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Phosphorous adsorption using Al^{3+}/Fe^{3+}-modified bentonite adsorbents—effect of Al^{3+} and Fe^{3+} combinations

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ABSTRACT

This study focused on assessing the impact of using a variety of Al^{3+} and Fe^{3+} combinations to prepare modified bentonite adsorbents to remove phosphorous from water. Eight adsorbents with various Al^{3+} and Fe^{3+} combinations were used; four where prepared by adding Al^{3+} then Fe^{3+} to the bentonite, and four were prepared by adding Fe^{3+} then Al^{3+} to the bentonite. The adsorption capacities and kinetics of the eight adsorbents were experimentally assessed and compared. The experimental results best fitted the Langmuir adsorption isotherm model and the kinetic data best fitted the pseudo-second-order kinetic model. The Langmuir maximum adsorption capacities of the various adsorbents were in the range of 5.6–11.3 mg P/g adsorbent. The results suggested that combining Al^{3+} and Fe^{3+} in preparing the adsorbents improved the adsorption capacity and adsorption rate compared to using Al^{3+} alone or Fe^{3+} alone. Furthermore, equal amounts of Al^{3+} and Fe^{3+} resulted in the maximum phosphorous adsorption capacities. Adding Al^{3+} then Fe^{3+} to the bentonite resulted in adsorbents with higher adsorption capacities and adsorption rates compared to adding Al^{3+} then Fe^{3+} to the bentonite. The adsorbent prepared using Fe^{3+} alone achieved higher adsorption capacity and adsorption rate than the adsorbent prepared using Al^{3+} alone, which achieved the least adsorption capacity among all adsorbents. The results confirmed that using Al^{3+} and Fe^{3+} to modify bentonite and produce phosphorus adsorbents is technically feasible and is subject to optimization.

Keywords: Phosphorus removal; Al^{3+}/Fe^{3+}-modified bentonite; Adsorption; Adsorption capacity; Adsorption rate

1. Introduction

Phosphorous enters the water environment from a variety of sources, including the following: waste from living organisms; fertilizer runoff; human-made products and wastes; and phosphorus-containing soils. Excessive phosphorus in water can cause serious environmental problems related to eutrophication. Various phosphorous control strategies have been used to reduce contamination of water bodies with phosphorous, including phosphorus removal from wastewater discharges. Phosphorous removal methods from wastewater include ion exchange, chemical precipitation, enhanced biological phosphorus removal, and

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adsorption. A variety of low-cost or readily available materials and by-products have been used as phosphorous adsorbents [1–17]. This study is focused on phosphorous removal from water using modified clay adsorbents prepared by adding a variety of Al^{3+} and Fe^{3+} combinations to bentonite.

Bentonite clay is typically incapable of significant phosphate adsorption [1]. However, modifying bentonite through incorporating Fe^{3+} or Al^{3+} polycations as pillars between bentonite sheets significantly improves phosphorous adsorption. Incorporating Al^{3+} or Fe^{3+} pillars between clay sheets, which is called pillaring, increases the specific area and enhances permanent porosity as Al^{3+} and Fe^{3+} act as pillars between the layers of clay leaving ample voids between the pillars [18–21]. The phosphorus removal mechanism of metal-modified clay adsorbents is ion exchange, whereby $H_2PO_4^-$ exchanges the OH^- functional groups on the adsorbent surfaces. The ion exchange mechanism is typically represented by the simplified reaction: $\text{Clay–Metal} \equiv \text{OH} + H_2PO_4^- \Leftrightarrow \text{Clay–Metal} \equiv H_2PO_4 + OH^-$. The ion exchange mechanism is manifested by the increase in metal-OH surface bonds and corresponding increase in OH^- concentration in solution following phosphate adsorption [2,4]. Furthermore, phosphorus adsorption is pH-dependent due to speciation of phosphoric acid and pH-dependent functional groups on the surfaces of modified clay adsorbents, with optimum adsorption typically achieved at pH values below 6 [1,2,4].

Previous studies [1–6] evaluated the effectiveness of Al^{3+}- and Fe^{3+}-modified clays to remove phosphorous from water. However, available studies did not adequately address the impact of combining Al^{3+} and Fe^{3+} in preparing modified clays on phosphorous adsorption. Therefore, this study was conducted to assess and compare the performance of modified clays prepared using Al^{3+} alone, Fe^{3+} alone and combinations of Al^{3+} and Fe^{3+} in terms of phosphorous adsorption capacity and adsorption rate.

