

## Research Article

# Kinetic and Thermodynamic Studies on the Phosphate Adsorption Removal by Dolomite Mineral

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Received 26 November 2014; Revised 15 January 2015; Accepted 26 January 2015

Academic Editor: Apostolos Giannis

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The efficiency of dolomite to remove phosphate from aqueous solutions was investigated. The experimental results showed that the removal of phosphate by dolomite was rapid (the removal rate over 95% in 60 min) when the initial phosphate concentration is at the range of 10–50 mg/L. Several kinetic models including intraparticle diffusion model, pseudo-first-order model, Elovich model, and pseudo-second-order model were employed to evaluate the kinetics data of phosphate adsorption onto dolomite and pseudo-second-order model was recommended to describe the adsorption kinetics characteristics. Further analysis of the adsorption kinetics indicated that the phosphate removal process was mainly controlled by chemical bonding or chemisorption. Moreover, both Freundlich and Langmuir adsorption isotherms were used to evaluate the experimental data. The results indicated that Langmuir isotherm was more suitable to describe the adsorption characteristics of dolomite. Maximum adsorption capacity of phosphate by dolomite was found to be 4.76 mg phosphorous/g dolomite. Thermodynamic studies showed that phosphate adsorption was exothermic. The study implies that dolomite is an excellent low cost material for phosphate removal in wastewater treatment process.

## 1. Introduction

Phosphorus is an indispensable element for animals and plants on the earth. However, excessive phosphorus in water bodies can cause eutrophication. When the concentration of phosphorus in water bodies is higher than 0.02 mg/L, the eutrophication would happen [1]. So it is necessary to eliminate phosphate ions from water.

Several techniques have been applied to the removal of phosphate from wastewater, and the frequently used methods include chemical precipitation [2], biological treatments [3], and adsorption [4]. Among these, adsorption is considered to be a reliable and effective technique for phosphate removal. To choose the adsorption method, both high adsorption capacity and low cost are key issues to be considered. A great attention has been paid to low-cost adsorbents over past years, especially to the natural mineral and industrial waste, such as limestone [5], iron based compounds [6], aluminum based compounds [7], natural zeolite [8], iron oxide tailing [9], ferric sludge [10], blast furnace slag [11], and other materials.

It is well recognized that dolomite is an effective and low-cost adsorbent for phosphate. However, related studies of adsorption mechanism of dolomite, such as the kinetic and thermodynamic adsorption of phosphate by dolomite minerals, had not been reported yet. It is of great importance to study the adsorption mechanism of phosphate by dolomite to clarify the adsorption phenomena and reaction processes and to determine the optimal adsorption conditions in practical production. Dolomite contains  $\text{Ca}^{2+}$ , which can be dissolved in the solution and can then react with phosphate anions to form phosphate precipitates, such as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  [12]. In a previous paper [13], the effects of initial phosphate concentration, reaction time, reaction temperature, and adsorbent dosage on the phosphate removal rates were investigated. The experiments of phosphate adsorption removal results show that the phosphate removal rates exceed 99%; the equilibrium phosphate concentrations after phosphate removal reaction completely accord with the requirement of national discharge standards of the second category pollution GB 1A (TP = 0.5 mg/L) in China.

The objective of the present study was focused on the phosphate adsorption kinetics and thermodynamics of dolomite. Several kinetic models including intraparticle diffusion model, pseudo-first-order model, Elovich model, and pseudo-second-order model were used to fit the kinetic experimental data and the corresponding kinetic parameters were calculated. The isotherm models of Langmuir and Freundlich equations were applied to evaluate the adsorption equilibrium.

## 2. Materials and Methods

**2.1. Materials.** Dolomite used in this research (mass percent CaO 29.68%, SiO<sub>2</sub> 5.13%, and MgO 16.55%) was obtained from Daye, Hubei, China; dolomite was crushed and sieved to smaller than 0.15 mm in particle size before it was used. An appropriate volume of 0.1 mol/L HCl (AR, Chemical Reagent Factory, Chongqing Chuandong Chemical (Group) Co., Ltd) or 0.1 mol/L NaOH (AR, Shanghai Fengxian Fengcheng Reagent Factory) was used to adjust the pH of the solution.

