Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.956341

56 (2015) 1949–1954
November

Taylor & Francis
Taylor & Francis Group

Kinetics and thermodynamics of efficient phosphorus removal by a complex material

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Received 23 November 2013; Accepted 1 August 2014

ABSTRACT

In this paper, we investigated the kinetics and thermodynamics of phosphorus adsorption by a new efficient phosphorus removal composite (EPRC). Kinetic analysis showed that the adsorption of phosphorus by EPRC is best described by a pseudo-first-order equation. Thermodynamic analysis showed that the Gibbs free energy (ΔG°) is negative, implying that the reaction is spontaneous. Moreover, the change in enthalpy (ΔH°) of phosphorus adsorption by EPRC was always greater than 60 kJ/mol, indicating that the adsorption was an endothermic chemical process. Furthermore, EPRC adsorbs phosphorus better at higher temperatures.

Keywords: Phosphorus removal; Adsorption; Kinetics; Thermodynamics; Efficient phosphorus removal composite

1. Introduction

With the rapid development of urbanisation and industrial and agricultural production, a large amount of nutrient-rich urban sewage and industrial and agricultural wastewater is discharged into natural bodies of water, which leads to rapid nutrient enrichment. Its impact on lakes, reservoirs and other enclosed bodies of water is particularly serious. Of all nutrients, the over-abundance or deficiency of phosphorus directly influences the growth and development of all organisms, including humans [1]. Additionally, phosphorus is the key nutrient leading to eutrophication and threatening the surface water quality worldwide [2,3]. It has been considered that phosphorus with concentration greater than 0.02 mg/L is very likely to result in the problem of eutrophication.

Currently, the major treatment technologies on phosphorus include chemical sedimentation, electrolysis, adsorption, membrane filtration and biological removal in both aqueous and soil system [4–8]. Among them, adsorption was considered as one of the most promising and feasible approaches, if efficient and economical adsorbent is readily to be used. Over the past decades, industrial waste residue has increasingly been used as the raw material on phosphorus adsorption for its easy access and low price. However, the original industrial waste residues are normally powdered type and cannot be easily separated from the bulk solution after the adsorption process. Therefore, further process to make the powdered industrial

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waste residues to a granular type is usually suggested prior to use [9].

This study investigated the kinetics and thermodynamics of phosphorus adsorption by a new efficient phosphorus removal composite (EPRC) under different initial phosphorus concentrations and different temperatures through pseudo-first-order and pseudo-second-order equations. The kinetic and thermodynamic properties of EPRC were also analysed to provide guidance for the further development and engineering application of this material.

2. Test materials and methods

EPRC is an EPRC whose principal component is salt mud, an industrial by-product from salt-refining by chlorine–alkali process. The actual composite of salt mud, varied with its different sources, normally contains 15–70% of $CaCO_3$, 8.5–30% of $Mg(OH)_2$ and a small portion of $BaSO_4$, Fe_2O_3, Al_2O_3, SiO_2, NaCl and mechanical impurities. Preparation method: put the dried salt mud into a grinder and crush it to 70–200 mesh; the filtered salt mud is the primary substrate. Add a certain amount of carbide slag, an industrial waste from the acetylene production containing $Ca(OH)_2$ and a little amount of organic and inorganic impurities, and mix well in a granulator. Add an appropriate foaming agent and water to the homogenator, and mix until the solution attains the appearance of a milky foam. Add multiple low doses of the foam into the mixed material, and then, granulate in the drum granulator, controlling the sphere particle size between 0.5 and 2 cm. Spray water onto the sphere after it has gelled for 6–8 h, and conserve it for one week at standard temperature and atmospheric pressure, spraying regularly with water to maintain certain humidity.

Regardless of the initial pH, the phosphorus removal effect of EPRC with a grain size of 0.5 cm was the best among three grain sizes (0.5, 1.0 and 2.0 cm) according to the results of previous research. We, therefore, focus on EPRC with a grain size of 0.5 cm in the current study.

Test method: transfer 250 mL of KH_2PO_4 solution at 5, 10, 15 or 20 mg/L in a neutral medium to each stoppered conical flask and add 2 g of EPRC with a grain size of 0.5 cm. Oscillate under a speed of 100 rpm at 25℃. Remove from the oscillators at regular intervals, filter the top of the supernatant and determine the concentration of the residual phosphorus to determine the adsorption under different initial phosphorus concentrations.