2. Materials and methods

The bentonite clay used in the study was obtained from a local supplier (Poudrszan Industrial and Mineral Group, Dubai, United Arab Emirates) in Dubai, United Arab Emirates. The preparation of the modified bentonite adsorbents followed previously reported procedures [1,4,10,19,20]. Two chemical solutions were used to prepare the modified bentonite adsorbents; Al^{3+} solution and Fe^{3+} solution. The Al^{3+} solution was prepared by mixing 300 mL 1 M Na_2CO_3 solution and 500 mL 0.5 M $AlCl_3{\cdot}6H_2O$ solution to obtain a mixture with [OH]:[Al] molar ratio of 2.4. The Fe^{3+} solution was also prepared by mixing 100 mL 1 M Na_2CO_3 and 500 mL 0.2 M $FeCl_3{\cdot}6H_2O$ to produce a mixture with [OH]:[Fe] molar ratio of 2.0. The modified adsorbents were prepared by mixing bentonite samples that were allowed to swell for 24 h with combinations of the Al^{3+} solution and Fe^{3+} solution to produce adsorbents with nominal $Al^{3+} + Fe^{3+}$ content of 10 mmol/g dry bentonite (Table 1). After mixing with metals, the modified bentonite samples were thoroughly washed with deionized water and centrifuged several times until their supernatants were free of chloride, as indicated by adding silver nitrate to the separated wash water. Following washing, the prepared adsorbents were dried at 105˚C for 24 h, ground using a ball mill then sieved. The experiments reported in this study were conducted using modified clays with particles sizes ranging from 75 to 150 μm.

Two sets of modified bentonite adsorbents were prepared; the first set was prepared by adding the Al^{3+} solution first to the bentonite then the Fe^{3+} solution (labeled as Al/Fe in Table 1) according to the ratios stated in Table 1. The second set was prepared by adding the Fe^{3+} solution first to the bentonite then the Al^{3+} solution (labeled as Fe/Al in Table 1).

The phosphate adsorption experiments were conducted in conical Erlenmeyer flasks filled with 50 mL of different concentrations (10–50 mg/L) synthetic phosphate solutions and 0.1 g bentonite adsorbents at pH 5. Mixing was achieved using a Lab-Line thermal shaker (Model No. 3527-6) for 9 h at 200 rpm and 25˚C. Following mixing, the suspensions were filtered, and the remaining concentrations of PO_4-P were measured in the supernatants using the ascorbic acid standard method [22]. The phosphate adsorption kinetic experiments were conducted using flasks filled with 50 mL of 20 mg/L phosphorus solution and 0.1 g adsorbents at pH 5. The experiments were stopped following predetermined mixing times, and the residual phosphate concentrations in the supernatants were measured.

3. Results and discussion

3.1. Adsorption capacity

The experimental phosphate adsorption results were represented using the Freundlich, Langmuir, and Temkin isotherm models, which are shown in Eqs. (1)–(3). The linear forms of the Freundlich and Langmuir models are presented in Eqs. (4) and (5):

$$Q_e = K_f C_e^{1/n} \quad (1)$$

Table 1
Combinations and order of Al^{3+} and Fe^{3+} added to bentonite to prepare the adsorbents

Metal mixed first with bentonite	Adsorbent label	Al^{3+} (mmol/g)	Fe^{3+} (mmol/g)	$Al^{3+} + Fe^{3+}$ (mmol/g)
Al^{3+} solution	Al/Fe 25/50	2.50	7.48	9.98
Al^{3+} solution	Al/Fe 50/50	4.99	4.99	9.98
Al^{3+} solution	Al/Fe 75/25	7.49	2.49	9.98
Al^{3+} solution	Al/Fe 100/0	9.98	0	9.98
Fe^{3+} solution	Fe/Al 25/75	7.48	4.99	9.98
Fe^{3+} solution	Fe/Al 50/50	4.99	7.49	9.98
Fe^{3+} solution	Fe/Al 75/50	2.49	9.98	9.98
Fe^{3+} solution	Fe/Al 100/0	0	9.98	9.98

$$Q_e = \frac{Q_m k_L C_e}{1 + K_L C_e} \tag{2}$$

$$Q_e = A + B \ln C_e \tag{3}$$

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

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \tag{5}$$

where Q_e = equilibrium adsorption capacity (mg P/g adsorbent); C_e = remaining P concentration in solution at equilibrium (mg/L); K_f and n = Freundlich isotherm constants; Q_m = Langmuir theoretical maximum adsorption capacity (mg P/g adsorbent); K_L = Langmuir isotherm constant (L/mg); and A and B = Temkin isotherm constants.

