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Exploratory study to assess the use of lanthanum-modified chitosan as a potential phosphorous adsorbent

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ABSTRACT

The main objective of this study was to explore the potential of a lanthanum-modified chitosan (La-Ct) as a phosphorus adsorbent and to compare its performance in removing phosphorus from wastewater with an aluminum-modified bentonite adsorbent (Al-Bt). The La-Ct adsorbent was initially prepared as a solution containing 112 mg La/g chitosan to which NaOH was added to form La-Ct flakes, which were collected using a mesh then washed, dried, and used for phosphorus removal. The Al-Bt adsorbent was prepared by adding a solution containing hydroxy-aluminum-polycations to bentonite suspended in distilled water. The resulting modified clay was filtered, washed, dried, and ground to a suitable size. The experimental phosphorus adsorption results for both adsorbents fitted well both, the Freundlich and Langmuir adsorption isotherms, with R^2 values above 0.9. The adsorption capacities reached 10.7 mg P/g for the Al-Bt adsorbent and 17.9 mg P/g for the La-Ct adsorbent. The kinetic study showed that the adsorption rates of the two adsorbents were well represented by the pseudo-second-order kinetic model, with adsorption rate constants of 0.00543 and 0.0021 g/(mg min) for the Al-Bt and La-Ct adsorbents, respectively. The study demonstrated that the La-Ct adsorbent was effective for phosphorus removal and significantly more efficient than the Al-Bt adsorbent.

Keywords: Phosphorus removal; Adsorption; Aluminum-modified clay adsorbent; Lanthanum-modified chitosan adsorbent; Wastewater treatment

1. Introduction

Excess P can be considered as one of the main causes of eutrophication in the receiving water bodies [1]. There are many strategies that can be applied to deal with excessive concentrations of P in water bodies. One of the best approaches is to limit phosphorus inputs into water bodies through source reduction, [2], controlling P-based detergents and domestic food additives [3] and minimizing phosphorus discharges in industrial effluents [4]. Despite all measures for minimizing P loads in wastewater having considerable P loads in wastewater is unavoidable. There are many treatment techniques for P removal such as chemical precipitation, biological removal, ion-exchange, and adsorption [5,6]. There are many. Adsorption of P is one of the techniques that lately started to gain popularity. One of the early P adsorption experiments was the use of alum sludge resulting from drinking water treatment works for removal of P from wastewater [7]. Other studies included adsorption using alumina treated with aluminum sulfate [8] and metal-modified bentonites such as Al, Fe, and La [9–12]. In general, P adsorbents can be classified into three main categories: natural materials, industrial by-products, and man-made products [13]. This study aims to investigate the use of lanthanum-modified chitosan (La-Ct) as an adsorbent for phosphorus removal.

Chitosan is a deacetylated derivative of chitin, a natural polysaccharide available in a wide range of living organisms.

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Recently, chitin and its deacetylated derivative chitosan have gained significant popularity in industrial, pharmaceutical, and environmental applications because they can be commercially extracted from shellfish processing wastes such as shrimp. Chitosan has been used as natural biopolymer in many environmental applications, for example, as a coagulant [14,15], a coagulant aid [16], an adsorbent for metals, and a base for many adsorbents.

Lanthanum is a rare earth element that has high selectivity to phosphorus [17]. Because of its selectivity and affinity to phosphorus, lanthanum has been used in the preparation of many adsorbents for phosphorous removal from water and wastewater. Lanthanum oxide was used in preparing activated carbon fibers loaded with La for phosphorus removal as it was found that this novel adsorbent could remove up to 97.5% of phosphorus in the solution [18]. Similarly, lanthanum oxide was used to modify natural zeolite for the preparation of La-zeolite adsorbent, which showed high removal efficiency and high regeneration potential. Regeneration experiments showed that adsorption capacity of the regenerated adsorbent never fell below 90% of the fresh adsorbent [19]. Lanthanum-modified bentonite (Phoslock®, Sydney, Australia) was also used for removal of phosphorous from water. Phoslock® was developed in the early 1990s by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia. Since the introduction of Phoslock®, many studies confirmed its phosphorous removal efficiency [20,21]. Incorporation of lanthanum into clay structures, such as bentonite, can result in a stable adsorbents in which La is locked inside the clay structure which minimizes the possibility of La leaching to water. Accordingly incorporation of lanthanum into clay structure, such as the case of Phoslock®, is considered to be environmentally safe [22].