Meanwhile, transfer 5 mg/L KH_2PO_4 in a neutral medium to a conical flask with stopper, and add 2 g of EPRC with a grain size of 0.5 cm. Oscillate at a constant temperature of 25℃ and 100 rpm rotational speed. Remove from the oscillators at regular intervals, filter the top of the supernatant and determine the concentration of the residual phosphorus. Repeat with temperatures of 5, 15 and 35℃ to determine the adsorption at different temperatures.

3. Kinetic and thermodynamic characterisation

3.1. Adsorption kinetics

3.1.1. Adsorption kinetic model

The kinetics of the adsorption of a solute onto a solid adsorbent can be described by pseudo-first-order and pseudo-second-order equations. The differential expression [10–13] of the pseudo-first-order equation is as shown in Eq. (1):

$$\frac{dc}{dt} = -k_1 c \tag{1}$$

This equation is commonly expressed as Eq. (2):

$$q_t = A(1 - e^{-k_1 t}) \tag{2}$$

The differential expression of the pseudo-second-order equation is shown in Eq. (3):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{3}$$

The integration of Eq. (3) can be expressed as Eq. (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

In the above formulas, c is the concentration of solute in solution (mg/L), q_t is the phosphorus adsorption capacity of EPRC (mg/g), t is the sorption time (h), k_1 is a kinetic rate constant (h^{-1}), A is a constant related to the initial concentration, k_2 is the rate constant of the second-order equation (g/(mg h)) and q_e is the equilibrium adsorption capacity of EPRC (mg/g).

3.1.2. The effect of initial phosphorus concentration

The dynamic characteristics of phosphorus removal from synthetic wastewater at different initial phosphorus concentrations are shown in Fig. 1. The phosphorus adsorption capacity of the material increases with

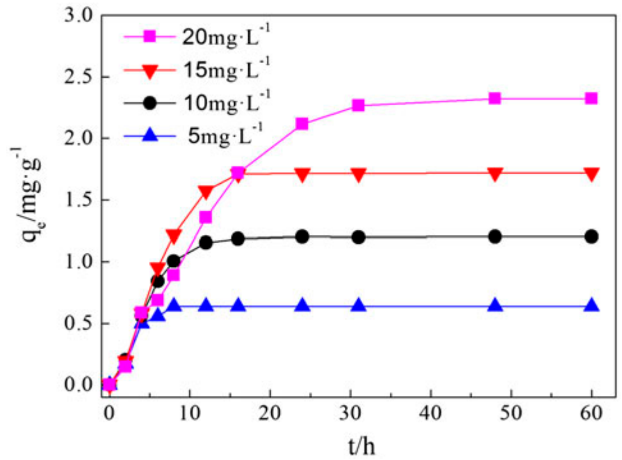

Fig. 1. The kinetics of phosphorus adsorption of EPRC at different initial phosphorus concentrations (Conditions: EPRC particle size 0.5 cm; concentration 8 g/L; mixing rate 100 rpm, 25℃).

increasing initial phosphorus concentration of the solution. When the phosphorus concentration increased from 5 to 20 mg/L, the equilibrium adsorption capacity of EPRC increased 2.6 fold, indicating that the initial phosphorus concentration is one of the main factors influencing the removal capacity. This effect is likely due to the increased availability of the phosphorus for adsorption. Higher phosphorus concentration in solution means greater probability of the phosphorus and the solid surface coming into contact. From Fig. 1, it can be seen that the initial phosphorus concentration significantly influenced the equilibrium time of adsorption: higher phosphorus concentrations retarded the adsorption process, so the time to achieve equilibrium increased. For an initial phosphorus concentration of 5 mg/L, the adsorption equilibrium time was approximately 10 h. When the concentration increased to 20 mg/L, the corresponding adsorption equilibrium time was above 48 h.

The observed phosphorus removal from the synthetic wastewater under different initial phosphorus concentrations were fitted into pseudo-first-order and pseudo-second-order equations (Fig. 1). The correlation coefficient of the pseudo-first-order equation described the process more accurately at different initial phosphorus concentrations ($R^2 > 0.95$). The value of the rate constant k_1 decreased with increasing phosphorus concentration, indicating that the larger the initial phosphorus concentration, the slower the process of the adsorption. It can be seen from the kinetic Eq. (2) that when $t \to \infty$, $q_t \to \infty$. As a result, the value of A reflects the equilibrium adsorption capacity of the material for phosphorus. The higher initial concentrations of phosphorus coming up with the greater values of A indicated that higher adsorbate concentration tends to enhance the adsorption capacity of the material.