**2.2. Experimental Methods.** Adsorption experiments were carried out as the following procedure. Firstly, a defined volume of phosphate stock solution was diluted to the experimental concentration by adding deionized water in 100 mL glass round-bottom flasks immersed in a thermostatic shaker bath. The pH of the solution was then adjusted to the desired value and a defined amount of adsorbent was added. The mixture was stirred at 250 rpm for a defined period, using a potentiometer to regulate the stirring speed. Then the liquid samples were collected and filtering process was applied to separate solid from liquid, and the filtrate was taken for P analysis.

To investigate the influence of pH on the phosphate adsorption by dolomite, experiments were carried out on the conditions of reaction temperature 20°C, stirring speed 250 rpm, dolomite dosage 10 g/L, initial phosphate concentration 50 mg/L, and reaction time 60 min. Phosphate adsorption kinetics studies were evaluated in the conditions with different adsorption time, different initial phosphate concentrations, and fixed dolomite dosage (10 g/L) and pH 9.5 at 20°C. Five levels of initial phosphate concentrations (10, 30, 50, 70, and 100 mg P/L) and adsorption time (20, 40, 60, 80, and 100 min) were used. The effect of adsorption temperature on phosphate removal was performed at four different temperatures (20, 40, 60, and 80°C) for 60 min with fixed dolomite dosage (10 g/L) and pH (9.5), and the initial phosphate concentration varies from 10 to 90 mg P/L.

The pH of solutions was measured by pH meter (Model Delta 320, METTLER-TOLED Instruments (Shanghai) Co., China). The phosphate concentration of all samples including wastewater was analyzed by bismuth phosphor molybdenum blue spectrophotometric method (Model TU-1810, Beijing Puxi Science and Technology Instrument Co. Ltd., China). Phase analyses of dolomite before and after phosphate adsorption were conducted by X-ray diffraction (XRD) (Model D/max 2500 PC, Rigaku, Japan) with Cu K $\alpha$  radiation.

**2.3. Data Evaluation.** In order to investigate the potential rate-controlling step of the phosphate adsorption process, several kinetics models, including intraparticle diffusion model, pseudo-first-order model, Elovich model, and pseudo-second-order model were employed to evaluate phosphate adsorption kinetics performance. The following equations were applied for describing the four kinetics models, respectively, [14–17]:

intraparticle diffusion model:

$$Q_t = c + k_m t^{1/2}, \quad (1)$$

pseudo-first-order model:

$$\frac{1}{Q_t} = \frac{k_1}{Q_e t} + \frac{1}{Q_e}, \quad (2)$$

Elovich model:

$$Q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta} \ln t, \quad (3)$$

pseudo-second-order model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \quad (4)$$

where  $t$  (h) is the contact time of adsorption experiment,  $Q_e$  (mg/g) and  $Q_t$  (mg/g) are, respectively, the adsorption capacity at equilibrium and at any time  $t$ ,  $\alpha$  (mg/(g·min)) is the initial adsorption rate constant and the parameter  $\beta$  (g/mg) is related to the extent of surface coverage and activation energy for chemisorption,  $k_1$  (1/min) is the rate constant of the pseudo-first-order model,  $k_m$  (mg/(g·min<sup>1/2</sup>)) is the rate constant of the intraparticle diffusion model and  $c$  is obtained from the intercept, and  $k_2$  (g/(mg·min)) is the rate constant of the pseudo-second-order model. The initial adsorption rate is  $k_2 Q_e^2$  (mg/(g·min)).

Adsorption isotherms data were evaluated using the Langmuir and Freundlich equations, respectively, expressed in the following equations [18, 19]:

$$Q_e = \frac{C_e b Q_{\max}}{(1 + b C_e)}, \quad (5)$$

$$Q_e = k C_e^{1/n}. \quad (6)$$

The linear equations of these two experiential models are as follows:

$$\frac{C_e}{Q_e} = \frac{1}{(b Q_{\max})} + \frac{C_e}{Q_{\max}}, \quad (7)$$

$$\log Q_e = \log k + \frac{(\log C_e)}{n}, \quad (8)$$

TABLE 1: Influence of pH value on phosphate removal by dolomite.