Many phosphorous removal studies have been conducted using metal-based bentonite adsorbents [9–11]. In this study, aluminum-modified bentonite (Al-Bt) was chosen as a control to compare its performance with the La-Ct adsorbent proposed in this study. No previous studies have investigated the use of La-Ct preparations for removal of phosphorus from water; however, previous studies investigated the use of La-Ct for removal of fluoride from water [23]. This study aims at investigating the efficiency of a proposed La-Ct adsorbent to remove phosphorus from water compared with an Al-Bt adsorbent.

2. Material and methods

2.1. Preparation of La-Ct

La-Ct was prepared according to the method described by Bansiwal et al. [24]. In a beaker, 20 g of $LaCl_3{\cdot}7H_2O$ was dissolved in 100 mL distilled water and in another beaker, 2 g of chitosan (medium molecular weight from Aldrich Cat No. 448877) was dissolved in 100 mL acetic acid (CH_3COOH) solution (1%, v/v). The two solutions were then mixed at a ratio of 1.5 mL lanthanum chloride solution to 50 mL chitosan solution, which is equivalent to 112 mg of La per gram of chitosan. The resulting La-Ct mixture was stirred with a magnetic stirrer for 3 h to ensure La adsorption onto chitosan. The mixed La-Ct solution was then added dropwise to a 6 N NaOH solution under vigorous stirring and the resulting mixtures were allowed to stabilize overnight. After stabilization, the mixture was screened using 65 μm screen to separate the La-Ct flakes. The separated flakes were washed with distilled water and dried in the oven at 60°C. After drying, the flakes were ground to a uniform size ranging from 75 to 150 μm.

2.2. Preparation of Al-Bt

In preparing the Al-Bt adsorbent, a hydroxy-aluminum-polycations pillaring solution was prepared by adding 300 mL of 1 M Na_2CO_3 dropwise to 500 mL 0.5 M $AlCl_3{\cdot}6H_2O$ solution at 60°, which corresponds to [OH]:[Al] molar ratio of 2.4. A 250 mL of the aluminum pillaring solution was then added to 10 g of presoaked Bentonite clay (Poudrszan Industrial and Mineral Group, Dubai, United Arab Emirates), with the resulting mixture completed to 1 L with distilled water. The addition of pillaring solution resulted in an overall [Al]/bentonite ratio of 7.8 mmol Al per gram of bentonite. After the addition of the pillaring solution to the bentonite clay, the content was mixed overnight, then filtered and washed with deionized water several times to get rid of chlorides. The presence of chlorides was tested in the separated wash water using an 0.1 N silver nitrate indicator solution. The prepared Al-Bt adsorbent was dried at 105°C and ground to a uniform size in the range of 75–150 μm.

2.3. Phosphate adsorption experiments

The efficiency of phosphate removal using the Al-Bt and the La-Ct adsorbents was measured experimentally using 50 mL of different initial phosphate concentrations ranging from 10 to 50 mg/L treated with 0.1 g of the two adsorbents. The initial pH was adjusted at 5. The adsorption experiments were conducted over a period of 9 h using a lab-line thermal shaker (Model No. 3527-6) at 200 rpm and 25°C. At the end of the experiments, the residual phosphate concentrations in the different flasks were measured according to standard methods for the examination of water and wastewater (Ascorbic Acid Method 4500-P). The phosphate adsorption kinetic experiments were performed using a 50 mL of 20 mg/L phosphate solution at pH 5 treated with 0.1 g adsorbents over a period of 6 h, with the residual phosphate concentrations measured in the different flasks at various time intervals.

