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Adsorption of phosphate into waste oyster shell: thermodynamic parameters and reaction kinetics

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ABSTRACT

The present study explored the feasibility of exploiting an oyster shell as an adsorbent to remove the phosphate pollutants under different laboratory experimental conditions. The batch sorption was investigated for the solution temperature and the size of the oyster shell fragments. The results demonstrated that phosphate uptake capacity (q_e) increased with an increase in the solution temperature from 20 to 30°C and a decrease in the oyster shell diameter from 590 to 180 μm at an initial phosphate solution concentration of 10 mg/L. The thermodynamic parameters of the adsorption process were calculated. The positive value of ΔH° (40.61 kJ/mol) indicated that the adsorption of phosphate on oyster shell was endothermic; the positive value of ΔS showed good affinity of the phosphate toward the oyster shell; the positive value of ΔG (12.60 kJ/mol) suggested that the adsorption of phosphate into an oyster shell was a nonspontaneous reaction. Following the evaluation of the thermodynamic parameters, different kinetic models, including pseudo-second-order, Elovich, and intra-particle diffusion kinetics models, were studied to evaluate the adsorption process of the phosphate into an oyster shell. The pseudo-second-order kinetic model best fitted the phosphate adsorption into a waste oyster shell. This showed that the chemisorption mechanism plays a significant role in the adsorption process. The linear form of Elovich model revealed that the actually reacting solid surface, oyster shell, was energetically heterogeneous. The intra-particle diffusion model demonstrated that the diffusion mechanism was not the dominant rate-limiting step. The above results successfully established good potentiality for the application of waste oyster shell as a phosphate pollutant removal source.

Keywords: Adsorption; Phosphate; Kinetics; Thermodynamics

1. Introduction

Phosphorus exists in natural water in various forms, such as orthophosphates and organic phosphates. It is also a crucial nutrient for plants, alga, and other biological organisms. However, domestic and industrially polluted water usually contains an excess amount of phosphorus. As a result, the removal of phosphorus from water is always an important environmental issue. Chemicals, such as lime alum and ferric chloride, are widely used to remove the phosphate pollutants from water [1]. However, these chemicals may produce sludge besides very costly. Therefore, chemical treatment for

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the phosphate removal has become an unattractive option. Sorption was later found to be a reliable method to remove phosphate pollutants. Recently, many low-cost sorbents for the phosphate removal, such as alum sludge [2], red mud [3], and fly ash [4], have been studied for potential economic and environmental benefits.

On the other hand, oyster shell, the common by-product of *Crassostrea gigas* in Taiwan, was usually deemed as waste. A large amount of oyster shells are casually dumped along the coast of Tong-shi, a sinking town located in Cha-yi, Taiwan. Several oyster shell piles not only occupy lands but also trigger a host of environmental and hygiene problems, such as mosquito breeding, potent smell, and poor drainage. The waste oyster shell piles in the sinking town may even lead to flooding if intense rapid rain fell. Nevertheless, an oyster shell has been found to serve as a new material for phosphate removal [5]. The oyster shell mainly comprises of calcium carbonate, which enables the oyster shell to adsorb the phosphate pollutant from water. The oyster shell is applied to contacted beds and membrane bioreactors as filtration media to improve the urban wastewater treatment [6,7].

The objective of the present research is to study the feasibility of using an oyster shell as an adsorbent for the phosphate removal from wastewater. In the present study, the adsorption of phosphate on different diameters of oyster shell fragments from aqueous solutions was measured in batch experiments under different temperatures and time intervals. The effects of temperature and diameter of oyster shell were studied respectively. Various kinetic models were employed to fit the experimental data and were also discussed. Through thermodynamic and kinetic studies, the feasibility of applying oyster shell as a phosphate removal source was assessed.

