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Sorption of aquatic phosphorus onto native and chemically-modified plant residues: modeling the isotherm and kinetics of sorption process

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ABSTRACT

Removal of phosphorus (P) as a pollutant from aqueous solutions by the biological materials is a new approach by which plant and microbial biomass are used as sorbents. In this research, the residues of sunflower, potato, canola, and walnut shell in the form of native and chemically modified were used as biosorbents to remove P from aqueous solutions. Sorption of P by these sorbents was studied using batch technique. The effect of pH and contact time was also investigated. Optimum pH for P sorption by sunflower, potato, canola, and walnut shell residues was found to be 5, 3, 5, and 3.5, respectively. The values of zero point charge (pH_{zpc}) measured for sunflower, potato, canola, and walnut shell residues were 6.06, 6.80, 6.15, and 5.85, respectively. Maximum sorption of P by native sorbents was found to be in the range of 2.8–4.3 $mg\,g^{-1}$. Chemical modification of the sorbents was carried out by urea, $FeCl_3$, and $CaCl_2$. The modification of sorbents increased the pH_{zpc} and consequently increased the P sorption. Phosphorus sorption isotherm was described well by Langmuir isotherm model. The speciation of P in solution was carried out by Visual Minteq program and indicated that the dominant species of P in solution of all sorbents was $H_2PO_4^-$. The P sorption kinetic followed the pseudo-second-order model. Scanning electron microscopy images revealed that modification of the sorbents resulted in the development of the porous surface with coarse fibrous texture making the surface more suitable for the attachment of reactive functional groups.

Keywords: Pollution; Sorption; Plant residues; Phosphorus; Isotherm; Kinetic

1. Introduction

One of the environmental serious problems is the pollution of soil and water by various pollutants. Phosphorus (P) is a useful element in providing requirements for humans, plants, and other organisms, but the additional concentration more than the critical level in water sources threats the health and the life of aquatic organisms seriously.

In surface freshwater systems, P is usually the limiting factor for algae growth, so the increase in P in surface freshwaters leads to excessive algae growth. Then, P removal has a great significance in controlling the algae bloom [1]. An excessive concentration of this nutrient in water is often responsible for eutrophication leading to short- and long-term environmental problems in lakes and water reservoirs, coastal areas, and other confined water bodies, and furthermore it is a threat to ecological health [2].

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Various techniques have been developed in order to remove P from water and wastewater [3] which includes chemical precipitation [4,5], adsorption using suitable materials [6], biological treatment [7], and crystallization [8]. Most of these methods are not suitable for small-scale industries due to the disadvantages such as high operation cost, incomplete removal, and high energy requirements.

Several studies have demonstrated that adsorption technique is a suitable and effective method rather than others in order to remove P from aqueous solutions. Recently, numerous attempts have been performed in finding inexpensive and effective sorbents produced from agricultural byproducts. The sorbents originated from agricultural byproducts are particularly advantageous due to their low-cost and high availability. In addition, the appropriate chemical composition in agricultural byproducts with high contents of carbohydrate polymers (e.g. cellulose and hemicelluloses) suggest a widespread potential application for sorbent production; this is due to the existence of large amount of easily available hydroxyl groups in cellulose and hemicelluloses, which can easily make a series of chemical reactions, such as esterification, etherification, and copolymerization [9]. The lignocellulosic materials exhibit interesting capacities for pollutants adsorption which can be increased by activation process or by chemical surface modification [10,11]. Benyoucef and Amrani [12] showed that chemical surface modification can enhance the capacity of sorbent for sorption of phosphate. There are few studies about sorption of P by native or modified agricultural by products. Chemical modification of these materials may cause to enhance their P sorption capacity.

In the previous studies, the biosorption of P by some plant residues has been less investigated. The novel points of the present study are: (1) the use of three various chemical agents to modify the plant residues, (2) employ the pH_{zpc} concept in justification of sorption mechanisms of P, and (3) the speciation of P solutions and determination of saturation index of P minerals in isotherm experiments. Our objectives in this study are: (1) investigation of sorption capacity of four native sorbents (sunflower, potato, canola, and walnut shell residues) to remove P from aqueous solutions, (2) chemical modification of these sorbents in order to enhance their sorption capacity, and (3) the study of isotherm and kinetic sorption of P by empirical models and also to know the prevalent species of P in sorption process.

