

54 (2015) 3031–3043 June



Trends of natural and acid-engineered pumice onto phosphorus ions in aquatic environment: adsorbent preparation, characterization, and kinetic and equilibrium modeling

Gholam Hossein Safari^a, Mansur Zarrabi^b, Mohammad Hoseini^a, Hossein Kamani^c, Jalil Jaafari^a, Amir Hossein Mahvi^{a,d,e,*}

^aSchool of Public Health, Tehran University of Medical Sciences, Tehran, Iran, Tel. +98 2122909114; Fax: +98 2166662267; email: hsafari13@yahoo.com (G.H. Safari), Tel. +98 2188954914; Fax: +98 2166662267; email: m_hoseini2174@yahoo.com (M. Hoseini), Tel. +98 2122909114; Fax: +98 2166662267; email: jalil.jaafari@yahoo.com (J. Jaafari), Tel. +98 2188954914; Fax: +98 2166662267; email: ahmahvi@yahoo.com (A. H. Mahvi)

^bFaculty of Health, Department of Environmental Health Engineering, Alborz University of Medical Sciences, Karaj, Iran, Tel. +98 9126952302; Fax: +98 2166662267; email: zarrabi62@yahoo.com

^cHealth Promotion Research Center and School of Public Health, Zahedan University of Medical Sciences, Zahedan, Iran, Tel. +98 5412428797; Fax: +98 2166662267; email: hossein_kamani@yahoo.com

^dCenters for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran ^eNational Institute of Health Research, Tehran University of Medical Sciences, Tehran, Iran

Received 29 August 2013; Accepted 30 March 2014

ABSTRACT

The objective of this study was to investigate the potential of natural and acid-modified pumice as an adsorbent in phosphorous removal from aqueous solution. Various experimental parameters such as initial phosphorous concentration, adsorbent dosage, contact time, and pH were investigated. The most common isotherms and the kinetic adsorption models were used for survey of phosphorous adsorption mechanism. Results indicated that pH plays a significant role in the adsorption of phosphorous. The adsorption capacity increased with increase in contact time and initial phosphorous concentration and after 30 and 45 min, reached equilibrium for modified and natural pumice, respectively. Maximum adsorption of phosphorous (9.74 mg/g) was obtained in the pH ranging from 5 to 7, pumice dosage of 2 g/L, and contact time of 30 min using the modified pumice. Further increase of adsorbent dosage over 2 g/L didn't have significant effect on the phosphorous adsorption. The experimental results showed that absorption process and equilibrium data were well fitted using the pseudo-second-order kinetic model ($R^2 > 0.99$) and Langmuir No 2 isotherm ($R^2 > 0.99$). The foreign anions such as Cl^{-} , NO_{3}^{-} , SO_{4}^{2-} , and HCO_{3}^{-} didn't have noticeable effects on the phosphorous adsorption. In general, the adsorption capacity of acid-modified pumice in the same conditions is more than natural pumice (55-60%). As general conclusion; modified pumice can be used successfully as low-cost and effective absorbent for phosphorous removal from aqueous solution.

Keywords: Phosphorous; Pumice; Adsorption; Equilibrium studies

^{*}Corresponding author.

^{1944-3994/1944-3986 © 2014} Balaban Desalination Publications. All rights reserved.

1. Introduction

The application of phosphorus is prevalent in many consumer products and industrial processes, especially in fertilizers, water softening, detergents, metallurgy, paints, food, and beverages, pharmaceuticals, and many others practical uses [1]. Phosphorous is commonly found in wastewater and surface water in the form of orthophosphorous, polyphosphorous, and organic phosphorous [2,3]. Municipal wastewater typically contains 4–15 mg/L phosphorus as PO_4^{3-} [4]. Phosphorous has been identified as one of the important components that often results in pollution of the aquatic environment [5]. Presence of the large amount of phosphorus in waters as a main nutrient in the growth of algal and other biological organisms, leads to eutrophication in water bodies such as lakes and ponds [6]. Eutrophication of the confined water bodies is one of the most serious aesthetic and environmental problems, which strongly threaten human and ecological health [7]. Such conditions can lead to excessive development of the aquatic plants and growth of algae, destruction of aquatic life and resorts as well as influence the water quality, mainly via consumption and depletion of dissolved oxygen [1,8,9]. Consequently, removal of phosphorous from surface waters and wastewaters is absolutely important in management and control of eutrophication, protection of water resources, water conservation, and prevents any aesthetic and environmental problems adverse [1,10,11]. Several techniques have been applied for phosphorous removal from surface waters and wastewaters, including physical [12,13], chemical [13-16], biological [17,18], and crystallization methods [19]. Among these methods, chemical precipitation and biological removal processes are the two widely accepted methods for phosphorous removal [2,5,6,20]. Biological removal is a low-cost process, but has disadvantages such as susceptibility to seasonal and daily variations in temperature and changes in the chemical composition [7,21]. Chemical precipitation is widely utilized for phosphorous removal, but high cost of used chemical, production of elevated sludge, and sludge dewatering problem restricts its application [21-24]. Moreover, with respect to thermodynamic and kinetic restrictions, complete removal is impossible by chemical precipitation and biological processes [7,25]. Therefore, in recent years, significant attention has been shifted to application of different types of sorbents due to high efficiency, low cost, and various characteristics [4,9,26]. So, the application of the adsorbents appears to be the most economical method for phosphorus removal from aqueous solution [26,27]. The removal of phosphorus using various types of adsorbents including aluminum and aluminum oxides [1,28], iron and iron oxides [29-32], fly ash [33], slag [34], red mud [35], bauxite [36], silicates [37,38], active carbon [39], and alunite [40] has been investigated. Due to numerous benefits of pumice and its availability in Iran, the aim of this study was to investigate the potential of natural and acid-modified pumice as an adsorbent in phosphorous removal from aqueous solution. Modification with various chemicals has been used by researchers to improve natural mediums adsorption properties [41]. In our previous works, we used natural and modified pumice for removal of fluoride [41], hardness agents [42], and toxic hexavalent chromium [43]. Therefore, in the present work, our data concerning adsorption of phosphorus from aqueous solution by natural and acid-modified pumice are presented. The HCl acid was used for this purpose, since it may remove some impurity from natural adsorbent and increase positive species on adsorbent surface, leading to improved adsorption capacity of negatively charged phosphorus ions.