3. Results and discussions

3.1. Phosphate adsorption isotherms

To compare the adsorption efficiency of the two adsorbents used in this study, the experimental phosphate adsorption results were fitted using the Langmuir and Freundlich isotherms, which are expressed in Eqs. (1) and (2):

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

$$Q_e = K_f C_e^{1/n} \tag{2}$$

As shown in Eqs. (1) and (2), the Q_e is the equilibrium adsorption capacity expressed in mg P per g of adsorbent used;

C_e represents the residual phosphorus concentration at equilibrium (mg/L); Q_m is the Langmuir theoretical maximum adsorption capacity, expressed in mg P per gram of adsorbent used; K_L is the Langmuir equation constant; and the K_f and n are the Freundlich equation constants.

To graphically present the Langmuir and Freundlich isotherms, the linear forms should be used. The linear forms of Langmuir and Freundlich equations can be expressed as shown in Eqs. (3) and (4):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \tag{3}$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

The phosphate adsorption isotherms of the two adsorbents are presented in Fig. 1. The experimental adsorption data were fitted to the linear forms of the Langmuir and Freundlich models (Eqs. (3) and (4), respectively), and the isotherms parameters were estimated, as presented in Table 1.

The obtained correlation coefficient (R^2) values suggest that the data were adequately fitted by the two isotherm models. In both models, the R^2 values were greater than 0.95, which agrees with earlier reported results for most phosphate adsorbents. As shown in Table 1, the Q_m values were 17.86 mg/g for the La-Ct adsorbent and 10.65 mg/g for the Al-Bt adsorbent. Apparently from the Q_m values, the La-Ct adsorbent achieved greater adsorption capacity than the Al-Bt adsorbent.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a number of active sites with a uniform adsorption power. Based on this assumption, once the active sites are filled, no further adsorption can take place at the adsorbent surface, which reaches a state of saturation and achieves the maximum adsorption capacity [25]. For Freundlich isotherm, the K_f and $1/n$ values reflect the adsorption capacity and adsorption intensity, respectively. The $1/n$ value reflects the heterogeneity factor. For efficient adsorbents the value of $1/n$ ranges from 0 to 1 [11], with $1/n$ values greater than one indicating chemical-based adsorption and $1/n$ values less than one reflecting physical adsorption. The values of K_f for the two adsorbents were 9.27 and 5.1, respectively, indicating higher adsorption capacity for the La-Ct adsorbent compared with the Al-Bt adsorbent. For both adsorbents, then $1/n$ values were less than 1 suggesting physical adsorption.

Table 1
Langmuir and Freundlich adsorption constant for La-Ct and Al-Bt adsorbents

Adsorbent	Langmuir			Freundlich		
	K_L	Q_m	R^2	$1/n$	K_f	R^2
La-Ct	0.851	17.86	0.98	0.199	9.27	0.95
Al-Bt	0.83	10.65	0.99	0.247	5.1	0.99

3.2. Effect of pH

The effect of pH on phosphate adsorption was studied over a pH range 5–8. This range was chosen because it covers the practical pH range for waters and wastewaters. The experiments were carried out using a 10 mg P/L solution and an adsorbent dose of 2 g/L with the initial pH adjusted to the desired value using 0.1 N NaOH solution. As shown in Fig. 2, the phosphate adsorption capacity of both adsorbents generally decreased as the pH increased. The decrease in the phosphate adsorption capacity is insignificant when pH changed from 5 to 6; however, the impact of pH was more significant at pH values greater than 6.