Initial pH	Residual phosphate concentration/(mg/L)	Phosphate removal rate/%
3.52	3.75	92.50
5.56	3.65	92.70
7.39	2.98	94.04
9.50	1.46	97.08
10.39	1.53	96.40
11.35	1.69	96.20
12.37	3.02	93.96

where  $C_e$  is the equilibrium concentration of phosphate in the solution (mg/L),  $Q_e$  is the phosphate concentrations in the solid adsorbent (mg/g),  $Q_{\max}$  is the maximum adsorption capacity (mg/g),  $k$  is a constant related to the adsorption capacity ( $\text{mg}^{-1/n}\text{L}^{1/n}\text{g}$ ),  $b$  is a constant related to the energy of adsorption (L/g), and  $n$  is a constant related to the energy of adsorption.

### 3. Results and Discussion

**3.1. Influence of pH.** The result of the influence of pH on the phosphate adsorption by dolomite was listed in Table 1. As can be seen from Table 1, the phosphate removal rate increases rapidly with pH value increasing when the pH value is lower than 9.5. This may be explained by the fact that the phosphate removal is related both to the dissolution of  $\text{Ca}^{2+}$  ions from adsorbent and to the polyprotic nature of phosphate [20]. For  $\text{KH}_2\text{PO}_4$  solution, the main orthophosphate compound is changed with the pH value (i.e., conversion of  $\text{H}_3\text{PO}_4 \Rightarrow \text{H}_2\text{PO}_4^- \Rightarrow \text{HPO}_4^{2-} \Rightarrow \text{PO}_4^{3-}$  with increasing pH). When pH value is about 9.5,  $\text{HPO}_4^{2-}$  is the dominant compound in the solution. It is known that calcium phosphate precipitation is the predominant mechanism in phosphorus immobilization at higher pH value [21]. Therefore, dolomite dissolves to emerge partial  $\text{Ca}^{2+}$ , and  $\text{Ca}^{2+}$  reacts with  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  to form calcium phosphate. The dolomite samples before and after reactions have been checked by XRD and the result was shown in Figure 1. The main components of the sample after reaction include dolomite, quartz, and hydroxyl apatite; the maximum diffraction peak intensities of dolomite, quartz, and hydroxyl apatite are 16393, 622, and 279, respectively. It is obvious from Figure 1 that phosphate precipitated with calcium as hydroxyl apatite. However, the phosphate removal rate decreases with pH value increasing when the initial pH value is above 9.5. Obviously, the dissolved  $\text{Ca}^{2+}$  concentration will decrease with the initial pH value increasing, which causes the inhibition of calcium phosphate precipitation and thus reduces phosphate adsorption. In addition,  $\text{OH}^-$  concentration in solution increases with the initial pH value increasing [22]. The inhibition of phosphate adsorption could also be ascribed to the competition between hydroxyl ions ( $\text{OH}^-$ ) and the phosphate ions on the dolomite surface. In addition, it can be seen from Table 1 that the phosphate removal rate achieves

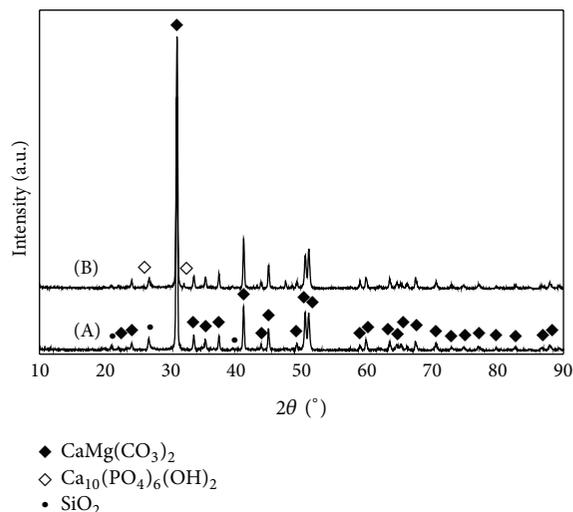


FIGURE 1: XRD patterns of the dolomite samples (A) before adsorption and (B) after adsorption (at pH value = 9.5).