The present study appears to be the first of its kind to evaluate the feasibility of applying waste oyster shell as a phosphate removal medium through thermodynamic and kinetic tests. If the natural oyster shell could be proven to be a good and efficient adsorbent for phosphorus removal, using an oyster shell to purify the water will not only save the cost for wastewater treatment, but will also give due consideration to solve the problem of solid pollutants of a waste oyster shell and thereby improve the eutrophication environment. Furthermore, utilizing abundant waste oyster shells for the adsorption of phosphate could enhance the life quality and make more land available for the local residents.

2. Experimental

2.1. Materials and methods

2.1.1. Preparation and characterization of the adsorbent, oyster shell

The present study, the waste oyster shell was harvested from the coastal town, Tung-shih, which is located in the south-western Taiwan. First, the waste oyster shell was collected and exposed to the sun for several months until all the organic matter, such as the carrion left in the oyster shell, had been decomposed thoroughly. The oyster shell was then washed with tap-water and brushed to remove away all the loose materials from the oyster shell surface. The oyster shell was air-dried naturally at a temperature of about 30℃ for 1–2 days and then was crushed by a pulverizer (Chin Kang Industry Co., Ltd., CK-125). Uneven diameters of the oyster shell powder were sieved by different dimensions of meshes to obtain a geometrical diameter from 180 to 590 μm and the oyster shell powder was later sbject to phosphate removal. In the present study, #30 represents the oyster shell powder between 425 and 590 μm, #40 stands for the diameter between 250 and 425 μm, #60 stands for the diameter between 180 and 250 μm, and #80 demonstrates the oyster shell powder between 149 and 180 μm, which are all corresponding to the ASTM standard [8].

Furthermore, to make sure that the water content of an oyster shell powder is rare, so that the water amount would not affect the experimental results, the water content of oyster shell powder is essential to estimate. Take approximately 10 g, 590 μm oyster shell powder and then place it into an oven and let it dry for approximately 8 hour. Next, take the oyster shell powder out and estimate the weights again. Subtract the weights estimated afterward from the weights estimated before and get the number, ΔW. Divide ΔW by the original weights and the water content, $W_c\%$, of the oyster shell was calculated. Generally, the water content of a naturally air-dried oyster shell is very limited.

2.1.2. Adsorbate

The solutions were prepared by dissolving a fixed amount of anhydrous potassium phosphate (KH_2PO_4) in distilled water at a concentration of 1,000 mg/L. When it is necessary, the solution can be diluted to different concentrations with distilled water.

2.2. Batch equilibrium and thermodynamic studies

The batch equilibrium study was conducted under agitation in a water bath shaker (YIH DER, BT-350) at various temperatures (20, 25 and 30°C) and natural pH surroundings, which was not adjusted by any artificial method, for 4 hour. The solution was mixed with 0.75 g oyster shell powder of different diameters and 100 mL of 10 mg/L phosphate solution to a series of conical flasks. After agitation, filter the oyster shell-phosphate mixture solution with glass filter papers and the air-extracting apparatus. The final phosphorus concentration was measured by using a UV/VIS spectrophotometer at an 880 nm wavelength after the samples were pretreated with the ascorbic acid method [9]. All the tests in this study were performed repeatedly three times. Then, the sorption capacity (q) and the distribution ratio (K_d) were calculated from Eqs. (1) and (2),

$$q = \frac{V(C_i - C_f)}{m} \text{ (mg/g)}, \tag{1}$$

where C_i (mg/L) and C_f (mg/L) represent the initial and final concentrations of the phosphate solution, respectively, V (L) is the volume of solution, and m (g) is the weight of the adsorbent.

Subsequently, to realize the thermodynamic properties of an adsorption process of phosphate into an oyster shell, the thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were required. With Eqs. (2)–(4)

$$K_d = \frac{\text{amount of phosphate in adsorbent}}{\text{amount of phosphate in solution}} \times \frac{V}{m} \text{ (L/g)}, \tag{2}$$

$$\Delta G^\circ = -RT \ln K_d, \tag{3}$$

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \tag{4}$$

where ΔG°, ΔH° and ΔS° mean the change of standard Gibbs free energy, enthalpy, and entropy, respectively; K_d is the distribution coefficient for the mix solution; T is the absolute temperature; R is the gas constant, the acquired thermodynamic parameters could be obtained by plotting.