3.3. Phosphate adsorption kinetics

As shown in Fig. 3, the equilibrium adsorption capacity of the La-Ct adsorbent was significantly higher than that of the Al-Bt adsorbent. The data show that about 75% and 90%

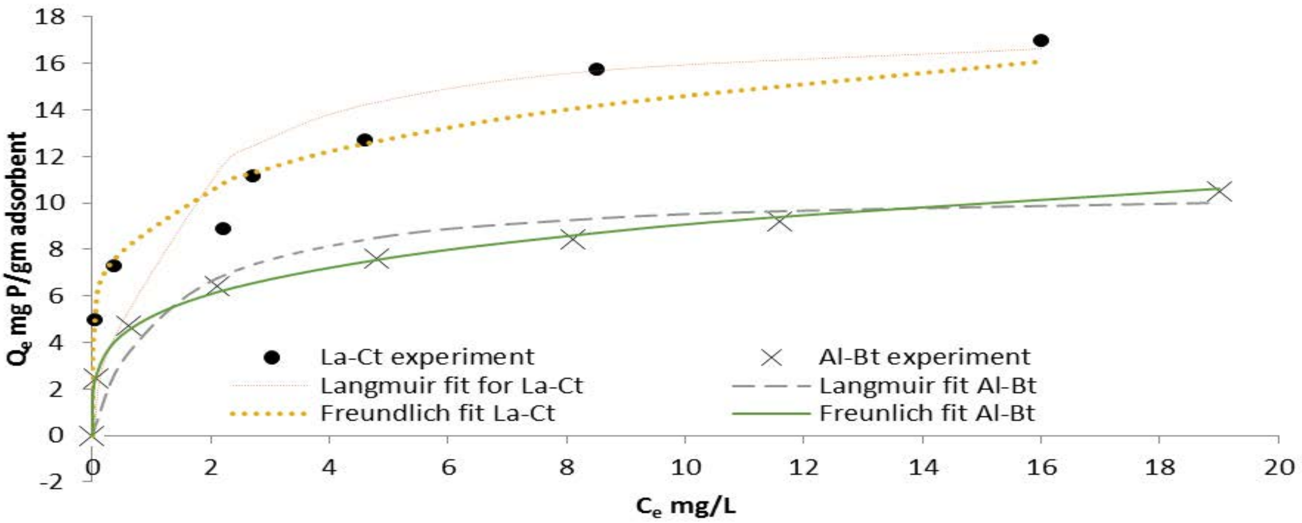

Fig. 1. Phosphorus adsorption isotherm for the La-Ct and Al-Bt adsorbents fitted to the Langmuir and Freundlich isotherms.