2. Materials and methods

2.1. Materials

Residues of sunflower (*Helianthus annuus*), potato (*Solanum tuberosum*), canola (*Brassica napus*), and walnut (*Juglans regia*) shell were gathered in harvesting season in Hamadan city, western Iran. In order to remove soluble materials in the residues, the samples were washed with distilled water for three times and then were dried in an oven at approximately 80°C for 24 h. The oven-dried samples were passed through a 1 mm sieve. Thereafter, the samples were maintained in special containers for subsequent experiments.

The stock solution of P was prepared by dissolving known quantity of KH_2PO_4 in deionized water. The stock solution was finally diluted to obtain standard solutions.

2.2. Chemical characterization of sorbents

In order to measure the pH of the washed residues, 25 ml distilled water was added to 2.5 g of residues and after 16 h of shaking of the samples, the suspensions were filtered and the pH of washings was measured with pH meter (13). The total amounts of Ca, Mg, K, and Na were determined using digestion by nitric acid [13]. The total concentration of N, C, and P was also measured by Kjeldahl digestion [14], combustion process [14], and Murphey and Riley [15] methods, respectively.

2.3. Modification of sorbents

Because of low capability of native sorbents to remove P from aqueous solutions, these sorbents were modified using three methods. For modifying the plant residues, three chemical materials, urea, $CaCl_2$, and $FeCl_3$ were selected. Because of specific interactions between the P ions and Ca^{2+} and Fe^{3+} cations, the $CaCl_2$ and $FeCl_3$ were selected. The selection of urea as a modifier of plant residues was due to the presence of nitrogen in urea structure, which probably can affect the amine groups of adsorbent structure.

2.3.1. Modification by urea

In the process of modification by urea, 10 g of each sorbent sample were agitated in the presence of urea (200 $g\,l^{-1}$) for 24 h, washed with deionized water, and then dried in oven (80°C) overnight [12].

2.3.2. Modification by $FeCl_3$

The modification of sorbents was carried out using the same procedure as previously described [16]. Ten grams of each sorbent was soaked with 200 ml of 0.01 M $FeCl_3$ solution at 70°C for 4 h. After heating for 4 h, a black slurry type of solid mass was obtained. It was followed by cooling it at room temperature until the iron(III)-loaded sorbent was obtained. The modified sorbent was rinsed with distilled water and filtered several times until the physically adhered iron (III) was removed. Finally, it was dried at 70°C for 4 h and stored in a specific container.

2.3.3. Modification by $CaCl_2$

Ten grams of each sorbent were soaked with 200 ml of 0.01 M $CaCl_2$ solution. After 24 h of shaking, the Ca-loaded sorbent was washed with distilled water and filtered several times until the physically adhered Ca was removed. Finally, it was dried at 70°C for 4 h and stored in a specific container.

2.4. Determination of the zero point of charge (pH_{zpc})

The pH, in which the net charge of the solid surface is zero, is referred to the zero point of charge (pH_{zpc}). The determination of pH_{zpc} of the samples was carried out using the same method described by Rivera-Utrilla et al. [17]: 20 ml of 0.01 M NaCl solution were placed in closed Erlenmeyer flasks. The pH of each solution in each flask was adjusted to be 2, 4, 6, 8, 10, and 12 by adding appropriate amounts of 0.1 M HCl or 0.1 M NaOH solutions. Then, 0.06 g of each sample was added and final pH was measured after 48 h at equilibrium at room temperature. The pH_{zpc} is the intersection point of final pH vs. initial pH curve with the line of blank samples. In this section, the pH_{zpc} of native and modified sorbents was measured.

2.5. Scanning electron microscopy micrographs

SEM technique (Model: Philips XL30) was employed to observe the surface physical morphology of the some used sorbents before and after sorption of P.

2.6. Sorption experiments

The effect of pH, contact time, and P concentration on P sorption were investigated. Batch experiments were carried out as P initial concentration was 100 mg l^{-1} and sorbent dose was 4 g l^{-1} at room temperature. After shaking, the solution samples were centrifuged and equilibrium concentration was determined using UV–visible spectrophotometer. All experiments were performed in duplicates.

