69.3	0.0478	0.9826

[a] Breakthrough concentration $C_t = 0.1C_0$.
[b] Exhaustion concentration $C_t = 0.9C_0$.

This equation implies that the 50% breakthrough line theoretically must pass through the origin of the graph depicting t vs. Z. However, the straight line of Fig. 7 at 50% breakthrough did not expectedly pass through the origin. According to similar results reported by Jusoh et al. [27], this deviation from the BDST model can possibly have resulted from the fact that the PO_4^{3-} adsorption on PAC sludge was quite complex in real wastewater and more than one rate limiting step was possibly involved.

4. Conclusions

In this study, spent PAC sludge was concluded to exhibit high reuse potential of adsorbing phosphate from real secondary effluent based on the following findings:

(1) The phosphate adsorption onto PAC sludge was rapid in the preliminary reaction stage and the kinetic data followed a pseudo-second-order model.
(2) The experimental results of phosphate adsorption on PAC sludge could be well explained by both the Langmuir and the Freundlich models; nevertheless, the Langmuir isotherm demonstrated more applicability than the Freundlich isotherm.
(3) The process of phosphate adsorption on PAC sludge was spontaneous and endothermic, and the adsorption reaction was favored at lower pH.
(4) PAC sludge could selectively adsorb phosphate ions and competing anions hardly interfered with the phosphate adsorption process.
(5) Phosphate could be successfully removed by PAC sludge through the fixed-bed column adsorption, and the BDST model was appropriate to describe the entire adsorption behavior.

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