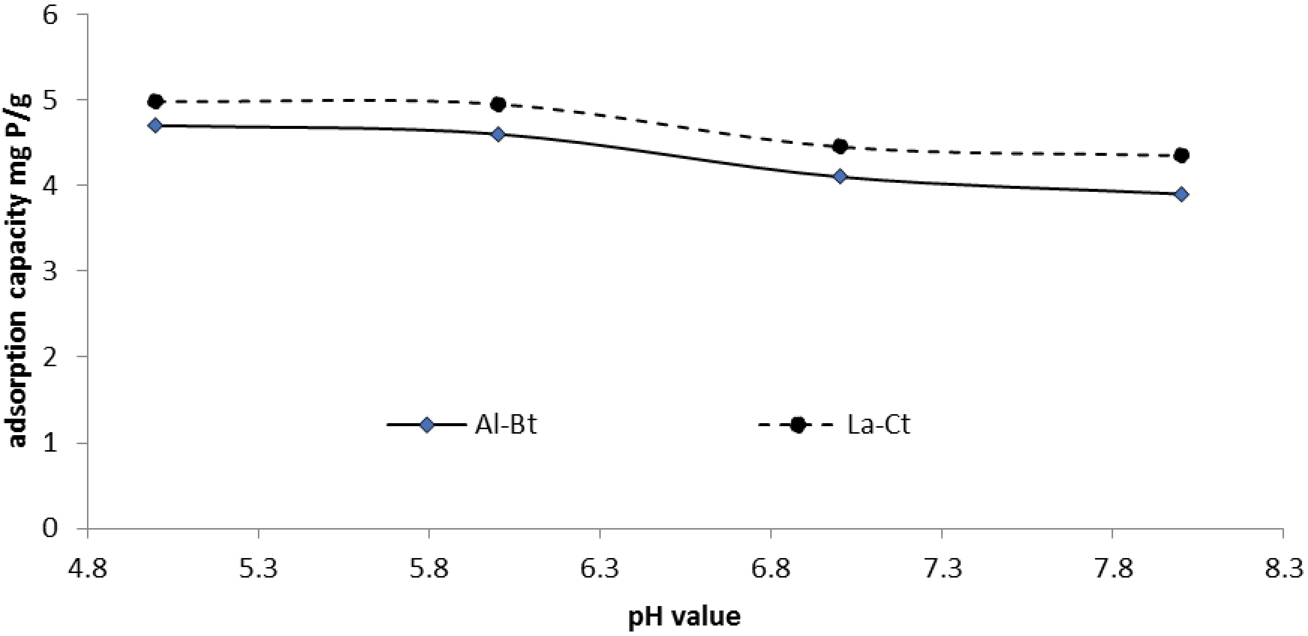

Fig. 2. Change of adsorption capacity of both adsorbents at a pH range from 5 to 8.

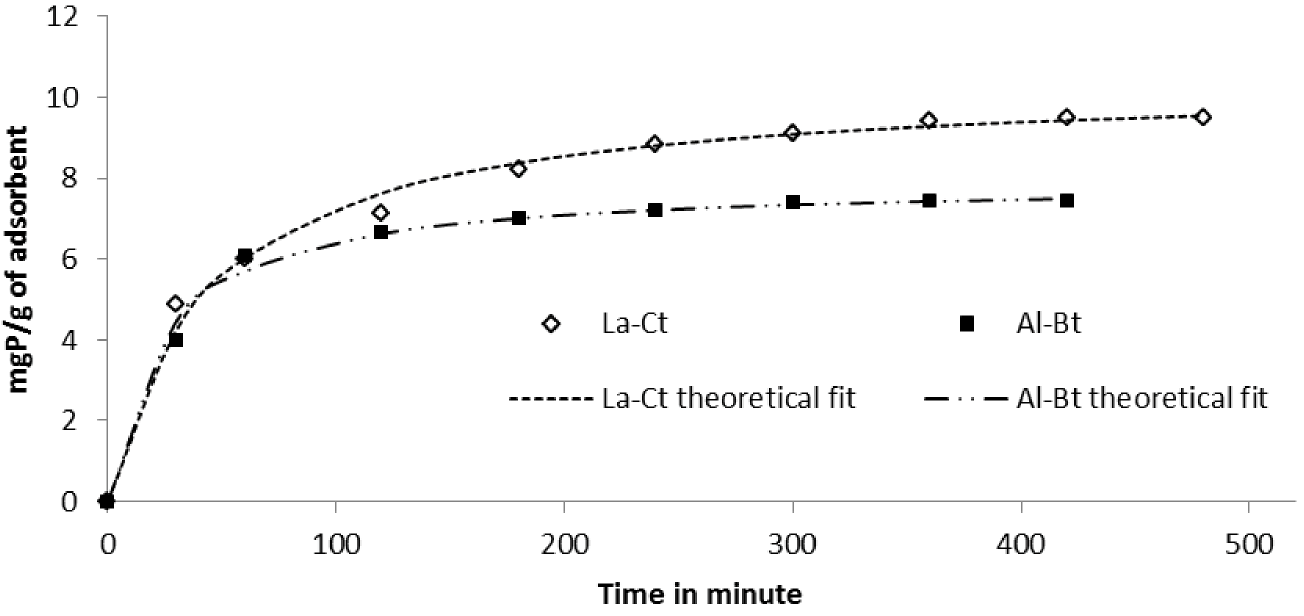

Fig. 3. Kinetics of phosphate adsorption onto the two adsorbents fitting with the theoretical pseudo-second-order kinetic equation.