2. Materials and methods

2.1. Preparation and characterization of the sorbent

In this study, pumice stone provided from Tikmeh Dash district of eastern Azerbaijan (Iran) with 85% porosity was used. The original pumice was crushed and sieved to desirable size (30-20 mesh). Natural pumice stone was thoroughly washed several times with distilled water in order to remove any impurities until the turbidity value became lower than 1 NTU and used as natural adsorbent after drying at 55°C for 24 h to remove the remaining water. To prepare the modified adsorbent, natural pumice was rinsed several times by double-distilled water and immersed in 1 N HCl acid for 24 h. After that, it was washed several times by distilled deionized water, until its effluent turbidity achieved less than 1 NTU and was ultimately dried at 60°C for 24 h and used as a modified adsorbent. The adsorbent morphology was observed with a scanning electron microscope (SEM, Philips-XL30, Holland) equipped with energy dispersive X-ray micro-analysis. The specific surface area of natural and modified adsorbent was measured using a nitrogen adsorption technique based on the Brunauer-Emmet-Teller isotherm model (Micromeretics/Gemini-2372). The functional groups on the surface of used adsorbents were analyzed using Fourier transform infrared spectroscopy (FTIR) at a wavelength of range $400-4,000 \text{ cm}^{-1}$ (Bruker-VERTEX 70, Germany). The chemical compositions of used adsorbents were determined by means of an X-ray fluorescence spectroscopy (XRF) instrument (Philips-Magix Pro, Netherland). The crystalline structures of the used adsorbents were determined using an X-ray diffractometer (XRD) which are collected by means of a PHILIPS Xpert pro with Cu K α as radiation (1.54056 A°) generated at 40 kV and 40 mA instrument. The diffractograms were obtained with a step width of 0.02° (2 θ) and a scan rate of 8°/min.

2.2. Chemicals and experimental procedure

Phosphorous stock solutions (100 mg/L) were prepared from analytical grade potassium dihydrogen phosphorous salt (KH₂PO₄) by using distilled deionized water and diluted as required. All experiments were performed in lab scale and batch system and at temperature of $24 \pm 2^{\circ}$ C using a 250 mL reactor. In all experiments, the sample volume was 100 mL. The solution was magnetically stirred at a speed of 200 rpm. The initial pH was adjusted with H₂SO₄ or NaOH prior to addition of adsorbent. All chemicals used in this study were of reagent grade and were used without further purification. Analytic reagents were obtained from Merck. In this study, effects of variable parameters such as pH (3-11), initial phosphorous concentration (5-25 mg/L), adsorbent dosage (0.5-8 g/L), and contact time on adsorption capacity were evaluated. After adjusting the pH of solution to the desired value, 100 mL sample of phosphorous solution was placed in a 250 mL reactor and required amount of adsorbent was added. The solution was magnetically stirred at 200 rpm at room temperature $(24 \pm 2^{\circ}C)$. Samples were collected at pre-selected intervals, and then samples were filtered through a membrane filter $(0.45 \,\mu\text{m})$ to determine the concentrations of phosphorous. Phosphorous concentration was measured by the molybdenum blue method. To measure residual phosphorous by this method, 10 mL Molybdenum acid ammonium solution, was added to the sample solution and after 10 min, the absorbance was determined at a wavelength of 470 nm using UV/Vis spectrophotometer (Shimadzo-1700, Japan) [44].