The amount of P sorbed by sorbents in the sorption system was calculated using Eq. (1):

$$Q_e(\text{mg g}^{-1}) = \frac{(C_i - C_e)V}{M} \tag{1}$$

where Q_e is the P sorbed at equilibrium (mg g^{-1}), and C_i and C_e are initial and equilibrium concentrations of the P, respectively (mg l^{-1}), V is the volume of aqueous phase (l), and M is sorbent dose (g).

The percent P removal (%) was calculated using Eq. (2):

$$\text{Removal}\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

2.6.1. Effect of pH

The effect of pH on removal of P was investigated at different pH values (2, 3, 4, 5, 6, 7, 8, 9, and 10). The initial concentration of P was 100 mg l^{-1}. The samples were shaken for 24 h at room temperature.

2.6.2. Effect of contact time

In order to optimize the contact time, sorption process was carried out at different shaking times (5, 10, 20, 50, 120, 200, 600, and 1,440 min) at optimum pH value obtained from pervious section. The initial concentration of P was 100 mg l^{-1}.

2.6.3. Sorption isotherms

The sorption isotherms were evaluated by contacting 0.05 g of sorbents with 25 ml of different initial concentration of P solution (0–300 mg l^{-1}). The mixture was shaked in a centrifuge tube at optimum contact time and pH. After shaking, the sorbents were separated by filtration and the equilibrium concentration of P in the aqueous solution was determined.

The experimental sorption isotherms were described by Freundlich and Langmuir models represented as Eqs. (3) and (4), respectively:

$$Q_e = K_{\text{Fr}} C_e^{\frac{1}{n}} \tag{3}$$

$$Q_e = \frac{K_L C_e Q_{\max}}{1 + K_L C_e} \tag{4}$$

where K_{Fr} and n are Freundlich equation constants, K_L is the Langmuir constant related to the energy of sorption ($\mathrm{l\,mg^{-1}}$), and Q_{max} is the maximum sorption capacity indicating amount of P per unit weight of adsorbent to form a complete monolayer on the surface.

The values of coefficient of determination (R^2) and standard error (SE) were calculated to determine the goodness-of-fit of kinetic and isotherm models, which were used to describe sorption of P.

2.6.4. Speciation of P in isotherm experiments

After performance of sorption isotherms of P by modified sorbents, speciation of P in the highest concentration of isotherms ($300\ \mathrm{mg\,l^{-1}}$) was carried out by Visual MINTEQ program and subsequently the saturation indices of P minerals were calculated.

2.6.5. The Kinetic of sorption of P

The kinetic of sorption of P was described using pseudo-first-order and pseudo-second-order equations which are mathematically expressed as Eqs. (5) and (6), respectively:

$$\ln(Q_f - Q_t) = \ln Q_f - K_1 t \tag{5}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_f^2} + \frac{t}{Q_f} \tag{6}$$

where Q_t and Q_f ($\mathrm{mg\,g^{-1}}$) are the amounts of P adsorbed on the sorbent at time t and equilibrium time, respectively, K_1 ($\mathrm{min^{-1}}$) and K_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) are the rate constant of sorption in pseudo-first-order and pseudo-second-order equations, respectively.

2.6.6. Statistical analysis

The statistical analysis of data was carried out using SAS program (v. 9.1).

3. Results and discussion

3.1. The characterization of sorbents

Some chemical properties of plant residues are given in Table 1. The pH of plant residues ranged from 5.1 to 6.2 and the maximum and the minimum pH were obtained for potato and canola residues. Also, total P, N, C, Na, K, Ca, and Mg concentration, and C/N, C/P ratios of plant residues were indicated in Table 1.

The $\mathrm{pH_{zpc}}$ of the sorbents is graphically shown in Fig. 1. In this figure, the final pH of sorbents in NaCl solution after 48 h vs. initial pH as well as the variation of pH of blank solutions (without sorbent material) is indicated. The intersection point of two lines is cut together, equaled to $\mathrm{pH_{zpc}}$. The $\mathrm{pH_{zpc}}$ of the sunflower, potato, canola, and walnut shell residues was 6.06, 6.8, 6.1, and 5.8, respectively.