The adsorption results of the different adsorbents are presented in Fig. 1 fitted with the Langmuir isotherm model. Among the three adsorption models, only the Langmuir isotherm consistently provided the best fit of the experimental data, with R^2 values in the range of 0.96–1.00 (Table 2). The Freundlich and Temkin isotherm models also adequately fitted the data, with R^2 values in the range of 0.63–0.96. The parameters of the three isotherm models are listed in Table 2. The Langmuir model assumes uniform energies of adsorption for a mono-surface layer of identical adsorption sites. The fact that the Langmuir model best fitted the experimental data is consistent with previously reported results [1,4,10] and indicates ion exchange as the main adsorption mechanism. The isotherms in Fig. 1 generally suggest that the adsorbents prepared by adding Al^{3+} first then Fe^{3+} to the bentonite achieved higher adsorption capacities than the adsorbents prepared by adding Fe^{3+} first then Al^{3+}.

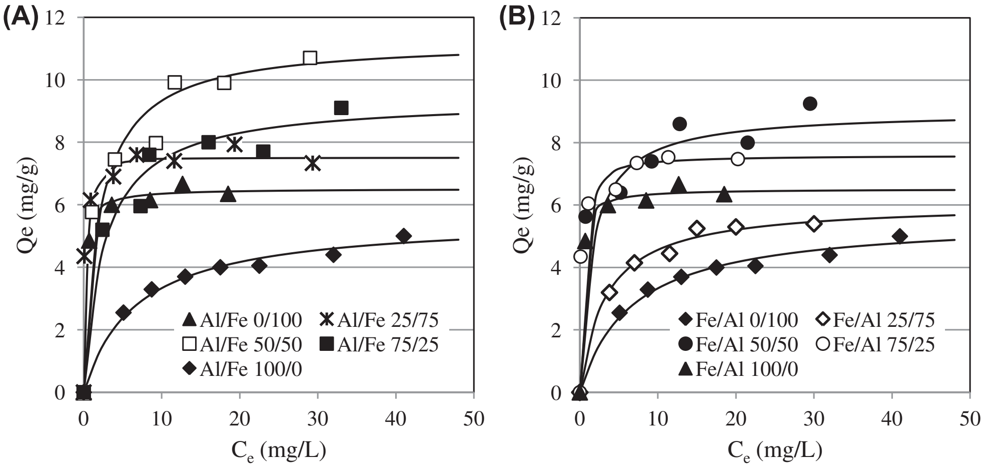

Fig. 1. Isotherms of the different adsorbents fitted with Langmuir adsorption equation: (A) adsorbents prepared by adding Al^{3+} first then Fe^{3+} to the bentonite in preparing the clay and (B) adsorbents prepared by adding Fe^{3+} first then Al^{3+} to the bentonite.

Table 2
Parameters of the Langmuir, Freundlich, and Temkin adsorption isotherms

	Langmuir			Freundlich			Temkin		
Adsorbent	K_L	Q_m	R^2	$1/n$	K_f	R^2	A	B	R^2
Al/Fe 25/75	18.75	7.5	1.00	0.10	5.87	0.90	−4.07	0.68	0.91
Al/Fe 50/50	0.48	11.3	0.99	0.21	5.54	0.94	−0.95	0.21	0.88
Al/Fe 75/25	0.38	9.9	0.98	0.22	4.32	0.78	−0.40	0.19	0.74
Al/Fe 100/0	0.15	5.6	0.99	0.29	1.68	0.96	−0.32	0.40	0.97
Fe/Al 25/75	0.30	6.1	1.00	0.27	2.32	0.94	−0.42	0.32	0.93
Fe/Al 50/50	0.63	9.0	0.96	0.16	5.47	0.72	−0.81	0.23	0.63
Fe/Al 75/25	3.33	7.6	1.00	0.11	5.72	0.96	−3.46	0.60	0.94
Fe/Al 100/0	3.91	6.5	1.00	0.08	5.16	0.90	−3.92	0.77	0.90