of the maximum adsorption capacities of the two adsorbents were reached in the first 2 h of adsorption. In case of the Al-Bt adsorbent, equilibrium was virtually reached within the first 4 h, however, the La-Ct adsorbent took a longer time to reach equilibrium. The kinetic adsorption results were consistent with results reported in previous studies in which equilibrium was reached within 3–8 h [9,26]. The kinetic adsorption data were fitted with the linear forms of the pseudo-first-order and pseudo-second-order reaction rate models, which are described in Eqs. (5) and (6) as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_t = phosphorus adsorbed (mg P/g adsorbent) at time t (minutes); q_e = phosphorus adsorbed in mg P/g adsorbent at equilibrium; k_1 = pseudo-first-order rate constant (min^{-1}), and k_2 = pseudo-second-order rate constant in g/(mg min).

The kinetic parameters for the pseudo-first-order and pseudo-second-order kinetic models are presented in Table 2 and Figs. 4(a) and (b). With regards to the R^2 values, it is clear that the experimental data fitted both the pseudo-first-order and pseudo-second-order for the La-Ct adsorbent; however, the data only fitted the pseudo-second-order adsorption for the Al-Bt adsorbent. However, despite the La-Ct data fitting both kinetic models, the pseudo-second-order model gave a value for q_e that is closer to the experimentally observed value than the pseudo-first-order model. This finding is in accordance with many other studies that reported that phosphate adsorption fits better with pseudo-second-order kinetics more than the pseudo-first-order kinetics.

3.4. Adsorption mechanism

Previous studies on Al-Bt suggested that the underlying phosphate adsorption mechanism is an ion-exchange mechanism with the OH^- functional surface group. On the other hand, there is limited information about the phosphorus adsorption mechanism by La-Ct adsorbent. As shown in Fig. 2, both adsorbents showed high removal efficiency at pH 5 and the removal efficiency decreased with increasing pH to 8, which supports the OH^- exchange mechanism. Kamble et al. [23] studied the adsorption of fluoride on La-Ct adsorbent and their study concluded that fluoride adsorption could be explained in terms of ligand exchange mechanism between fluoride ion and hydroxide ion coordinated on lanthanum immobilized on chitosan. This can be simplified by the following reactions [23]:

$$\mathrm{Ct-NH_3-La\,(H_2O)_n^{2+} \leftrightarrow Ct-NH_3-La\,(H_2O)_{n-1}\,OH^+ + H^+}$$

$$\mathrm{Ct-NH_3-La\,(H_2O)_{n-1}\,OH^+ + A^- \leftrightarrow Ct-NH_3-La\,(H_2O)_{n-1}\,A^+ + OH^-}$$

where Ct is chitosan and A^- is any anion, such as fluoride or phosphate anion. The authors believe that phosphate adsorption onto La-Ct follows the same mechanism of fluoride adsorption explained by Kamble et al. [23]. Similarly, the Al-Bt adsorption can be explained by the following simplified exchange mechanism where the phosphate anion exchanges with the OH^- functional groups on the adsorbent surfaces. The ion exchange mechanism can be represented by the following simplified reactions:

$$\mathrm{Bt-Al\,(H_2O)_n^{2+} \leftrightarrow Bt-Al-(H_2O)_{n-1}\,OH^+ + H^+}$$

$$\mathrm{Bt-Al-(H_2O)_{n-1}\,OH^+ + A^- \leftrightarrow Bt-Al-(H_2O)_{n-1}\,A^+ + OH^-}$$

where Bt is bentonite and A^- refers to anions.

In general, the dependence of phosphorus adsorption on pH suggests that adsorption is due to OH^- group exchange, as indicated by similar phosphorus adsorption trends observed with pH change in the range of 5–8 in Fig. 2.

3.5. Regeneration of the adsorbents

As shown in Fig. 2, there was an overall reduction in the adsorption capacity of both adsorbents due to pH increase.