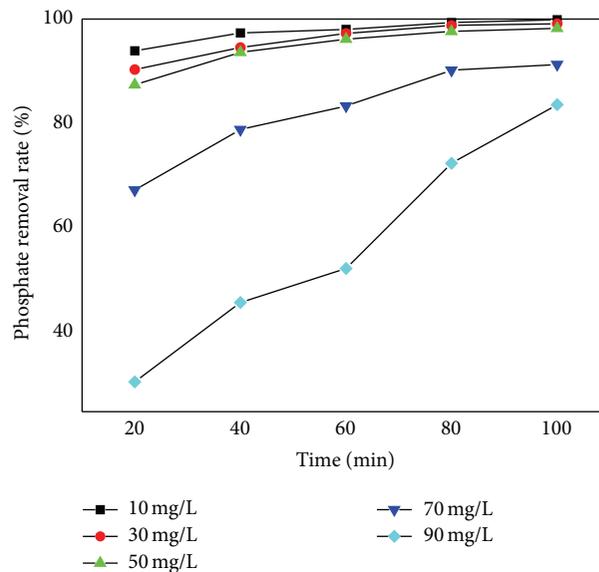


FIGURE 2: Kinetics of phosphate adsorption by dolomite.

92.50% when the pH value is 3.52. Considering the fact that the calcium phosphate precipitation can be neglected when the pH value is relatively low [21], it is clear that the considerable phosphate removal rate (92.50%) at  $\text{pH} = 3.52$  is fulfilled by the process of phosphate adsorption to dolomite. So, it can be concluded that adsorption to dolomite is the main phosphate removal process in present work. Although dolomite contains Mg element, previous works reported that the phosphate removal by fixation with  $\text{Mg}^{2+}$  ions was not accomplished or it was low [23]. So the main effective component for phosphate adsorption on dolomite is  $\text{Ca}^{2+}$ .

**3.2. Adsorption Kinetics.** Figure 2 showed the kinetics results of phosphate removal by dolomite. Results indicated that