The Langmuir theoretical maximum adsorption capacities, as indicated by Q_m, of the different adsorbents are compared in Table 2 and Fig. 2. The data show that the maximum Q_m values were for the Al/Fe 50/50 adsorbent (Fig. 1(A)) and for the Fe/Al 50/50 adsorbent (Fig. 1(B)). The minimum Q_m value was for the Al/Fe 100/0. The order of Q_m for the adsorbents to which Al^{3+} was added first was as follows: Al/Fe 50/50 > Al/Fe 75/25 > Al/Fe 25/75 > Al/Fe 0/100 > Al/Fe 100/0. The order of Q_m for the adsorbents to which Fe^{3+} was added first was as follows: Fe/Al 50/50 > Fe/Al 75/25 > Fe/Al 100/0, Fe/Al 25/75 > Fe/Al 0/100. Overall, the order of the Q_m values was as follows: Al/Fe 50/50 > Al/Fe 75/25 > Fe/Al 50/50 > Fe/Al 75/25 > Al/Fe 25/75 > Fe/Al 100/0 > Fe/Al 25/75 > Al/Fe 100/0. The results suggest that combining Fe^{3+} and Al^{3+} improves the adsorption capacity and that equal amount of Fe^{3+} and Al^{3+} result in the maximum adsorption capacity. The results show that Q_m increased as Al^{3+} or Fe^{3+} increased up to 50% then decreased as Al^{3+} or Fe^{3+} increased above 50%. The results also show that adsorbents prepared by adding Al^{3+} first then Fe^{3+} achieved higher Q_m values than adsorbents prepared by adding Fe^{3+} first then Al^{3+}. On the other hand, the adsorbent prepared using Fe^{3+} alone achieved a higher adsorption capacity (Q_m = 6.5 mg/g for Fe/Al 100/0) than the adsorbent prepared using Al^{3+} alone (Q_m = 5.6 mg/g for Al/Fe 100/0).

3.2. Adsorption kinetics

The kinetic adsorption results were fitted with pseudo-first-order and pseudo-second-order reaction rate models, which are described in Eqs. (6) and (7). The linear forms of the pseudo-first-order rate and pseudo-second-order rate models are presented in Eqs. (8) and (9), respectively. The initial pseudo-second-order adsorption rate can be approximated by from Eq. (8) when t approaches zero (i.e. q_t

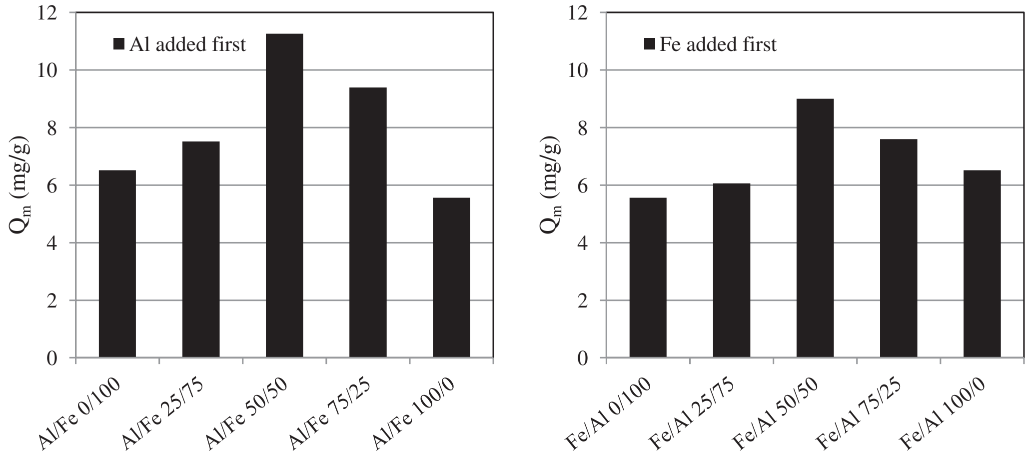

Fig. 2. Comparison of the maximum Langmuir phosphorus adsorption capacities (Q_m) of the prepared adsorbents.