2.3. Kinetic studies

The kinetic study procedure was identically processed to those of equilibrium tests. In the kinetic study, the geometrical size of 180–250 μm oyster shell powder was employed to adsorb the phosphate at various temperatures (20, 25 and 30°C) and natural pH surroundings. Aqueous samples were withdrawn at suitable time intervals and phosphate concentrations was identically measured. q_t (mg/g), the amount of adsorption at that time interval, was evaluated by Eq. (5), where C_i and C_t (mg/L) demonstrate the phosphate concentration in aqueous solution at initial and any time t, V (L) is the volume of solution, and m (g) is the mass of adsorbent used.

3. Results and discussion

3.1. The effect of temperature

The effect of temperature on the phosphate uptake capacity was studied. Fig. 1 shows that as the temperature rises, the phosphate uptake capacity (q_e) of the oyster shell also increases. This phenomenon indicates that the adsorption of phosphate on the waste oyster shell favors being processed at higher temperature, which helps us to elucidate that phosphate adsorption into an oyster shell is an endothermic process. This may be due to the fact that the increasing temperature could provide more calcium hydrolysis complexes for phosphate precipitation since the content of an oyster shell is mainly filled with calcium carbonate. Owing to the above observation, it is believed that the adsorption process involves not only physical but also chemical adsorption. Similar results and trends were also observed by the phosphate removal process on an iron hydroxide-eggshell waste [10].

3.2. The effect of particle size

The effect of particle size upon phosphate adsorption on the oyster shell was investigated in the range

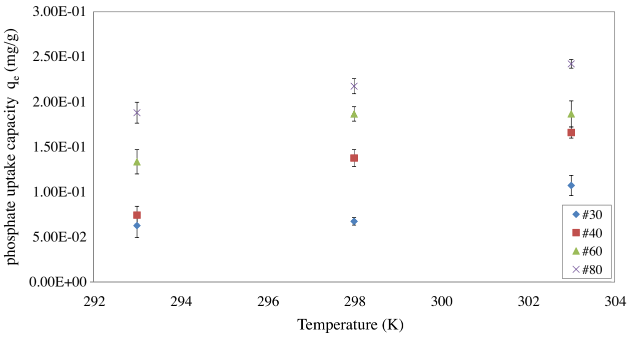

Fig. 1. The relationship between the phosphate uptake capacity (q) and the temperature performed with various sizes of oyster shells. All of the tests have independently repeated three times in each specific condition ($n = 3$).

from 150 to 590 μm. The research results are presented in Fig. 1, which indicates that as the particle size decreased, the phosphate uptake capacity (q_e) increased. It may be due to the fact that the surface area increased as the particle size decreased. This study also presents similar results compared with previous research [11,12]. However, there may not be a linear relationship between the phosphate uptake capacity and particle size of the oyster shell since by nature the oyster shell powder did not distribute uniformly. Fig. 1 also reveals that the temperature effect on the phosphate uptake capacity is noticeable for a bigger particle size. At the highest processing temperature (30℃), the phosphate uptake capacity of #30 and #40 oyster shell powder was higher than that at 25 and 20℃. However, for smaller particle diameters, this phenomenon was not very much apparent, which might be on account of an uneven distribution of the oyster shell. The oyster shell used in the experiment was not subject to any artificial treatment, so the distribution of components, surface roughness, and density of an oyster shell were not uniform. Besides, this phenomenon was obvious for the oyster shell of a bigger dimension as the filtration for a bigger scalar oyster shell may not be as pure as the filtration for an oyster shell of a smaller size. Similar results were observed in the previous study regarding the chemical–mechanical characteristics of a crushed oyster shell [13] (see Fig. 1).