The measurement of $\mathrm{pH_{zpc}}$ of sorbent can provide useful information about the mechanism of uptake of cations and anions from the aqueous solutions. The amount of net charge and characterization of sorbent surface are two important factors affecting sorption process. Although structure of these materials is mainly made from cellulose, hemicelluloses, and lignin they are generally similar in structure, the type of functional groups and their acidic and basic properties are different.

The SEM micrographs of native sorbents are shown in Fig. 2. These images present morphologic status of the sorbents as uneven and porous structure and heterogeneous surface. According to these images, it can be said that morphological properties of these materials are detectable.

3.2. Effect of pH on P sorption

Results of the effect of pH on P sorption by sorbents are shown in Fig. 3. The P sorption by native sorbents was studied in pH ranged from 2 to 10. Increase in pH from 2 to 5 caused to an increase in P sorption by sunflower residues, but pH change from 5 to 10, decreased P sorption. Desire range of pH for P sorption by this sorbent was 3–6. Also, the optimum pH range of pH for P sorption by potato, canola, and walnut shell residue was 3–5, 3–6, and 2.5–4, respectively.

Krishnan and Haridas [16] reported that P sorption by coir pith was desired in the range of pH 2–5. The $\mathrm{pH_{zpc}}$, P speciation in solution, and its affinity to sorption sites and surface chemistry indicate the dependency of sorption to pH [16]. The $\mathrm{pH_{zpc}}$ obtained for sunflower, potato, canola, and walnut shell residues were 6.06, 6.80, 6.15, and 8.85, respectively. Based on the definition of $\mathrm{pH_{zpc}}$, the trend of P sorption in $\mathrm{pH_s}$ lower than $\mathrm{pH_{zpc}}$ toward $\mathrm{pH_{zpc}}$ should be descending. The optimum pH of P sorption by all sorbents was less than their $\mathrm{pH_{zpc}}$ and the amount of sorption was decreased toward $\mathrm{pH_{zpc.}}$ These results suggest that the major part of P sorption has electrostatic nature and

Table 1
Chemical properties of plant residues

Residues	pH	Na (mg g^{-1})	K (mg g^{-1})	Ca (mg g^{-1})	Mg (mg g^{-1})	P (mg g^{-1})	N (mg g^{-1})	C (mg g^{-1})	C/N	C/P
Sunflower	5.6	1.5	32.5	8.7	4.1	2.1	4.8	421	87.7	200.5
Potato	6.2	5.4	67.7	18.9	7.2	2.0	17	430	25.3	215.0
Canola	5.1	5.1	21.9	12.3	4.8	0.7	6.7	465	69.4	664.3
Walnut shell	5.4	4.9	20.6	6.2	2.9	1.2	4.9	516	105.3	430.0

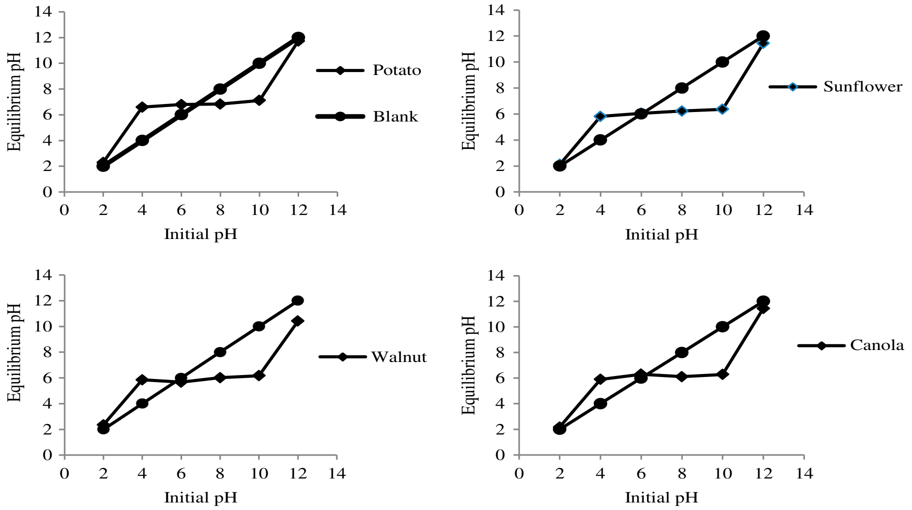

Fig. 1. pH_{ZPC} of plant residues (intersection of two curves equaled to pH_{ZPC}).