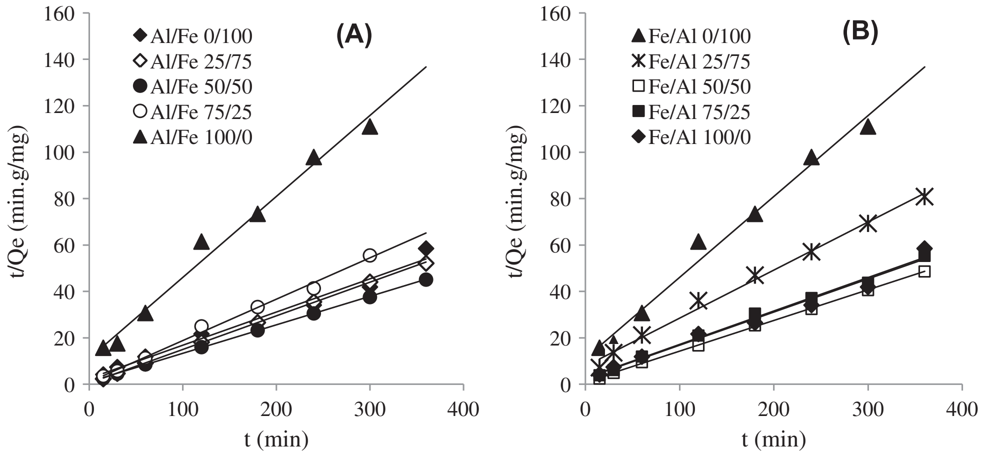

Fig. 3. Linear form of the pseudo-second-order reaction rate model applied to the phosphate adsorption kinetic data obtained using the various adsorbents (A) Al added first and (B) Fe added first.

approaches zero and $q_e - q_t$ approaches q_e). The initial adsorption rate is presented in Eq. (10):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

$$\log\frac{(q_e - q_t)}{q_e} = -k_1 t \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{9}$$

$$\frac{dq_t}{dt} = k_2 q_e^2 \tag{10}$$

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

Table 3
Parameters of the pseudo-second-order kinetic models for the various adsorbents

Adsorbent	k_2	q_e	$k_2q_e^2$ (initial rate)	R^2
Al/Fe 25/75	0.026	6.9	1.25	1.00
Al/Fe 50/50	0.014	8.2	0.94	1.00
Al/Fe 75/25	0.029	5.6	0.92	0.99
Al/Fe 100/0	0.011	3.0	0.09	0.99
Fe/Al 25/75	0.005	4.8	0.13	0.99
Fe/Al 50/50	0.017	7.6	0.96	1.00
Fe/Al 75/25	0.008	6.9	0.37	1.00
Fe/Al 100/0	0.008	7.0	0.40	0.98

Among the two kinetic models, the pseudo-second-order rate model best fitted the experimental data and gave R^2 values above 0.98 (Fig. 3 and Table 3) for all adsorbents. Pseudo-second-order kinetic models were widely reported to best fit phosphorus adsorption kinetic results obtained using Al^{3+}- and Fe^{3+}-modified clays [1,3]. The appropriateness of the pseudo-second-order rate model indicates that the rate-limiting step was possibly chemisorption and/or phosphorus diffusion in the pores of the modified clay adsorbents. The pseudo-second-order reaction rate model parameters obtained for the various adsorbents are summarized in Table 3.

The data in Table 3 show that the pseudo-second-order adsorption rate constant, k_2, was achieved by the adsorbent with the highest adsorption capacity (i.e. Al/Fe 50/50). The order of the initial adsorption rate for the adsorbents to which Al^{3+} was added first then Fe^{3+} was as follows: Al/Fe 25/75 > Al/Fe 50/50 > Al/Fe 75/25 > Al/Fe 100/0. The order of the initial pseudo-second-order adsorption rate for the adsorbents to which Fe^{3+} was added first then Al^{3+} was as follows: Fe/Al 50/50 > Fe/Al 100/0 > Fe/Al 75/25 > Fe/Al 25/75. The results generally suggest that the adsorbents prepared by adding Al^{3+} then Fe^{3+} to the bentonite achieved higher initial adsorption rates than the adsorbents prepared by adding Fe^{3+} first then Al^{3+}.

The maximum equilibrium adsorption capacity, q_e, values predicted by the pseudo-second-order models for the various adsorbents are shown in Fig. 4. In general, the equilibrium q_e values in Fig. 4 were lower than the Langmuir Q_m values shown previously in