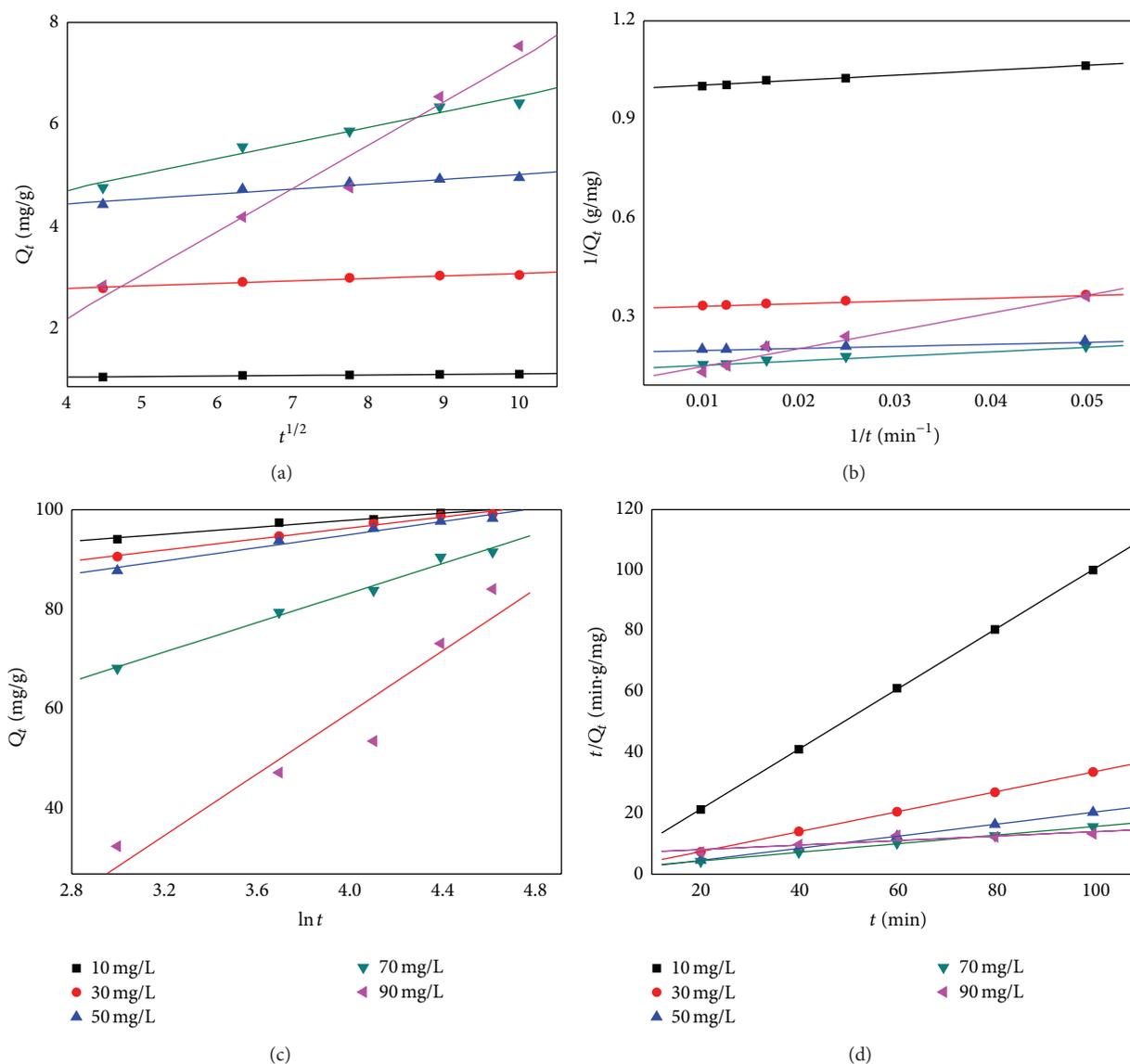


FIGURE 3: The kinetic plots for sorption of phosphate using different models: (a) intraparticle diffusion model; (b) pseudo-first-order model; (c) the Elovich model; and (d) pseudo-second-order model.

the rate of phosphate removal by dolomite was quite rapid. The phosphate removal rate increased rapidly before 80 min. With the adsorption time further increasing, the phosphate removal rate increased slowly.

The experimental data were employed to derive the kinetic parameters using the four different models. The fitting of the experimental data to the linear forms of the four adsorption kinetics models was shown in Figures 3(a)–3(d), respectively. The parameters obtained using these four models are listed in Table 2. It is seen that the pseudo-second-order model shows a good agreement with the experimental data; the correlation coefficients ( $R^2$ ) of pseudo-second-order model in all different initial phosphate concentrations are all above 0.99, which are higher than those of Elovich model, intraparticle diffusion model, and pseudo-first-order model. In adsorption processes, a pseudo-second-order mode is generally interpreted to mean that the mechanism of the process

is mainly controlled by chemical bonding or chemisorption. This would imply that the cause of phosphate adsorption onto the dolomite involves valency forces through sharing or exchanging electrons between sorbate and sorbent [24].

**3.3. Adsorption Isothermal Models.** Figure 4 showed the effect of adsorption temperature on phosphate removal. It can be seen from Figure 4 that the adsorption reaction nearly reached equilibrium at initial phosphate concentration at about 50 mg/L under the experimental conditions tested.

The plots of fitting the experimental data to the linear forms of Freundlich and Langmuir models were shown in Figure 5. The values of the Freundlich and Langmuir constants and the correlation coefficients for dolomite are presented in Table 3. Results showed that Langmuir equation gave a better fit than the Freundlich equation according to their correlation coefficients. In all cases, correlation

TABLE 2: Estimated kinetic model parameters for phosphate adsorption by dolomite.