3. Results and discussion

3.1. Adsorbent characteristics

In our previous works, we used natural and various modified pumices for the removal of fluoride [41], hardness [42], and chromium [43]. In those works, we discussed the natural and modified pumice in depth and then, here, we avoid the discussion on prepared adsorbents. In brief, the chemical composition of natural pumice according to XRD analysis is presented in Table 1

Chemical	composition	of	the	natural	pumice	(w/w)
measured	by XRF techni	ique				

Component	% (w/w)	Component	% (w/w)
SiO ₂	63.45	SrO	0.09
Al_2O_3	17.24	MgO	1.03
TiO ₂	0.37	K ₂ O	2.16
P_2O_5	0.21	SO_3	0.16
CaO	3.22	Na ₂ O	2.00
Fe ₂ O ₃	2.86	Cl	0.30

Table 1. The main chemical components of natural pumice sample were SiO₂ (i.e. 63.45%) and Al₂O₃ (i.e.17.24%), resembling natural zeolite composition [43]. Modification of natural pumice with HCl leads to improvement in the specific surface of natural pumice from 2.34 to $27.2 \text{ m}^2/\text{g}$ according to the BET isotherm model. The remarkable improvement of the surface area can be attributed to the removal of components occupying the pores of the pumice resulting in more accessible pores and consequently larger surface area. In addition, in our previous works, we used the surface-modified pumice with HCl for removal of negatively charged acid black dye [45] and magnesium chloride-modified pumice for removal of phosphorus [46]. In those works, we exactly explained that surface modification of natural pumice will improve the specific surface area on one hand (in the case of HCl) and also will improve the positive charge of adsorbent surface on the other hand (in the case of magnesium chloride). Therefore, modification of pumice with HCl may improve its porosity and positive charge on adsorbent surface which leads to increase in phosphorous adsorption capacity.

Fig. 1 shows the XRD pattern on natural and modified pumice. As seen, the XRD patterns were not changed remarkably after modification with acid, showing that acid modification did not change the structural framework of the sample. The peaks that appeared at $2\theta = 12.0^{\circ}$, 26.0°, 28.0°, 32.5°, 33.0°, 33.5°, 34.5°, and 28.0° can be ascertained as crystalline phases, while the appearance of a dome between $2\theta = 20$ –40 can be considered as evidence for the presence of some amorphous phase in both samples [43].

Fig. 2 shows the SEM micrographs of the natural and modified pumice adsorbents at magnification of 2.00 KX. The natural pumice surface seems to be irregular in texture with larger grains and sharper edges, while modification with HCl leads to restructured texture with smoother surface.

Fig. 3 shows the FTIR of the natural and modified pumice at wavelengths ranging from 400 to $4,000 \text{ cm}^{-1}$.



Fig. 1. XRD patterns for the natural (a) and modified (b) pumice.

Overall, the IR spectra of the natural and modified pumice appeared to be roughly similar and compatible with those reported in the literature [41–43].

3.2. Effect of agitation time and initial phosphorous concentration

To evaluate the effect of agitation time and initial phosphorous concentration on phosphorous adsorption capacity, experiments were conducted in different concentrations of phosphorous with adsorbent dosage of 2 g/L, pH 5, and various agitation times. Fig. 4 shows that the adsorption of phosphorous increased with increasing the agitation time and remained approximately constant after 30 and 45 min for acid-modified pumice and natural pumice, respectively.

Furthermore, the adsorption of phosphorous increased with increasing initial phosphorous concentration. Therefore, with increasing initial solute concentration from 5 to 25 mg/L, the absorption capacity was increased from 1.76 to 9.74 and from 0.96 to 5.85 mg/g



Fig. 2. SEM micrographs of the natural pumice adsorbent (a) and the HCl-modified adsorbent (b).

for modified and natural pumice, respectively. Our results were well in agreement with the previously published works, showing that the higher the initial solute concentration, the higher the removal efficiency [41–43]. One reason for this phenomenon is due to increasing of phosphorous transfer from



Fig. 3. FTIR spectra of the natural pumice (a) adsorbent and the HCl-modified adsorbent (b).

solution to the surface of adsorbent particles, resulting in the increase of the mass transfer driving force between solid and liquid phases and higher free bands of adsorbent in lower concentration of phosphorous [45,46]. These results are in good agreement with other results obtained in phosphorous adsorption onto coir pith [47] and slag [48].

3.3. Effect of adsorbent dosage

The adsorption of phosphorous increased with increasing adsorbent dosages due to increasing the adsorption active sites and the total available surface areas of the adsorbent. Further increase of adsorbent dosage over 2 g/L didn't have significant effect on the phosphorous adsorption (Fig. 5). Therefore, the optimum dose of adsorbent was found to be 2 g/L for adsorption of phosphorous by pumice. These results are in good agreement with results obtained in fluoride adsorption by pumice [49].