Table 2
Parameters of the pseudo-first-order and pseudo-second-order kinetic models for phosphate adsorption removal using the two adsorbents shown in Fig. 4

Pseudo-first-order			Pseudo-second-order			Experimental value
K_1	q_e	R^2	K_2	q_e	R^2	$q_{e\,\mathrm{exp}}$
0.0093	6.73	0.985	0.002188	10.42	0.999	9.5
0.002	4.23	0.751	0.005427	7.9	0.999	7.45

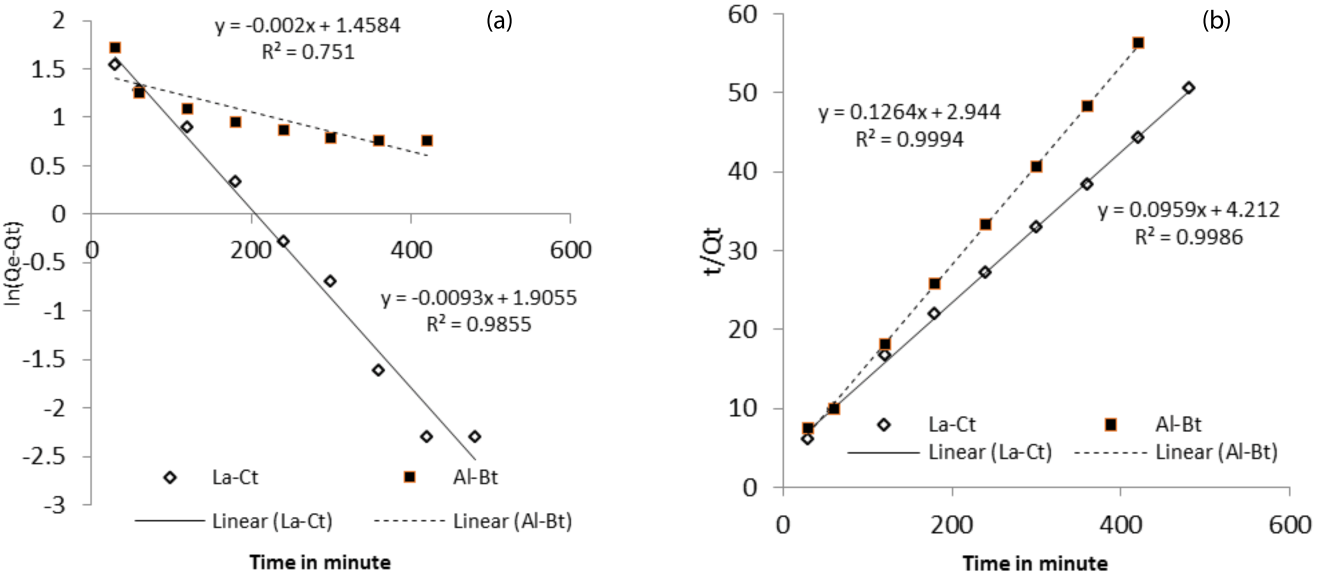

Fig. 4. Phosphate adsorption kinetics of the La-Ct and Al-Bt adsorbents: (a) data fitted to the pseudo-first-order reaction rate model, and (b) data fitted to the pseudo-second-order reaction rate model.