Intraparticle diffusion model: $Q_t = c + k_m t^{1/2}$				
Initial phosphate concentration/(mg/L)	$c$	$k_m/(mg/(g \cdot min^{1/2}))$	$R^2$	SD
10	0.8990	0.0104	0.9401	0.00661
30	2.5134	0.0490	0.9518	0.02769
50	4.0065	0.0966	0.9222	0.07055
70	3.4407	0.3089	0.9682	0.14076
90	-1.3036	0.8581	0.9630	0.4227
Pseudo-first-order model: $1/Q_t = k_1/Q_e t + 1/Q_e$				
Initial phosphate concentration/(mg/L)	$k_1/(min^{-1})$	$Q_e/(mg/g)$	$R^2$	SD
10	1.5421	1.0110	0.9821	0.0039
30	2.5160	3.0426	0.9805	0.0022
50	3.1923	5.0669	0.9989	0.0004
70	9.5929	6.9324	0.9826	0.0035
90	57.4628	10.4811	0.9631	0.0201
Elovich model: $Q_t = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t$				
Initial phosphate concentration/(mg/L)	$\alpha/(mg/(g \cdot min))$	$\beta/(g/mg)$	$R^2$	SD
10	3.7975	0.2751	0.9766	0.41284
30	6.1505	0.1757	0.9866	0.48756
50	7.5168	0.1471	0.9731	0.82918
70	30.7053	0.0655	0.9886	1.20612
90	20.0906	0.0314	0.9182	0.95821
Pseudo-second-order model: $t/Q_t = 1/k_2 Q_e^2 + t/Q_e$				
Initial phosphate concentration/(mg/L)	$k_2/(g/(mg \cdot min))$	$Q_e/(mg/g)$	$R^2$	SD
10	0.5637	1.0148	1.0000	0.2412
30	0.1168	3.0586	0.9999	0.0901
50	0.0602	5.0743	1.0000	0.0185
70	0.0129	7.0877	0.9985	0.1978
90	0.0008	13.6519	0.9903	1.1780

TABLE 3: Characteristic parameters and determination coefficients of the experimental data according to Freundlich and Langmuir equations.

Temperature ( $^{\circ}C$ )	Langmuir equation				Freundlich equation			
	$b$ (L/g)	$C_e/Q_e = 1/(bQ_{max}) + C_e/Q_{max}$	$Q_{max}$ (mg/g)	$R^2$	SD	$k$ ( $mg^{1-1/n} L^{1/n} g$ )	$1/n$	$R^2$
20	11.56	4.76	0.9958	0.2871	2.48	0.276	0.6645	0.2096
40	9.64	4.00	0.9857	0.7333	1.67	0.326	0.6334	0.2100
60	5.83	3.71	0.9812	0.9462	1.45	0.336	0.6924	0.1856
80	3.06	3.25	0.9694	1.4949	1.20	0.345	0.6270	0.1998

coefficients corresponding to Freundlich equation were lower than those corresponding to Langmuir equation. The fact that dolomite has a relatively higher monolayer adsorption capacity supports the possibility of the adsorption mechanism. The value of the Langmuir constant  $Q_{max}$  was found to be 4.76 mg/g. Comparisons with other adsorbents indicate that the adsorption capacity of dolomite is good. For example, it was reported that adsorption capacities of hematite [25] and furnace slag [26] were 3 mg/g and 0.65 mg/g P, respectively.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter  $R_0$  [27]:

$$R_0 = \frac{1}{(1 + bC_0)}, \quad (9)$$

where  $b$  is the Langmuir constant,  $C_0$  is the initial concentration (mg/g), and  $R_0$  values indicate the type of isotherm. The value of  $R_0$  indicates the type of the isotherm to be either for unfavorable adsorption,  $R_0 > 1$ , for linear adsorption,  $R_0 = 1$ , for favorable adsorption,  $0 < R_0 < 1$ , or for irreversible adsorption,  $R_0 = 0$ .

In the present work, the  $R_0$  values on the initial phosphate concentrations of 10 mg/L, 30 mg/L, 50 mg/L, and 90 mg/L are in Table 4. The  $R_0$  values were found to be between 0 and 1 for all the concentrations of phosphate studied; therefore, the phosphate adsorption by dolomite belonged to favorable adsorption.

3.4. *Thermodynamic Parameters of Adsorption.* From Figure 4, the phosphate removal rate decreased with the

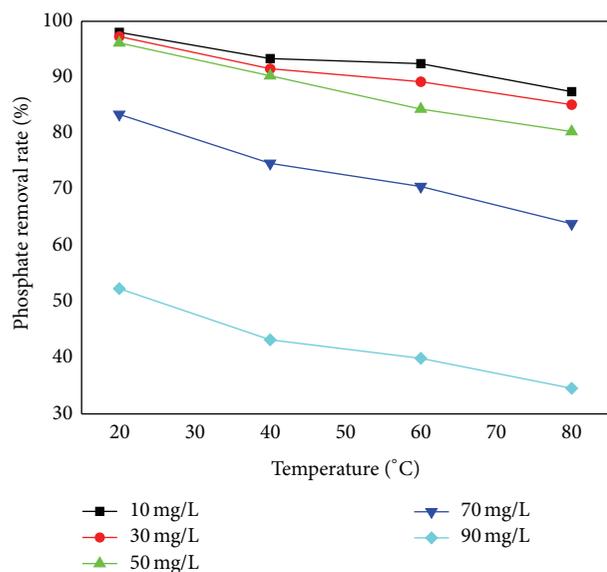


FIGURE 4: Effect of adsorption temperature on phosphate removal.