3.3. Effect of pH

The pH of the solution is a principal variable in the adsorption process. To investigate the effect of solution pH, experiments were performed in pH





Fig. 4. Effect of agitation time and initial phosphorous concentration on adsorption capacity: (a) modified pumice (b) natural pumice (adsorbent dose 2 g/L and pH 5).

ranging from 5 to 11 under the following conditions: adsorbent dosage of 2 g/L, phosphorous concentrations of 5-25 mg/L, and agitation time of 30 and 45 min for modified and natural pumice, respectively. As shown in Fig. 6, solution pH plays a significant role in the adsorption process, and the adsorption capacity is absolutely dependent on the pH. Based on the results, the adsorption capacity increased with the increasing pH from 3 to 5, which approximately stayed constant in the range of 5-7 and decreased with increasing pH from 7 to 11. Therefore, maximum adsorption of phosphorous was obtained in pH of 5-7. Phosphorous, depending on the system pH, can be in various forms, such as H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} . The predominant species of phosphorous at pH 3 is H₃PO₄ which is poorly attached to the adsorption sites. With increase in pH, the other species of phosphorous such as $H_2PO_4^-$ and HPO_4^2 are dominant, which can be absorbed well. In the alkaline pH, the amount of OH ions increased as a competitor ion with species of PO_4^{3-} for adsorption on the active sites of adsorbent

Fig. 5. Effect of adsorbent dose on adsorption capacity: (a) modified pumice, agitation time 30 min and (b) natural pumice, agitation time 45 min.

[14,27]. Moreover, in higher pH, ionization of adsorbent and adsorbed leads to make repulsion force in adsorbent surface, which results in a decrease in the adsorption capacity of phosphorous [50]. Based on studies performed, maximum adsorption of phosphorous using red mud and activated alum has been obtained in pH ranging from 5 to 7 and 6.5, respectively [35,51]. On the other hand, influence of solution pH on phosphorous removal efficiency can be explained with zero point charge of natural and modified pumice. In our previous works, the zero point charge was 6.3 [42] and 7.2 [45] for natural and HCl-modified pumice, respectively. Based on zero point charge for natural and modified pumice, at higher and lower values, the surface of pumice is occupied by OH⁻ and H⁺ ions, respectively. In a solution containing negatively charged phosphorus ions, electrostatic attraction between the positively charged pumice and the negatively charged phosphorus ions lead to increase in removal efficiency.



Fig. 6. Effect of pH on adsorption capacity: (a) modified pumice, agitation time 30 min and (b) natural pumice, agitation time 45 min.



Fig. 7. Comparison of the efficiency of natural and modified pumice on adsorption capacity: (adsorbent dose 2 g/L and pH 5).

Table 2

Effects of addition of foreign anions on the adsorption of phosphorous

Species	Removal of phosphorous (%)
PO_4^{3-} alone	78
$PO_4^{\frac{3}{4}} + SO_4^{2-}$	72
$PO_{4}^{3-} + HCO_{3}^{-}$	75
$PO_4^{3-} + NO_3^{-}$	73
$PO_4^{3-} + Cl^{-}$	73

3.4. Comparison of efficiency of natural and modified pumice

Fig. 7 illustrates the efficiency of natural and modified pumice at various concentrations of phosphorous. Natural pumice has some impurity and low sorption capacity and it is also negatively charged [52,53]. Therefore, the objective of adsorbent modification using acid is an improvement of positive surface charges of adsorbent and its adsorption capacity. So,



Fig. 8. Fitting of experimental data onto isotherm model (a) Langmuir 1, (b) Langmuir 2, (c) Freundlich, and (d) Temkin.



Fig. 8. (Continued).

modified pumice has high adsorption capacity (9.74 mg/g) compared to natural pumice (5.85 mg/g). In general, adsorption efficiency of modified pumice in stable condition is 55–60% higher than natural pumice.

Table 4Adsorption characterization based on the RL values

R _L	Adsorption process
$R_{\rm L} > 1$	Unfavorable
RL = 1	Linear
0 <rl<1< td=""><td>favorable</td></rl<1<>	favorable
RL = 0	Irreversible

3.5. Effect of foreign ions

To evaluate the influence of foreign anions such as Cl⁻ (70 mg/L), NO₃⁻ (50 mg/L), SO₄²⁻ (60 mg/L), and HCO₃⁻ (100 mg/L) on the phosphorous adsorption, experiments were performed with adsorbent dosage of 2 g/L, phosphorous concentration of 25 mg/L, agitation time of 30 min, and pH 5. The results showed that these anions did not produce a noticeable effect on the phosphorous adsorption (Table 2). The effect of these anions on the phosphorous adsorption was as in the order of:

$$SO_4^{2-} > NO_3^- > Cl^- > HCO_3^-$$

These results are in good agreement with other studies carried out in phosphorous adsorption by Fe(III)/Cr(III) hydroxide [2] and $ZnCl_2$ -activated coir pith carbon [27].

3.6. Adsorption isotherm

Data analysis obtained from the isotherm studies were applied in explaining the reaction of adsorbent

Table 3 Characteristics and isotherm constants for phosphorous adsorption on modified and natural pumice