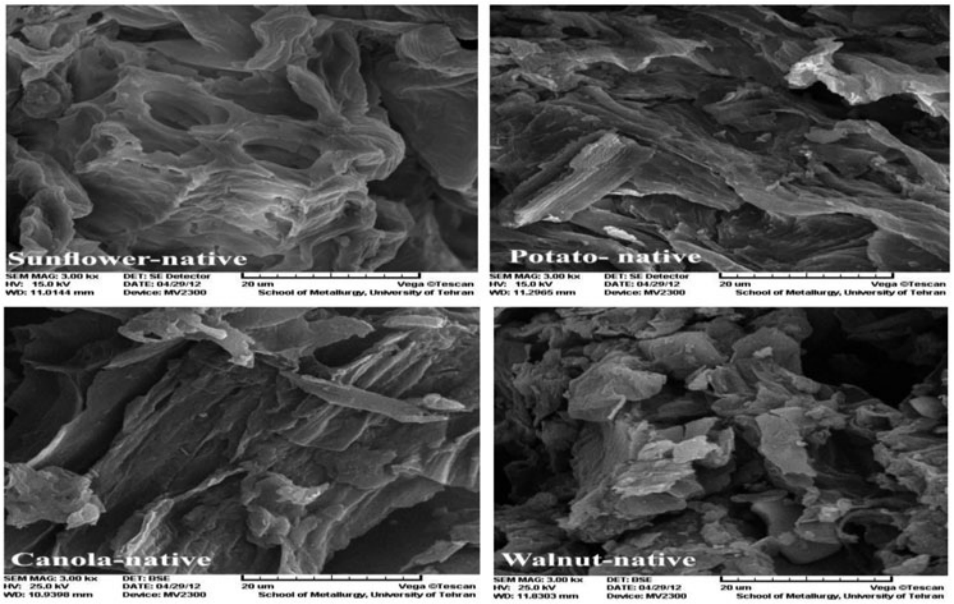

Fig. 2. SEM micrographs of native sorbents.

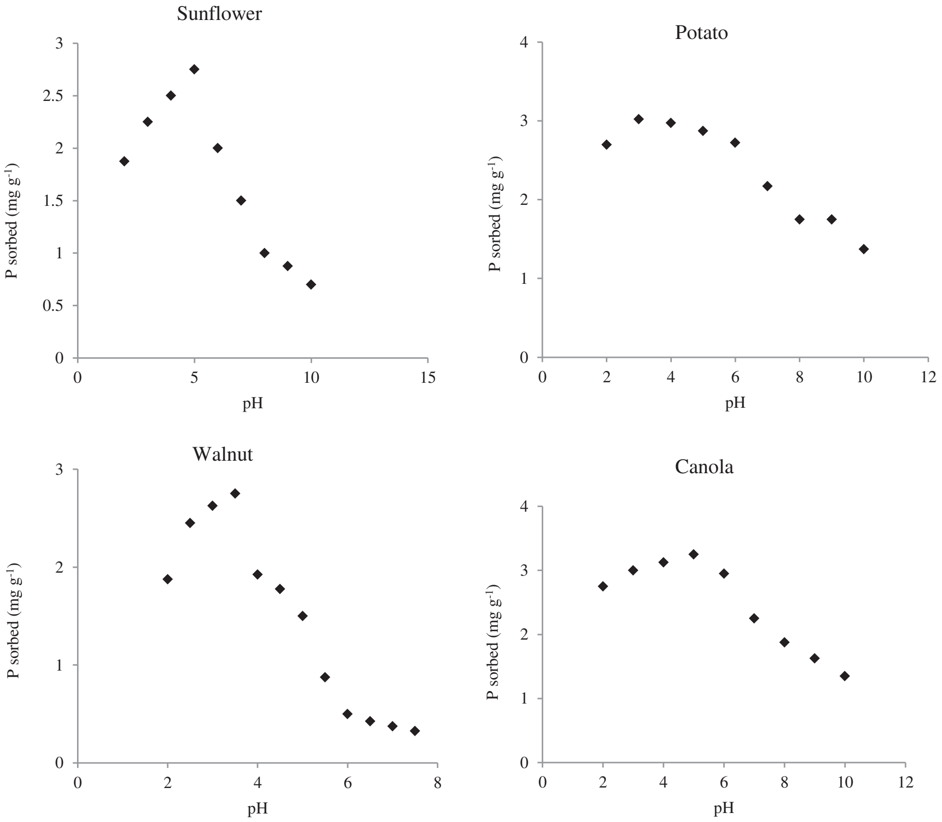

Fig. 3. The effect of pH on sorption of P.