TABLE 4: Computation result of  $R_0$ .

$b$ (L/g)	$C_0$ (mg/L)				
	10	30	50	70	90
	$R_0$				
11.56	0.0086	0.0029	0.0017	0.0012	0.0010
9.64	0.0011	0.0004	0.0002	0.0002	0.0001
5.83	0.0169	0.0057	0.0034	0.0024	0.0019
3.06	0.0316	0.0108	0.0065	0.0046	0.0036

TABLE 5: Thermodynamic parameters for the adsorption of phosphate on dolomite.

Temperature (K)	$\Delta G^\theta$ (KJ/mol)	$\Delta H^\theta$ (KJ/mol)	$\Delta S^\theta$ (J/K/mol)
293	-3.06		
313	-2.71	-5.85	-10.17
333	-2.45		
353	-2.25		

increase of adsorption temperature, especially for the sample with relatively high initial phosphate concentration. Which indicates that phosphate adsorption on the dolomite is exothermic reaction.

The change of Gibbs free energy is obtained using the following relationship:

$$\Delta G^\theta = -RT \ln k, \quad (10)$$

where  $R$  is the gas constant,  $k$  is the equilibrium constant (obtained from Freundlich equation), and  $T(K)$  is the temperature. The negative values of  $\Delta G^\theta$  indicate the spontaneous nature of adsorption (Table 5). The standard Gibbs free energies ( $\Delta G^\theta$ ) of the adsorption by dolomite were -3.06, -2.71, -2.45, and -2.25 KJ/mol at 293, 313, 333, and 353 K, respectively. The increase in  $\Delta G^\theta$  values for minerals with the

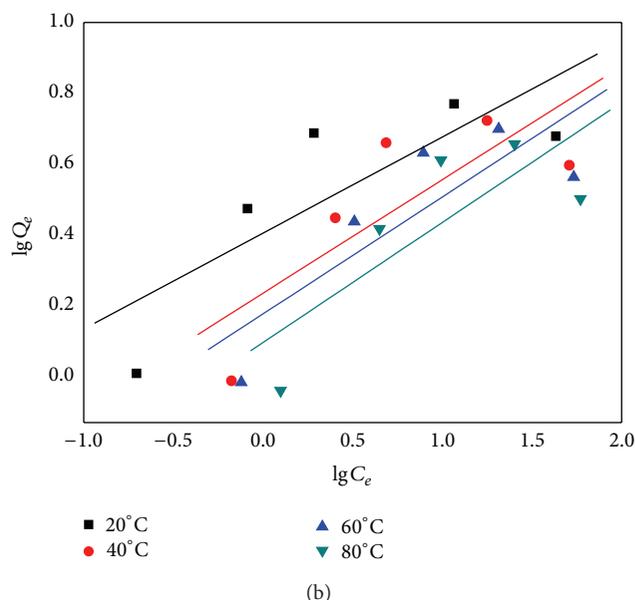
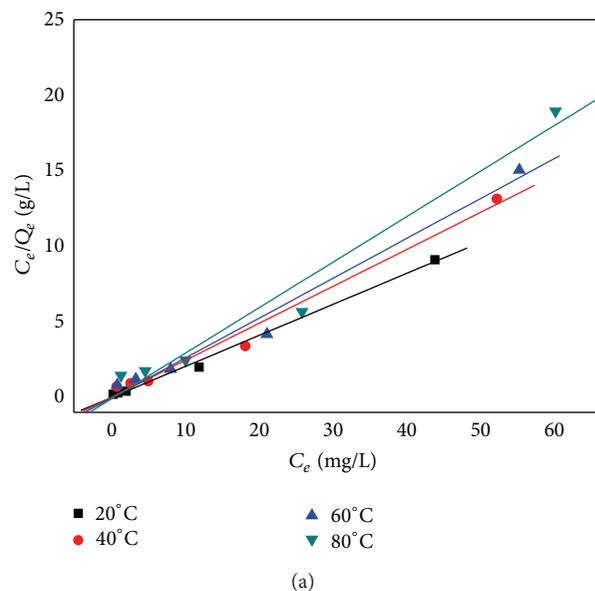


FIGURE 5: Linearized form plots of Langmuir (a) and Freundlich (b) isotherms for phosphate adsorption by dolomite.

temperature decreasing indicated that the adsorption is easier at low than at high temperature.