Isotherm model	Principle equation	Linear equation	Parameters	Modified pumice	Natural pumice
Freundlich	$q_{\rm e} = K_{\rm f} C_{\rm e}^{\frac{1}{n}}$	$\log \left(q_{\rm e}\right) = \log K_{\rm f} + 1/n \log C_{\rm e}$	R^2	0.970	0.998
	,		K _f	1.00	4.56
I	$q_{\rm m}bC_{\rm e}$	$C_{\rm e}$ $C_{\rm e}$ 1	n	0.53	0.75
Langmuir 1 $q_e = \frac{f_{me}}{1 + bC_e}$	$\frac{1}{q_{\rm e}} = \frac{1}{q_{\rm m}} + \frac{1}{q_{\rm m}b}$	R^2	0.950	0.959	
			$q_{\rm m}$	5.46	9.43
		1 1 1	b	0.191	0.032
Langmuir 2		$\frac{1}{-} = \frac{1}{-12} + \frac{1}{-}$	R^2	0.995	0.998
0		$q_{\rm e} q_{\rm m} b C_{\rm e} q_{\rm m}$	$q_{\rm m}$	5.46	8.06
	DT		b	0.191	0.036
Temkin	$q_{\rm e} = \frac{KT}{L} \ln (k_t C_{\rm e})$	$q_{\rm e} = B_1 \ln(k_{\rm t}) + B_1 \ln(C_{\rm e})$	R^2	0.831	0.911
	b_1		b_1	20.45	60.07
			κ _T	1.26	2.67

Table 5		
RL values in	different concentrations	of phosphorous

	Modified pumice		Pumice		
Phosphorous conc. (mg/L)	b (L/mg)	$R_{\rm L}$	b (L/mg)	R _L	
5	0.191	0.51	0.036	0.84	
10		0.34		0.73	
15		0.25		0.64	
20		0.20		0.58	
25		0.17		0.52	

Table 6

Specifications of the kinetics models investigated in this study

Kinetics model	Principle equation	Linear equation
Pseudo-first-order model	$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_1(q_{\mathrm{e}} - q_{\mathrm{t}})$	$\log\left(1 - \frac{q_{\rm t}}{q_{\rm e}}\right) = -\frac{k_1}{2.303}t$
Pseudo-second-order model	$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_2(q_{\mathrm{e}} - q_{\mathrm{t}})^2$	$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{1}{q_{\rm e}} t$
Modified pseudo-first-order model	$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_{\mathrm{m}}\frac{q_{\mathrm{e}}}{q_{\mathrm{t}}}(q_{\mathrm{e}}-q_{\mathrm{t}})$	$\ln\left(1-rac{q_{ m t}}{q_{ m e}} ight)+rac{q_{ m t}}{q_{ m e}}=-k_{ m m}t$
Intra-particle diffusion model	_	$q = k_{\rm i} t^{0.5} + c$

with adsorbed material and optimizing the amount of absorbent [54]. To investigate the equilibrium adsorption isotherm, experiments were performed with fixed adsorbent dosage (2g/L) and various initial phosphorous concentrations (5-25 mg/L) for 180 min contact time at pH 5, temperature of 25°C, and 200 rpm. In this research, experimental data of adsorption equilibrium were assessed using Langmuir 1 and 2, Freundlich, and Temkin isotherms. Fig. 8 shows a plot of the linearized forms of the isotherm models used in this study. Analysis of linear regression showed that the adsorption of phosphorous using modified and natural pumice followed by Langmuir and Freundlich isotherm models, respectively. Based on the results, the Langmuir 2 isotherm model represented the best fit with experimental data ($R^2 > 0.99$) compared to the other isotherm models. These results are in good agreement with other studies carried out in phosphorous adsorption by modified activated alumina [55], modified clinoptilolite [56], and simple and modified nanozeolite Y [57]. Characteristics and parameters obtained from isotherm studies are listed in Table 3. The basic features of Langmuir isotherm can be described by a constant known as equilibrium parameter R_L [53,58,59]:



 $R_{\rm L} = 1/(1 + bC_0)$

Fig. 9. Plots of the pseudo-second-order kinetics at: adsorbent dose, 2 g/L; pH 5.0; temperature, 25°C: (a) acid-treated pumice and (b) natural pumice.

	Modified pumice					Pumice	Pumice		
Phosphorous conc. (mg/L)	$\overline{R^2}$	ge (exp)	ge (calc)	<i>k</i> ₂	R^2	q _{e (exp)}	<i>q</i> e (calc)	<i>k</i> ₂	
5	0.990	1.78	2.05	0.063	0.990	0.99	1.17	0.059	
10	0.994	3.78	4.27	0.035	0.980	2.06	2.50	0.026	
15	0.992	5.57	6.53	0.022	0.987	3.28	3.87	0.019	
20	0.993	7.80	8.85	0.017	0.987	4.72	5.61	0.012	
25	0.993	9.77	10.98	0.014	0.098	5.95	6.84	0.012	

Table 7 parameters of the pseudo-second-order kinetic model at various initial phosphorous concentrations

where *b* is the Langmuir constant, C_0 is the initial concentration (mg/g), and R_L values illustrate the type of adsorption process. The R_L values in the range of 0–1 illustrate favorable adsorption (Table 4). The R_L values were in the range of 0–1 for all the phosphorous concentrations assessed.