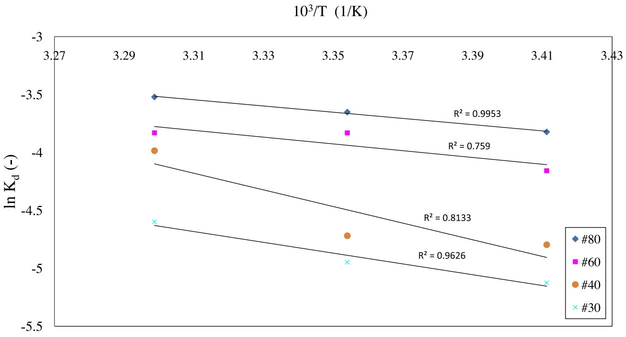

Fig. 2. Van't Hoff plot for the adsorption of the phosphate into an oyster shell at various temperatures.

3.3. Thermodynamic parameters

The thermodynamic parameters demonstrate the feasibility and spontaneous nature of an adsorption process. Parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can be determined by Eqs. (1)–(4) as mentioned in the experimental method.

With Eqs. (1) and (3), the ΔG values of #30, #40 (see Fig. 2), #60, and #80 oyster shell were gained and known to be 11.59, 9.99, 9.65, and 8.87 kJ/mol at a temperature of 30℃, while the ΔG° value of #30, #40, #60, and #80 oyster shell were estimated to be 12.26, 10.35, 9.49 and 9.05 kJ/mol at temperature of 25℃ and 12.49, 11.81, 10.13, and 9.32 kJ/mol at a temperature of 20℃, respectively. Owing to the positive Gibbs free energy value, it suggests that the adsorption reaction requires the energy to transform the reactants into products. A similar trend was shown in the adsorption process of various dyes on natural adsorbents such like *Paulownia tomentosa* Steud. leaf powder and hazelnut shell [14–16]. However, other studies that used industrial by-products, such as layered double hydroxides [17] and β-MnO_2 [18], to investigate the phosphate adsorption processes report negative ΔG, which means that phosphate adsorption on those media is spontaneous. This may be in reference to the pretreatment of the different phosphate adsorbents, since most of the industrial by-products are manufactured at high temperature and under high pressure condition or subjected to a complex pretreatment such as soaking with sulfuric acid [10,19]. Besides, as the Gibbs free energy decreased with decreasing particle size, it indicated that the adsorption process applied with smaller oyster shell particles was favorable. With Eqs. (2) and (3), the ΔS values were gained and known to be positive. This phenomenon suggested a good affinity of the adsorbate, phosphorus ions, toward the adsorbent, oyster shell [10,14]. The randomness increased during the adsorption process. An identical observation was reported previously for the adsorption of crystal violet dyes in activated carbon [20]. However, it is found that the ΔS value decreased as the particle size decreased in this study. The randomness may reduce when the particle size becomes small. Also, with Eqs. (2) and (3), the ΔH° values of #30, #40, #60, and #80 oyster shell were obtained and known to be 38.73, 59.71, 22.32, and 25.60 kJ/mol, respectively. It is learned that the phosphate adsorption process was endothermic in the experiment. The ΔH° values indicated the presence of an energy barrier in the adsorption process [10]; similar results are gained from an adsorption of the phosphate into an Aleppo pine adsorbent [21]. The enthalpy value decreased as the oyster shell powder became small and it indicated that the energy barrier in the adsorption process weakened as the particle size of the oyster shell reduced (see Table 1).