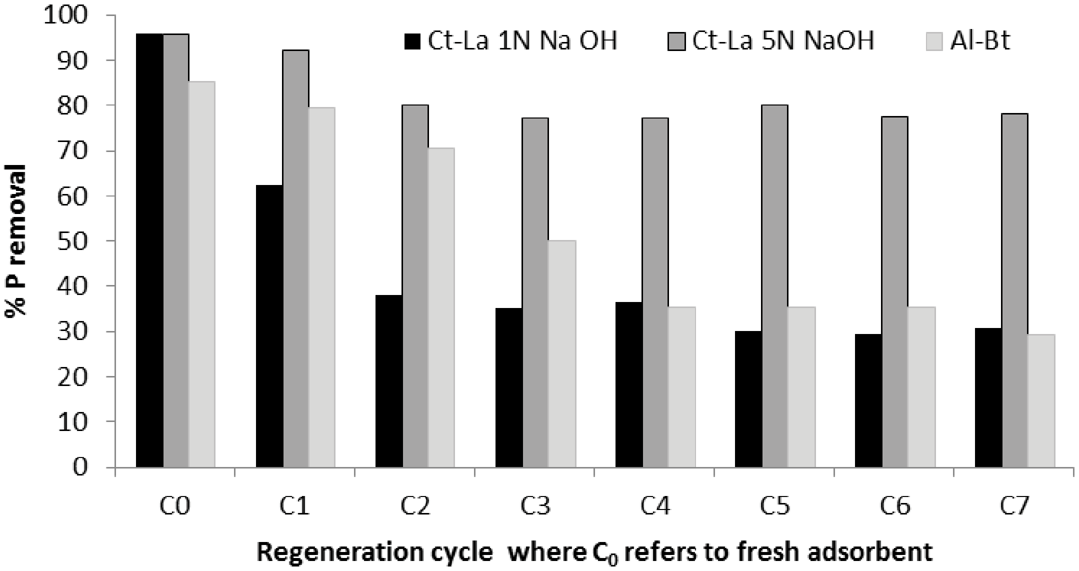

Fig. 5. Performance of La-Ct versus Al-Bt over seven cycles of regeneration.

Furthermore as discussed earlier, the phosphate adsorption mechanism is more likely an ion exchange mechanism with the OH^- functional surface group. Accordingly, regeneration could be achievable through increasing the concentration of OH^- in solution. The data in Fig. 5 show the performance of La-Ct and Al-Bt over seven regeneration cycles. Aluminum bentonite was regenerated using 0.05 M NaOH solution to maintain the pH of the solution in the range of 9–9.5 as it was observed that at higher pH values the physical consistency of the Al-Bt adsorbent was compromised. This observation is consistent with findings reported previous studies [27] on the stability of bentonite structure at extreme pH values, which may result in mobilizing the silica and alumina in clay structure. In contrast, the La-Ct adsorbent was stable at high pH and accordingly, 1 and 5 N NaOH solutions were used for regeneration. In case of Al-Bt adsorbent, the efficiency of phosphorus removal dropped from 85% for fresh adsorbent to 50% after the third generation cycle, and then significantly dropped to 29% in the seventh regeneration cycle. Moreover, the amount of modified bentonite recovered after repeated regeneration decreased due to loss of the adsorbent during regeneration. On the other hand for the La-Ct adsorbent, regenerated using 1 N NaOH was not efficient and the efficiency dropped from 95% for fresh adsorbent to 62% and 38% in the first and second regeneration cycles. However, improved results were achieved using 5 N NaOH for regeneration, with the efficiency dropping from 95% for fresh adsorbent to 78% after the seventh regeneration cycle. Therefore, it may be concluded that the La-Ct adsorbent had higher reuse potential compared with the Al-Bt adsorbent due to its stability during regeneration at high pH.

4. Conclusions

This study concludes that the La-Ct adsorbent is a promising adsorbent that can be used for removal of phosphates from water and wastewater. The study showed that the La-Ct adsorbent was significantly more efficient than the Al-Bt adsorbent. Comparison of the two adsorbents showed that the adsorption capacities for Al-Bt and La-Ct adsorbents were 10.71 and 17.9 mg P/g, respectively. Kinetic studies showed that the two adsorbents were well presented by the pseudo-second-order kinetics model, with the reaction rate constants equal to 0.00543 g/(mg min) for the Al-Bt adsorbent and 0.0021 g/(mg min) for La-Ct adsorbent. The adsorption capacities of both adsorbents declined as the pH increased from 5 to 8. Further studies should be conducted to assess the impact of competing anions found on waters and wastewaters on phosphate removal using the La-Ct adsorbent.

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