3.7. Phosphorous adsorption kinetics

The studies of adsorption kinetics are used to determine the absorption efficiency and the kind of adsorption mechanism. In this research, the phosphorous adsorption kinetic data were investigated with pseudo-first-order model, pseudo-second-order model, modified pseudo-first-order model, and intra-particle diffusion model. Specifications of the kinetic models investigated in this study are listed in Table 6. To evaluate the phosphorous adsorption kinetic by modified and natural pumice, experiments were performed in various initial phosphorous concentrations the (5-25 mg/L), adsorbent dosage of 2 g/L, pH 5, temperature of 25°C with the contact times of 60 and 90 min for modified and pumice, respectively. Based on the obtained results, the pseudo-second-order model represented the best fit with experimental data ($R^2 > 0.99$) compared to the other kinetic models. The high values of $(R^2 > 0.99)$ at all various initial concentrations of phosphorous indicated that the adsorption of phosphorous using modified and natural pumice was followed by the pseudo-second-order kinetic model. Therefore, mechanism of the phosphorous adsorption predominantly is managed by chemical bonding or chemisorptions. Plots of the pseudo-second-order kinetic model at various initial phosphorous concentrations are illustrated in Fig. 9 and parameters of the model are presented in Table 7. These results are in good agreement with other studies carried out in phosphorous adsorption with iron hydroxide-eggshell [4], electrocoagulated metal hydroxides sludge [8], ZnCl2-activated coir pith carbon [27], modified coir pith [47], calcined alunite [58], red mud [59], and dolomite [60].

4. Conclusion

In this study, the adsorption of phosphorous was investigated using the natural and modified pumice. The results indicated that the adsorption capacity of acid-modified pumice is more than natural pumice at all concentrations used in this research. Operating parameters, such as, initial phosphorous concentration, contact time, adsorbent dosage, and pH have effect on the absorption process of phosphorous. The adsorption capacity increased with increase in contact time and initial phosphorous concentration and after 30 and 45 min, reached equilibrium for modified and natural pumice, respectively. The solution pH plays an important role in the adsorption process of phosphorous, and maximum adsorption of phosphorous (9.74 mg/g) was obtained in the pH ranging from 5 to 7, pumice dosage of 2g/L and agitation time of 30 min using the modified pumice. The foreign anions such as Cl⁻, NO₃⁻, SO₄²⁻, and HCO₃⁻ didn't have noticeable effects on the phosphorous adsorption. The experimental results also showed that absorption process and equilibrium data were well fitted by pseudo-second-order kinetic models (R^2 > 0.99) and isotherm of Langmuir no 2 ($R^2 > 0.99$). This means that absorption process occurs as a monolayer and dominantly managed by chemical bonding or chemisorptions. Based on the above good results, the acid-modified pumice could be considered as a low-cost and effective absorbent for the removal of phosphorous from aqueous solution.

Acknowledgments

The financial and technical support of this research was provided by the Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences. All authors gratefully acknowledged the Tehran University of Medical Sciences.

References

- K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphorous species from solution by adsorption onto calcite used as adsorbent, J. Hazard. Mater. 139 (2007) 447–452.
- [2] C. Namasivayam, K. Prathap, Recycling Fe(III)/Cr(III) hydroxide, an industrial solid waste for the removal of phosphate from water, J. Hazard. Mater. 123 (2005) 127–134.
- [3] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, The adsorption of phosphate from an aquatic environment using metalloaded orange waste, J. Colloid. Interface. Sci. 312 (2007) 214–223.
- [4] N.Y. Mezenner, A. Bensmaili, Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste, Chem. Eng. J. 147 (2009) 87–96.
- [5] Y. Seida, Y. Nakano, Removal of phosphate by layered double hydroxides containing iron, Water Res. 36 (2002) 1306–1312.
- [6] S. Karaca, A. Gürses, M. Ejder, M. Açıkyıldız, Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite, J. Hazard. Mater. 128 (2006) 273–279.
- [7] D. Zhao, A.K. Sengupta, Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers, Water Res. 32 (1998) 1613–1625.
- [8] A. Golder, A. Samanta, S. Ray, Removal of phosphate from aqueous solutions using calcined metal hydroxides sludge waste generated from electrocoagulation, Sep. Purif. Technol. 52 (2006) 102–109.
- [9] Y. Zhao, J. Wang, Z. Luan, X. Peng, Z. Liang, L. Shi, Removal of phosphate from aqueous solution by red mud using a factorial design, J. Hazard. Mater. 165 (2009) 1193–1199.
- [10] H. Liu, X. Sun, C. Yin, C. Hu, Removal of phosphate by mesoporous ZrO₂, J. Hazard. Mater. 151 (2008) 616–622.
- [11] S.-L. Wang, C.-Y. Cheng, Y.-M. Tzou, R.-B. Liaw, T.-W. Chang, J.-H. Chen, Phosphate removal from water using lithium intercalated gibbsite, J. Hazard. Mater. 147 (2007) 205–212.
- [12] A. Omoike, G. Vanloon, Removal of phosphorus and organic matter removal by alum during wastewater treatment, Water Res. 33 (1999) 3617–3627.
- [13] T. Clark, T. Stephenson, P. Pearce, Phosphorus removal by chemical precipitation in a biological aerated filter, Water Res. 31 (1997) 2557–2563.
- [14] L. Ruixia, G. Jinlong, T. Hongxiao, Adsorption of fluoride, phosphorous, and arsenate ions on a new type of ion exchange fiber, J. Colloid. Interface. Sci. 248 (2002) 268–274.
- [15] A.H. Mahvi, S.J.A.d. Ebrahimi, A. Mesdaghinia, H. Gharibi, M.H. Sowlat, Performance evaluation of a continuous bipolar electrocoagulation/electrooxidation-electroflotation (ECEO-EF) reactor designed for simultaneous removal of ammonia and phosphorous from wastewater effluent, J. Hazard. Mater. 192 (2011) 1267–1274.
- [16] H. Gharibi, A.H. Mahvi, M. Chehrazi, R. Sheikhi, S.S. Hosseini, Phosphorous removal from wastewater effluent using electro-coagulation by aluminum and iron plates, Anal. Bioanal. Chem. 2 (2010) 165–177.