Table 1
Thermodynamic parameters for the adsorption of phosphate on oyster shell under various temperatures and various particle sizes

Temperature (K)	Particle size (μm)	ΔG (kJ/mol)	$T\Delta S$ (kJ/mol)	ΔH° (kJ/mol)
303.15	590	11.59	27.51	
	425	9.99	49.38	
	250	9.65	13.47	
	180	8.87	16.82	
298.15	590	12.26	27.06	38.73
	425	10.35	48.57	59.71
	250	9.49	13.24	22.32
	180	9.05	16.54	25.60
293.15	590	12.49	26.62	
	425	11.81	47.75	
	250	10.13	13.02	
	180	9.32	16.26	

3.4. Kinetic models

Implementing the rate of adsorption process is probably the most significant factor in an adsorption system design as both the residence time and the reactor dimensions are controlled by reaction kinetics [22]. Consequently, it is necessary to understand the detail of reaction kinetics in the given adsorption system. Several kinetic models, such as pseudo-second-order model and intra-particle diffusion, were used to analyze the adsorption of phosphate into an oyster shell. Fig. 3 in line with these kinetic models showed the linearized forms and the evaluated results were discussed as follows.

3.4.1. Pseudo-second-order model

The pseudo-second-order model determines the parameters directly by the experiments, which means that this approach did not have the problem of assigning an adsorption capacity in previous. Parameters, such as the rate constant of pseudo-second-order and the adsorption capacity, can be obtained from the equation without knowing any factor beforehand [23]. Hence, the study chose the pseudo-second-order model as a possible way to characterize the reaction kinetics of the adsorption process.

The pseudo-second-order kinetic equation is represented as Eq. (5) [24],

$$\frac{t}{q_t} = \frac{1}{K_2 \times q_e^2} + \frac{t}{q_e}, \tag{5}$$

where K_2 is the rate constant of pseudo-second-order adsorption (g/mg min). Also, the initial adsorption rate, h (mg/g min), is expressed as Eq. (6).

$$h = K_2 \times q_e^2. \tag{6}$$

The values of K_2, h, and q_e were known from the slopes and intercepts of the plots gained by plotting t/q vs. time t (Fig. 3(a)). It can be learned from Table 2 that the kinetics of phosphate adsorption into the oyster shell followed this model with coefficients of determination (r^2-value) averagely about 0.973. Table 2 also reveals that the sorption capacity at equilibrium (q_e) increased as the temperature enhanced. In addition, the initial adsorption rate, h, and the rate constant, K_2, were both raised as the temperature enhanced. These results indicated that chemisorption may play a significant role in the adsorption process of phosphate into the waste oyster shell [10]. Further, comparing this study to part of our previous research [25], which is modified and plotted in Fig. 3(b), it can be found that when the contact time extended, the data conformed to well fit the pseudo-second-order model too ($r^2 = 0.9991$).

3.4.2. Elovich model

The Elovich equation was used to decide the reaction kinetics of chemisorptions of gases into heterogeneous solids [26]. In recent times, this equation has been frequently applied to describe the adsorption process of pollutants from an aqueous solution or the