3.1.3. *The impact of temperature*

The dynamic characteristics of phosphorus removal from synthetic wastewater of EPRC at different temperatures are shown in Fig. 2. The impact of temperature on adsorption capacity is minimum in the range of tested temperature, while its impact on the adsorption equilibrium time is clear: when the temperature is 35℃, the adsorption equilibrium time is approximately 5 h, but at 15℃, it is over 30 h. This is likely ascribed to a greater diffusion rate of phosphorus from the surface to the inside of the material and thus allowing more available adsorption sites on the surface, making the process of the adsorption faster.

The observed phosphorus removal from the synthetic wastewater under different initial phosphorus concentrations were fitted into pseudo-first-order and pseudo-second-order equations (Fig. 2). Similar to what was observed in response to initial phosphorus concentrations, the pseudo-first-order equations described the process more accurately at different temperatures ($R^2 > 0.95$). The value of the rate constant k_1 increased with increasing temperature, indicating that the higher the temperature is, the faster the process of the adsorption and the greater the value of A. Thus, raising the temperature increases the phosphorus adsorption capacity of the material (Table 1).

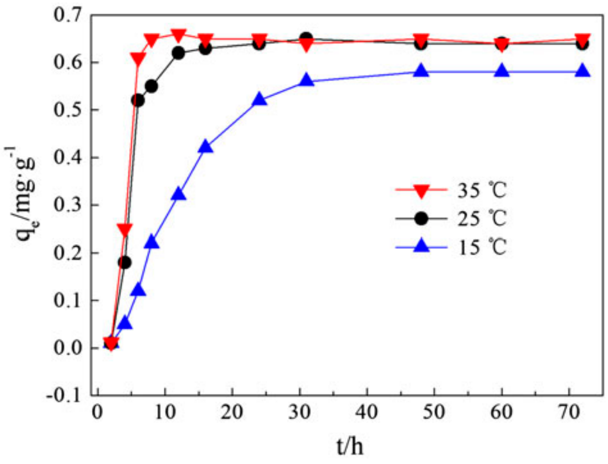

Fig. 2. The kinetics of phosphorus adsorption of EPRC at different temperatures (Conditions: EPRC particle size 0.5 cm; initial P concentration 5 mg/L; mixing rate 100 rpm).

Table 1
The kinetics parameters and correlation coefficients of phosphorus adsorption at different initial phosphorus concentrations

Initial phosphorus concentration (mg/L)	The pseudo-first-order equation			The pseudo-second-order equation			
	A	k_1 (h^{-1})	R^2	k_2 ($\mathrm{g\,mg^{-1}\,h^{-1}}$)	h ($\mathrm{mg\,g^{-1}\,h^{-1}}$)	q_e ($\mathrm{mg\,g^{-1}}$)	R^2
5	0.64974	0.29043	0.95987	0.60079	0.303029	0.7102	0.91187
10	1.23004	0.17672	0.97601	0.15616	0.306708	1.40145	0.93779
15	1.78182	0.13259	0.97039	0.07060	0.310590	2.09745	0.93441
20	2.47240	0.06665	0.98565	0.01835	0.191219	3.2281	0.97100

3.2. Adsorption thermodynamics

3.2.1. Adsorption isotherms

The test results of the material adsorbed phosphorus removal isotherms are shown in Fig. 3. The isothermal adsorption process of EPRC was divided into two clear phases (Fig. 3). In the initial stage, the adsorption isotherms are relatively steep, and the phosphorus adsorption capacity of the material increases rapidly with the increase in the equilibrium concentration. When the concentration surpassed a certain threshold, the change in adsorption capacity became more gradual, and the slope of the curve levelled off. The chemical adsorption of the phosphate ions in solution on the calcium, magnesium and other metal oxides contained in the material often proceeds rapidly and thus mainly occurs in the initial stage of adsorption (Table 2).