- [17] H. Stensel, R. Sedlak, Principles of Biological Phosphorus Removal, Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice, 2nd ed., Lewis Publishers for the Soap and Detergent Association, New York, NY, 1991, pp. 141–166.
- [18] A. Mahvi, R. Nabizadh, M. Pishrafti, T. Zarei, Evaluation of single stage USBF in removal of nitrogen and phosphorus from wastewater, Eur. J. Sci. Res. 23 (2008) 204–211.
- [19] E. Moreno, K. Varughese, Crystal growth of calcium apatites from dilute solutions, J. Cryst. Growth 53 (1981) 20–30.
- [20] F. Gan, J. Zhou, H. Wang, C. Du, X. Chen, Removal of phosphate from aqueous solution by thermally treated natural palygorskite, Water Res. 43 (2009) 2907–2915.
- [21] Y. Li, C. Liu, Z. Luan, X. Peng, C. Zhu, Z. Chen, Z. Zhang, J. Fan, Z. Jia, Phosphate removal from aqueous solutions using raw and activated red mud and fly ash, J. Hazard. Mater. 137 (2006) 374–383.
- [22] N. Bektas, H. Akbulut, H. Inan, A. Dimoglo, Removal of phosphate from aqueous solutions by electro-coagulation, J. Hazard. Mater. 106 (2004) 101–105.
- [23] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
- [24] S. Yeoman, T. Stephenson, J. Lester, R. Perry, The removal of phosphorus during wastewater treatment: a review, Environ. Pollut. 49 (1988) 183–233.
- [25] L.M. Blaney, S. Cinar, A.K. SenGupta, Hybrid anion exchanger for trace phosphate removal from water and wastewater, Water Res. 41 (2007) 1603–1613.
- [26] S. Tian, P. Jiang, P. Ning, Y. Su, Enhanced adsorption removal of phosphate from water by mixed lanthanum/aluminum pillared montmorillonite, Chem. Eng. J. 151 (2009) 141–148.
- [27] C. Namasivayam, D. Sangeetha, Equilibrium and kinetic studies of adsorption of phosphate onto ZnCl₂ activated coir pith carbon, J. Colloid. Interface. Sci. 280 (2004) 359–365.
- [28] B.B. Johnson, A.V. Ivanov, O.N. Antzutkin, W. Forsling, 31P nuclear magnetic resonance study of the adsorption of phosphate and phenyl phosphates on γ -Al₂O₃, Langmuir 18 (2002) 1104–1111.
- [29] Z. Hongshao, R. Stanforth, Competitive adsorption of phosphate and arsenate on goethite, Environ. Sci. Technol. 35 (2001) 4753–4757.
- [30] X. Huang, Intersection of isotherms for phosphate adsorption on hematite, J. Colloid. Interface. Sci. 271 (2004) 296–307.
- [31] R.-S. Juang, J.-Y. Chung, Equilibrium sorption of heavy metals and phosphorous from single-and binary-sorbate solutions on goethite, J. Colloid. Interface. Sci. 275 (2004) 53–60.
- [32] S.-H. Lin, H.-C. Kao, C.-H. Cheng, R.-S. Juang, An EX-FAS study of the structures of copper and phosphate sorbed onto goethite, Colloids. Surf., A, 234 (2004) 71– 75.
- [33] S. Lu, S. Bai, L. Zhu, H. Shan, Removal mechanism of phosphate from aqueous solution by fly ash, J. Hazard. Mater. 161 (2009) 95–101.
- [34] E. Oguz, Thermodynamic and kinetic investigations of PO₃₋₄ adsorption on blast furnace slag, J. Colloid. Interface. Sci. 281 (2005) 62–67.
- [35] C.-J. Liu, Y.-Z. Li, Z.-K. Luan, Z.-Y. Chen, Z.-G. Zhang, Z.-P. Jia, Adsorption removal of phosphate

from aqueous solution by active red mud, J. Environ. Sci. 19 (2007) 1166–1170.