Other thermodynamic parameters such as enthalpy change ( $\Delta H^\theta$ ) and entropy change ( $\Delta S^\theta$ ) are evaluated using van't Hoff equation. The negative values of  $\Delta G^\theta$  indicate the spontaneous and highly favorable nature of adsorption:

$$\log k = \frac{\Delta S^\theta}{(2.303R)} - \frac{\Delta H^\theta}{(2.303RT)}. \quad (11)$$

Values of  $\Delta H^\theta$  and  $\Delta S^\theta$  were calculated from the slope and intercept of van't Hoff linear plot of  $\log k$  versus  $1/T$  (Figure 6) and were listed in Table 5. The negative value of  $\Delta H^\theta$  confirms the exothermic nature of phosphate

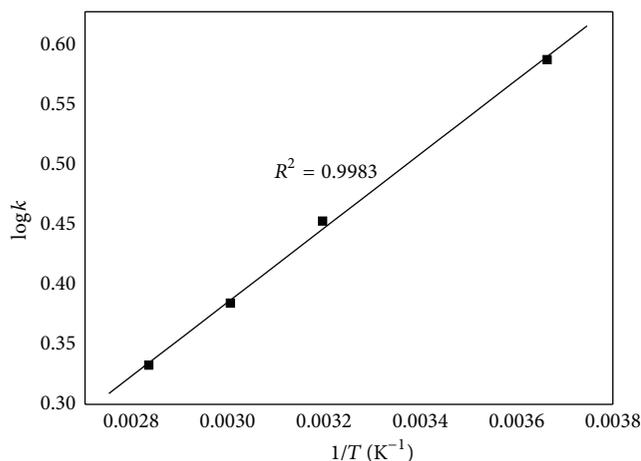


FIGURE 6: Plot of  $\log k$  versus  $1/T$  for phosphate adsorption by dolomite.

adsorption onto dolomite. The negative value of  $\Delta S^\ddagger$  suggests that the randomness at the solid/solution interface decreases during the phosphate adsorption, and it governs the possibility of chemical adsorption. Entropy of activation can be regarded as a measure of the “saddle point energy” over which reactant molecule must pass as activated complex;  $\Delta S^\ddagger$  conveys whether a particular reaction proceeds faster or slower than another individual reaction [28].

It is well known that phosphate adsorption reaction belongs to endothermic reaction for most adsorbents, for example, Fe(III)/Cr(III) hydroxide, red mud, and iron oxide tailings [29–31]. Considering the fact that the reaction of phosphate adsorption onto dolomite is exothermic, a relatively high phosphate removal rate is expected to be obtained at room temperature, and the energy consumed to heat up can be saved, which favors the industrial application of dolomite in phosphate removal.

#### 4. Conclusions

- (1) Dolomite removes phosphate from aqueous solution rapidly. Phosphate may be removed by adsorption and/or by precipitation of calcium phosphate.
- (2) The adsorption kinetics characteristics of phosphate on dolomite were well described by pseudo-second-order model. The mechanism of the phosphate removal process is mainly controlled by chemical bonding or chemisorption.
- (3) Equilibrium isotherm adsorption data obey Langmuir isotherms. The maximum adsorption capacity of dolomite is 4.76 mg/g P.
- (4) Thermodynamic studies indicated that the phosphate adsorption on dolomite was exothermic.
- (5) Dolomite can be used as an effective and low-cost adsorbent for the removal of phosphate.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

#### Acknowledgments

This research was funded by Research Foundation of Chongqing University of Science & Technology, Project no. CK2014Z23. This work was also financially supported by the National Natural Science Foundation of China (Grant no. 51174246 and Grant no. 51204221) and the Scientific and Technological Research Program of Chongqing Municipal Education Commission (no. KJ131417).

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