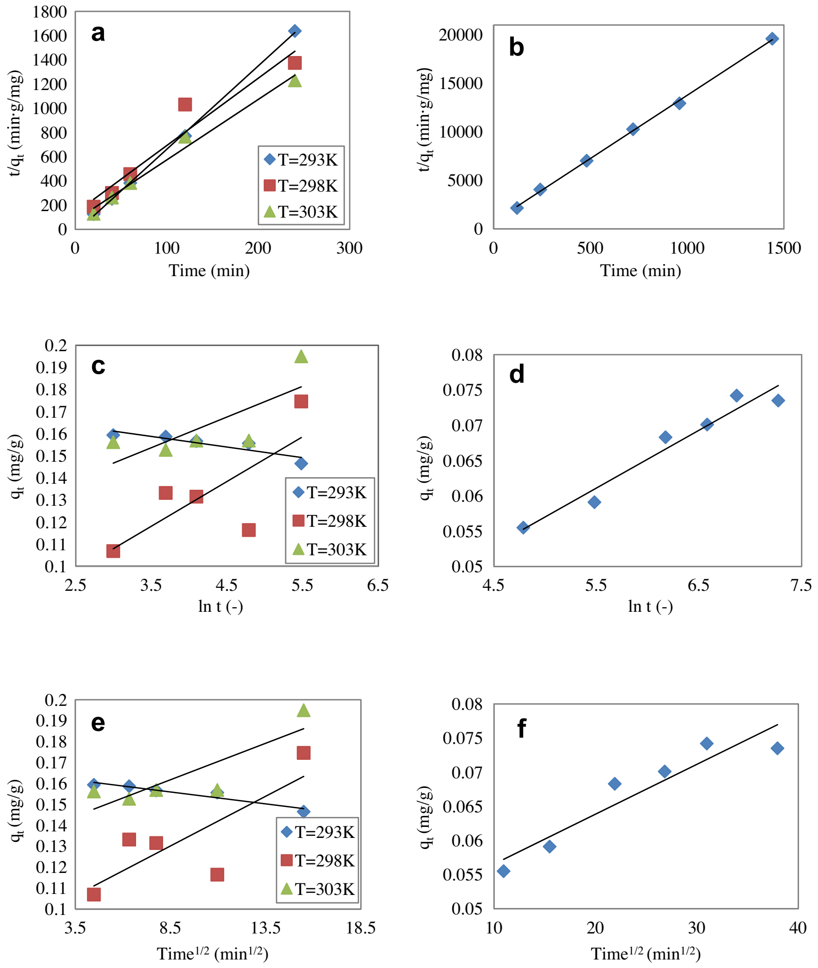

Fig. 3. Plots of (a) pseudo-second-order model, (b) pseudo-second-order model for long time interval, (c) Elovich model, (d) Elovich model for long time interval, (e) intra-particle diffusion model, and (f) intra-particle diffusion model for a long time interval. All the data for long time interval condition are obtained and modified from our previous research [25].

phosphate adsorption into soils [27–29]. The Elovich equation assumes that the actual reacting solid surfaces, such as an oyster shell, are energetically heterogeneous [30]. Eventhough the Elovich equation has often been used to explain the chemisorption process, this equation does not propose any definite fundamental kinetics for an adsorption system. Namely, this equation was considered as a semi-empirical equation [30].

The linear form of the Elovich equation is shown as Eq. (7)

Table 2
Parameters for kinetic models of pseudo-second-order, Elovich, and intra-particle diffusion

	Pseudo-second-order model					Elovich model			Intra-particle diffusion model	
Temp. (K)	q_{ex} (mg/g)	k_2 (g/mg min)	q_e (mg/g)	h (mg/g min)	r^2	a_e (mg/g min)	b_e (g/mg)	r^2	K_{dif} (min$^{1/2}$)	r^2
303.15	0.195	0.336	0.200	0.013	0.9844	26.525	71.942	0.5720	0.0350	0.7298
298.15	0.175	0.227	0.180	0.007	0.9346	0.210	49.505	0.5650	0.0048	0.6310
293.15	0.146	−1.768	0.145	−0.037	0.9992	0.000	−208.333	0.8006	−0.0011	0.9088