The adsorption isotherms at different temperatures fit well into both the Langmuir [14] and Freundlich [15] equations as shown in Fig. 3 and Table 3. From Table 3, it can be seen that the fit of the Freundlich equation is better than that of the Langmuir equation ($R^2 > 0.96$) at the same temperature, indicating that the Freundlich equation provides a more accurate model of phosphorus adsorption on EPRC II. The values of $1/n$ are less than 0.5, indicating that the phosphorus is easily adsorbed, and when the temperature increases, the value of $1/n$ decreases, indicating that raising the temperature enhances the adsorption strength of the material.

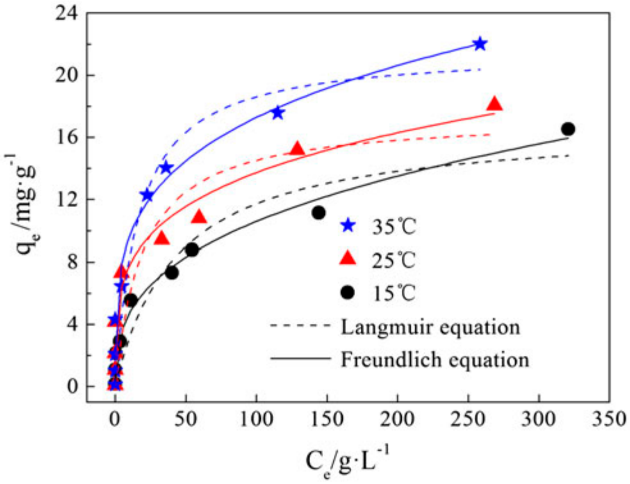

Fig. 3. The adsorption isotherms of EPRC (Conditions: EPRC particle size 0.5 cm; concentration 4 g/L; mixing rate 100 rpm).

3.2.2. Thermodynamic properties

To understand the driving forces of the adsorption process, we can examined the change of the standard thermodynamic functions calculated using the data.

The relationships between the change in standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) and the thermodynamic equilibrium constant are shown as follows [16]:

$$\ln(K_d) = \frac{-\Delta H^\circ}{R{\cdot}T} + \frac{\Delta S^\circ}{R} \tag{5}$$

$$\Delta G^\circ = \Delta H^\circ - T{\cdot}\Delta S^\circ \tag{6}$$

In the above formulas, R stands for the ideal gas constant (8.314 J/mol K), and T stands for absolute temperature (K). If we treat our experimental system as an ideal solution, we can combine Eqs. (5) and (6) to define the apparent Gibbs free energy change ΔG°:

$$\Delta G^\circ = -\mathrm{RT}\ln(K_d) \tag{7}$$

K_d can be calculated by the definition $K_d = q_e/C_e$ (where q_e stands for the equilibrium adsorption capacity (mg/g) and C_e stands for the concentration of phosphorus in solution at equilibrium (mg/g)). Drawing a figure based on the values of $\ln(q_e/C_e)$ and q_e and the intercept of the q_e and $\ln(q_e/C_e)$ plot, the

Table 2
The kinetic parameters and correlation coefficients of phosphorus adsorption at different temperatures

	The pseudo-first-order equation			The pseudo-second-order equation			
Temperature (℃)	A	k_1 ($\mathrm{h^{-1}}$)	R^2	k_2 ($\mathrm{g\,mg^{-1}\,h^{-1}}$)	h ($\mathrm{mg\,g^{-1}\,h^{-1}}$)	q_e ($\mathrm{mg\,g^{-1}}$)	R^2
15	0.63645	0.06035	0.97654	0.06799	0.045208	0.81543	0.95247
25	0.64675	0.28890	0.96381	0.59227	0.298109	0.70946	0.91758
35	0.64960	0.43056	0.95460	1.10988	0.522792	0.68632	0.91416

Table 3
The parameters and correlation coefficients of EPRC at different temperatures

	Langmuir equation: $q_e = \frac{bq_mC_e}{1+bC_e}$			Freundlich equation: $q_e = K_fC_e^{\frac{1}{n}}$		
Temperature (℃)	q_m ($\mathrm{mg\,g^{-1}}$)	b ($\mathrm{L\,mg^{-1}}$)	R^2	K_f	$1/n$	R^2
15	16.82365	0.02299	0.91496	2.10627	0.35079	0.99003
25	17.35564	0.05117	0.84414	4.38888	0.24756	0.96713
35	21.64279	0.06133	0.93486	5.34254	0.25493	0.97428

intersection of the straight line and the vertical axis gives the value of $\ln(K_d)$ [17].