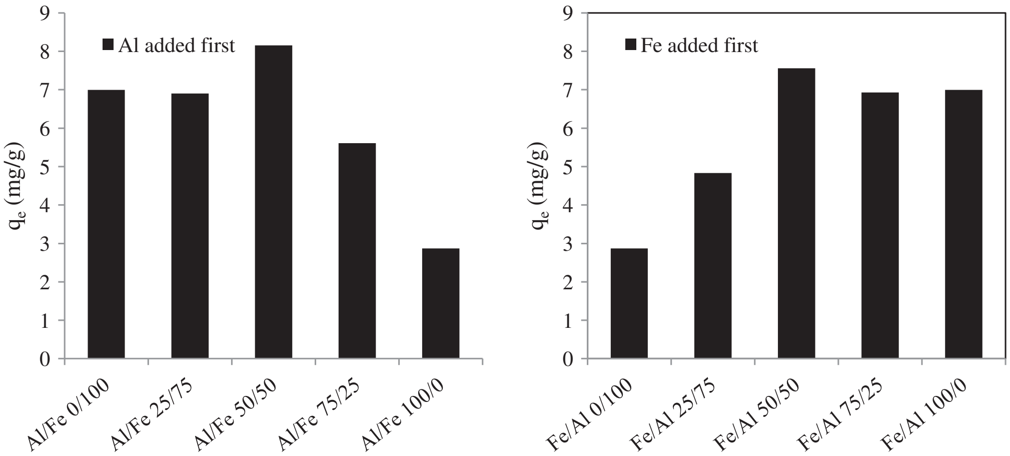

Fig. 4. Comparison of the pseudo-second-order equilibrium phosphorus adsorption capacities (q_e) of the tested adsorbents.

Fig. 2 but followed generally similar trends except for the Fe/Al 100/0 adsorbent. The kinetic results confirm that equal amounts of Al^{3+} and Fe^{3+} gave the best adsorption results and that adsorbent prepared using Fe^{3+} alone achieved higher adsorption capacity and adsorption rate than the adsorbent prepared using Al^{3+} alone, which achieved the least adsorption capacity among all adsorbents. The results also suggest that Fe^{3+} performed better than Al^{3+} in terms of improving bentonite phosphorus adsorption capacity, and therefore, adsorbents prepared by adding Fe^{3+} after Al^{3+} possibly increased Fe^{3+} exposure to phosphorus and thus performed better than adsorbents prepared by adding Al^{3+} after Fe^{3+}.

4. Summary and conclusions

Modification of bentonite through incorporating Al^{3+} and/or Fe^{3+} polycations in the clay matrix significantly enhanced the capacity of bentonite to achieve phosphorus adsorption. The experimental phosphorus adsorption data best fitted the Langmuir adsorption isotherm compared with the Freundlich and Temkin isotherms. The applicability of the Langmuir isotherm indicates the uniform nature of adsorption sites, which supports the ion exchange phosphorus adsorption mechanism. Similarly, the kinetic experimental data best fitted the pseudo-second-order kinetic model compared with the pseudo-first-order kinetic model, which indicates that the rate-limiting step for phosphorus adsorption was possibly chemisorption and/or diffusion in the pores of the modified clay adsorbents. The experimental results suggest that using Al^{3+} and Fe^{3+} combined to produce modified Al^{3+}/Fe^{3+}-adsorbents is superior, in terms of adsorption capacity and adsorption rate, to using Al^{3+} alone or Fe^{3+} alone. The maximum adsorption capacities were achieved by the adsorbents prepared using equal amounts of Al^{3+} and Fe^{3+}, while the least adsorption capacity was achieved by the adsorbent prepared using Al^{3+} alone. The results also suggested that Fe^{3+} performed better than Al^{3+} in terms of improving bentonite phosphorus adsorption capacity in two ways: (1) Fe^{3+} alone produced a better adsorbent than Al^{3+} alone and (2) adsorbents prepared by adding Fe^{3+} after Al^{3+} possibly increased Fe^{3+} exposure to phosphorus and thus performed better than adsorbents prepared by adding Al^{3+} after Fe^{3+}. Additional studies are needed to confirm and explain observed Fe^{3+} performance compared with Al^{3+} in terms of improving bentonite phosphorus adsorption capacity.

List of symbols

Q_e — equilibrium adsorption capacity (mg P/g adsorbent)
C_e — remaining P concentration in solution at equilibrium (mg/L)
K_f — Freundlich isotherm equation proportionality constant
n — Freundlich isotherm adsorption intensity constant
Q_m — Langmuir theoretical maximum adsorption capacity (mg P/g adsorbent)
K_L — Langmuir isotherm constant (L/mg)
A — Temkin linear equation intercept constant
B — Temkin linear equation slope constant
q_t — phosphorus adsorbed (mg P/g adsorbent) at time t (min)
k_1 — pseudo-first-order adsorption rate constant (min^{-1})

k_2 — pseudo-second-order adsorption rate constant in g/(mg min)

t — adsorption time (min)

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