$$q_t = \frac{\ln a_e \times b_e}{b_e} + \frac{1}{b_e} \times \ln t, \tag{7}$$

where a_e (mg/g min) demonstrates the initial adsorption rate, while b_e (g/mg) is related to the distribution of activation energies [30] and the extent of surface coverage [31]. A plot of q_t vs $\ln t$ (Fig. 3 (c)) would generate a linear relationship and the values of a_e and b_e were acquired from the slope and intercept. The calculated parameters are listed in (Table 2). It could be seen from Table 2 that the initial adsorption rates, a_e and b_e, both increased with the rising temperature. A similar trend that the initial adsorption rate (a_e) grows with the temperature was found in the phosphate adsorption into a waste egg-shell [10]. The effect of temperature on the initial adsorption rate (a_e) usually indicates that the activation energy exists for an adsorption process. Various activation energy values of activation energy are be considered to be a potent implication for surface heterogeneity [32]. This is also consistent with the rich surface of heterogeneous components of the natural oyster shell, which can supply a source of empty sites for ion exchange or physical adsorption [29]. Accordingly, the corresponding values of b_e are different from temperature to temperature. As the temperature increased, b_e was supposed to decrease because there may be less surface area under a higher temperature condition. Nevertheless, the results of this study did not agree with the previous research [10]. More data are proposed to measure further examination of the relationship between temperature and the constants a_e and b_e. Plus, the r^2 values were not very high in this kinetic model. The regression analysis showed that the Elovich model may not fit very well for the phosphate adsorption into the oyster shell in short time intervals (20 min). Statistically, these data were not significant when the Elovich model was employed to describe the phosphate adsorption process. On the other hand, in contrast with part of our previous study (Fig. 3(d)), which was processed in long time intervals (more than 120 min), it revealed a high performance with a r^2 value of 0.9519 for the Elovich model. The results implied that the Elovich model applied properly for the phosphate adsorption into an oyster shell in a long time interval. Identical results were reported on the arsenic adsorption into goethite [30]. Yet, the slow adsorption may not be a consequence of diffusion but rather it could be due to either the heterogeneity of the surface site bonding energy or any other reaction controlling for the phosphate removal from the solution [33].

3.4.3. Intra-particle diffusion model

Since the pseudo-second-order and Elovich models could not identify the diffusion behavior during the adsorption process, the kinetic results were then analyzed by the intra-particle diffusion approach developed by Weber and Morris [34]. Diffusion behavior, such as internal diffusion and liquid film diffusion, may be the rate-limiting step of the adsorption process [14,15]. The rate for intra-particle diffusion is evaluated by Eq. (8),

$$q_t = K_{\mathrm{dif}} \times t^{1/2} + C, \tag{8}$$

where C is a constant gained from intercept (mg/g), K_{dif} is the intra-particle diffusion rate constant (mg/g min$^{1/2}$) gained from the slope, and q_t is the uptake of phosphate in that time interval.

If intra-particle diffusion is the dominant rate-limiting step, q_t vs. the square root of time ($t^{1/2}$) would be linear and the lines are supposed to pass through the origin [34]. However, the results of this research shown in Fig. 3(e) and (f) did not pass through the origin, which helps us to infer that the intra-particle diffusion was not the only rate-limiting step. Other kinetic mechanisms may also play a role in the phosphate adsorption process into an oyster shell. All of the above-discussed kinetic models may operate simultaneously. Besides, K_{dif} is known to increase with the rising temperature, which is due to promotion of the pore diffusion in sorbent particles. Nevertheless, the trend was not observed in the solution temperature range from 25 to 30℃. It is also noticed that the intra-particle diffusion model may not work well for the phosphate adsorption into oyster shell at a low temperature (20℃) in this study. At a low temperature (20℃), the capacity for phosphate uptake did not enhance too significantly with time. Similar results are reported in the phosphate adsorption into dolomite at 20℃ in the previous research [35]. By comparing the present study to our previous research carried out in long time intervals (Fig. 3(f)), it is found that there was no apparent difference in the corresponding values of r^2 (about 0.8884) when the adsorption process was analyzed with intra-particle diffusion. This suggests that the contact time may be not the most crucial factor affecting the intra-particle diffusion kinetic model.