- [36] H.S. Altundoğan, F. Tümen, Removal of phosphates from aqueous solutions by using bauxite. I: Effect of pH on the adsorption of various phosphates, J. Chem. Technol. Biotechnol. 77 (2002) 77–85.
- [37] T. Kasama, Y. Watanabe, H. Yamada, T. Murakami, Sorption of phosphates on Al-pillared smectites and mica at acidic to neutral pH, Appl. Clay Sci. 25 (2004) 167–177.
- [38] E.W. Shin, J.S. Han, M. Jang, S.-H. Min, J.K. Park, R.M. Rowell, Phosphate adsorption on aluminumimpregnated mesoporous silicates: Surface structure and behavior of adsorbents, Environ. Sci. Technol. 38 (2004) 912–917.
- [39] D. Bhargava, S. Sheldarkar, Use of TNSAC in phosphorous adsorption studies and relationships. Literature, experimental methodology, justification and effects of process variables, Water Res. 27 (1993) 303–312.
- [40] M. Özacar, Phosphorous adsorption characteristics of alunite to be used as a cement additive, Cem. Concr. Res. 33 (2003) 1583–1587.
- [41] M. Sepehr, V. Sivasankar, M. Zarrabi, M. Senthil Kumar, Surface modification of pumice enhancing its fluoride adsorption capacity: An insight into kinetic and thermodynamic studies, Chem. Eng. J. 228 (2013) 192–204.
- [42] M. Sepehr, M. Zarrabi, H. Kazemian, A. Amrane, K. Yaghmaian, H.R. Ghaffari, Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems, Appl. Surf. Sci. 274 (2013) 295–305.
- [43] M. Noori Sepehr, A. Amrane, K.A. Karimaian, M. Zarrabi, H.R. Ghaffari, Potential of waste pumice and surface modified pumice for hexavalent chromium removal: Characterization, equilibrium, thermodynamic and kinetic study, J. Taiwan. Inst. Chem. Eng. 45 (2014) 635–647.
- [44] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.
- [45] K.A. Krishnan, A. Haridas, Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith, J. Hazard. Mater. 152 (2008) 527–535.
- [46] A. Drizo, C. Forget, R.P. Chapuis, Y. Comeau, Phosphorus removal by electric arc furnace steel slag and serpentinite, Water Res. 40 (2006) 1547–1554.
- [47] A.H. Mahvi, B. Heibati, A. Mesdaghinia, A.R. Yari, Fluoride adsorption by pumice from aqueous solutions, J. Chem. 9 (2012) 1843–1853.
- [48] N.M. Agyei, C. Strydom, J. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag,

ordinary Portland cement and related blends, Cem. Concr. Res. 32 (2002) 1889–1897.

- [49] N.p. Chi, B.z. Dong, Y. Liao. Advanced phosphorous removal by adsorption onto activated alum porcelain in simulation water, in the 4th International Conference on Bioinformatics and Biomedical Engineering (iCBBE), Chengdu, 2010, pp. 1–4.
- [50] B. Ersoy, A. Sariisik, S. Dikmen, G. Sariisik, Characterization of acidic pumice and determination of its electrokinetic properties in water, Powder Technol. 197 (2010) 129–135.
- [51] M.R. Samarghandi, M. zarrabi, M. Noorisepehr, A. Amrani, G.H. Safari, S. Bashiri, Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions: kinetic, equilibrium and thermodynamic studies, Iran. J. Environ. Health. Sci. Sci. Eng. 9 (2012) 33–44.
- [52] B. Hameed, Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue, J. Hazard. Mater. 162 (2009) 939–944.
- [53] C.S. Ding, F.M. Ni, Y.L. Zou, Q.F. Zhu, Behavior of phosphorus adsorption from aqueous solutions on modified activated alumina, Adv. Mat. Res. 152 (2011) 945–949.
- [54] M. Malakootian, N. Yousefi, N. Jaafarzadeh Haghighifard, Kinetics modeling and isotherms for adsorption of phosphorous from aqueous solution by modified clinoptilolite, Water. Waste. 4 (2011) 21–29.
- [55] M.T. Samadi, M.H. Saghi, K. Ghadiri, M. Hadi, M. Beikmohammadi, Performance of simple nano zeolite Y and modified nano zeolite Y in phosphor removal from aqueous solutions, Iran, J. Health. Environ. 3 (2010) 27–33.
- [56] S. Ghadiri, R. Nabizadeh, A. Mahvi, S. Nasseri, H. Kazemian, A. Mesdaghinia, S. Nazmara, Methyl tertbutyl ether adsorption on surfactant modified zeolites, Iranian Iran, J. Environ. Health. Sci. Eng. 7 (2010) 241– 252.
- [57] M.R. Boldaji, A. Mahvi, S. Dobaradaran, S. Hosseini, Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water, Int. J. Environ. Sci. Technol. 6 (2009) 629–632.
- [58] M. Özacar, Equilibrium and kinetic modelling of adsorption of phosphorus on calcined alunite, Adsorption 9 (2003) 125–132.
- [59] W. Huang, S. Wang, Z. Zhu, L. Li, X. Yao, V. Rudolph, F. Haghseresht, Phosphate removal from wastewater using red mud, J. Hazard. Mater. 158 (2008) 35–42.
- [60] S. Karaca, A. Gürses, M. Ejder, M. Açıkyıldız, Kinetic modeling of liquid-phase adsorption of phosphate on dolomite, J. Colloid. Interface. Sci. 277 (2004) 257–263.