The value of K_d can also be calculated using the constants of the Freundlich and Langmuir adsorption isotherm models. Because the Freundlich equation provided a better fit for our data, we obtained the value of K_d (Table 4) by fitting the EPRC adsorption isotherms to the Freundlich equation at three different temperatures (T = 288 K, 298 K and 308 K). The graphs of $\ln(K_d)$ and $1/T$, from which the values of ΔH° and ΔS° can be calculated (Table 4), are depicted in Fig. 4.

Table 4 suggested that regardless of the model used, ΔG° is always negative and ΔH° and ΔS° are always positive. ΔG° is always negative regardless of temperature, indicating that the adsorption of phosphorus is spontaneous. The smaller the value of ΔG° is, the easier the reaction occurs. Raising the temperature facilitated the adsorption process.

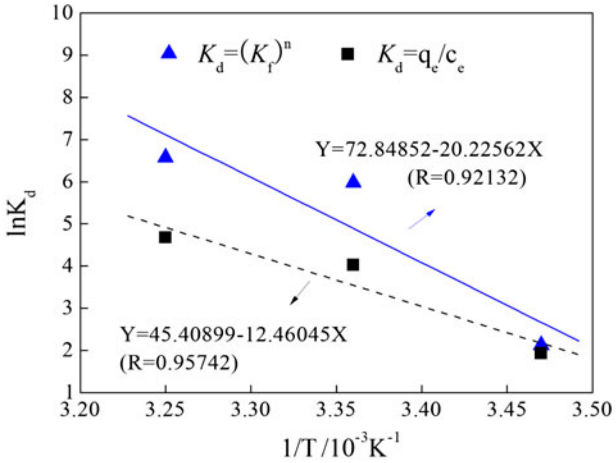

Fig. 4. The influence of temperature on the equilibrium adsorption coefficients.

ΔH° reflects the thermal effects under a constant pressure. When its value exceeds zero, the process of phosphorus adsorption is endothermic, so raising the temperature will increase the adsorption of phosphorus on the material. Von Open B and others

Table 4
The thermodynamic properties of phosphorus adsorption by EPRC at different temperatures

Formula used to calculate K_d	T (K)	K_d	ΔG° ($\mathrm{kJ\,mol^{-1}}$)	ΔH° ($\mathrm{kJ\,mol^{-1}}$)	ΔS° ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
$K_d = (K_f)^n$	288	8.3607	−6.27502	168.1558	605.6626
	298	393.3141	−12.3316		
	308	715.6431	−18.3883		
$K_d = \dfrac{q_e}{C_e}$	288	6.9074	−5.13256	103.5962	377.5303
	298	55.6510	−6.89114		
	308	107.1147	−10.5988		

determined the extent of heat adsorption caused by a variety of forces: the van der Waals force is 4–14 kJ/mol, hydrophobic bond strength is approximately 5 kJ/mol, hydrogen bonding is 2–40 kJ/mol and base coordination and chemical bonds are greater than 60 kJ/mol. ΔH° is always greater than 60 kJ/mol (Table 4), so the adsorption of phosphorus is on the order of chemical bonds.

ΔS° reflects the orderliness of the material in a system. The values in Table 4 are all positive, indicating that the entropy of system increases; ergo, the system becomes more disordered. Therefore, the degree of disorder following the adsorption of phosphorus on the material phosphorus increases. This effect is mainly due to the hydration of the adsorbate in solution. When hydrated ions or molecules of the adsorbate are adsorbed, the bonds with water may be dissociated, and the disorder of the solution increases. This process increases the entropy of the system such that $\Delta S^\circ > 0$ [18].

4. Conclusion and applications

The kinetics of phosphorus removal using EPRC under different conditions were well fitted both by pseudo-first-order and pseudo-second-order equations ($R > 0.9539$). Higher initial phosphorus concentrations yielded slower equilibrium rates but greater adsorption capacities. Phosphorus adsorption in this study is thermodynamically favourable, indicating that raising the temperature is beneficial for phosphorus removal. In conclusion, the EPRC is a new and promising material which could be potentially applied on removal of phosphorous in wetland, municipal wastewater treatment as well as lakes and rivers.

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