3.5. Evaluation of oyster shell as phosphate adsorbent

In this study, #30, #40, #60, and #80 oyster shells were used; the activation time for equilibrium is 4 hour; the adsorbate concentration is 10 mg/L; the

Table 3
Phosphate removal capacity of the materials investigated

Material	Diameter (μm)	q_e (mg/g)	Initial P concentration (mg/L)	Contact time (hour)	Refs.
Oyster shell	180				
Gravel	<2000	0.03	0–320	20	[36,37]
Opoka	250	0.10	5–25	24	[37,38]
Granulated slag	80–4,750	0.16	N/A	N/A	[37]
Sand	0–500	0.13–0.29	100–1,000	24	[39]
LECA	<2,000	0.16	0–320	24	[40]
Limestone	250–2,000	0.25	2.5–40	24	[41]
Electric arc furnace steel slag	2,500–10,000	1.25–2.35	0–320	24	[41]
Filtralite	500–4,000	1.39	N/A	N/A	[39]
Red mud gypsum	<2,000	5.07	0–800	24	[42]
Crystalline slag	0–125	18.94	50–500	150	[43]
Blast furnace slag	9,500–19,000	44.25	0–600	48	[44]
Fly ash	<150	63.22	0.31–3,100	4	[45]

phosphate uptake capacity (q_e) of #30, #40, #60, and #80 oyster shell for the adsorption process is 0.061, 0.139, 0.179, and 0.214 mg/g at a temperature of 25°C, respectively. To evaluate the feasibility of using an oyster shell as an adsorbent to remove the phosphate, the phosphate uptake capacity of oyster shell is compared with those of other materials.

The results of comparison are listed in (Table 3). The effect of applying an oyster shell to remove the phosphate is better than using gravel, opoka, and sand as an adsorbent to the remove phosphate wastes, while the effect of applying oyster shell to adsorb phosphate is almost the same with using some kinds of sand, granulated slag, light expanded clay aggregates (LECA), and limestone to adsorb phosphate. It might be owing to the fact that there are more adsorbing sites on the oyster shell surface and the oyster shell is composed of lot of calcium, which could form a complex ion with the phosphate. Accordingly, the oyster shell presents a better effect on the removal of phosphate. However, compared to other materials such as electric arc furnace steel slag [41], red mud gypsum [42], etc. the effect that oyster shell demonstrates on removing the phosphate that oyster shell demonstrates is not that good. It might be due to the particle size of an oyster shell being bigger than these materials. Additionally, most of these materials are treated at a high temperature before used so that there may be a physical or a chemical difference such as the change in the structure upon material surface and hence improves the effect of adsorbing the phosphate into the solution [38]. Nonetheless, these kinds of materials usually cost much more than using an oyster shell as the phosphate adsorbent. Plus, these sources may cause any other pollution to the environment.

4. Conclusion

The present study demonstrated that waste oyster shell could feasibly remove the phosphate pollutants. Based on the batch experiments, it is known that the phosphate uptake capacity of an oyster shell enhanced with an increase in temperature and a decrease in the oyster shell powders' dimension. This tendency has shown that phosphate adsorption into an oyster shell favored the surroundings at a high temperature. The thermodynamic parameters were evaluated in the present study. The positive ΔH° revealed that the adsorption process was an endothermic process, while the positive ΔS° suggested a good affinity of phosphate toward an oyster shell; the positive ΔG° indicated that the adsorption process is nonspontaneous. As the temperature rose, the Gibbs free energy decreased, which showed that the adsorption process required energy to transform the reactants into products. On the other hand, the kinetic study was considered for the reaction kinetics. Three kinetic models, pseudo-second-order, Elovich, and intra-particle diffusion, were applied to the experimental data. The pseudo-second-order model appeared to best fit the dynamical adsorption behavior. It was also discovered that the intra-particle diffusion was not the only rate-controlling step. To illustrate the potential of the oyster shell as a phosphate pollutant adsorbent, various phosphate removal sources were compared: an oyster shell is better than a material such as gravel owing to its abundant adsorbing sites; if by contrast with industrial by-products like fly ash, an oyster shell demonstrates weaker effect due to its relatively rare surface area. However, these media are not as environmentally friendly as an oyster shell is. According to the results reported here, a waste oyster shell can be an effective adsorbent for the phosphate removal.

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