the quantity of difference between optimum pH and pH_{zpc} represent electrostatic aspect of sorption. This difference for different sorbents was not the same and suggesting the diversity in sorbents nature, functional groups type, and subsequently in the level of electrostatic nature of sorption. Therefore, it can be concluded that the removal of P by these sorbents is not only electrostatic but also other mechanisms like specific sorption or precipitation are involved in the removal of P from solution. In low pH_s (less than pH_{zpc} of sorbents), functional groups of biomass surfaces have positive charges and so the electrostatic sorption of orthophosphate and P ions with negative charge by sorbent surface is favorable.

Speciation of P in different pH_s are shown in Fig. 4. Since in the range of pHs 2–5, the dominant species of P in solution is primary orthophosphate ($H_2PO_4^-$), so P sorption within this pH range mainly occurs as $H_2PO_4^-$. It has been reported that the mechanism of P sorption is ligand exchange with hydroxyl accompanied by the formation of inner square complex [16]. Phosphorus sorption by potato and walnut shell residues decreased after pH 3 and 3.5, respectively, which was probably due to the increase in phosphoric acid in solution, which could not be adsorbed by biomass surface. Notably, the decrease in P sorption in high pHs is reasoned to electrostatic repulsion force between phosphate ions and negative charges on sorbent surface.

3.3. The effect of time contact on P sorption

The effect of contact time on P sorption by sunflower, potato, canola, and walnut shell residues was investigated at time which ranged 5–1,440 min at optimum pH (sorbent dose of 4 mg l^{-1} and P concentration of 100 mg l^{-1}). The effect of contact time on P sorption was shown in Fig. 5. Phosphorus sorption by sunflower residue was initially rapid, but the sorption rate decreased over time, so the optimum time was obtained to be 110 min. Phosphorus sorption by potato residue also occurred in two phases, rapid and slow, and the optimum time was found to be 300 min. The optimum time for sorption of P by canola and walnut residues was 160 and 300 min, respectively

The rapid phase of P sorption by sorbents is likely due to the single-layer sorption of P on sorbents surface [18]. Krishnan and Haridas [16] reported that

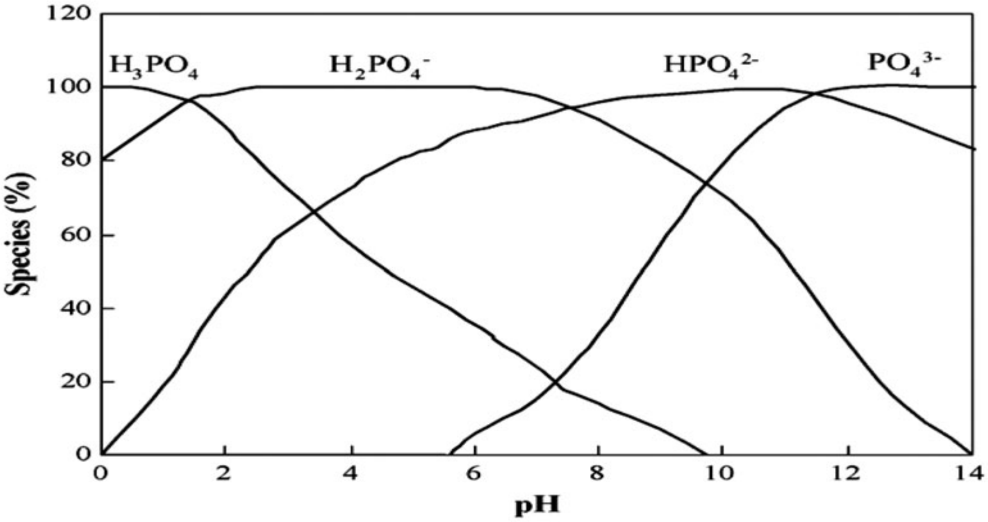

Fig. 4. Speciation of P as a function of pH [16].

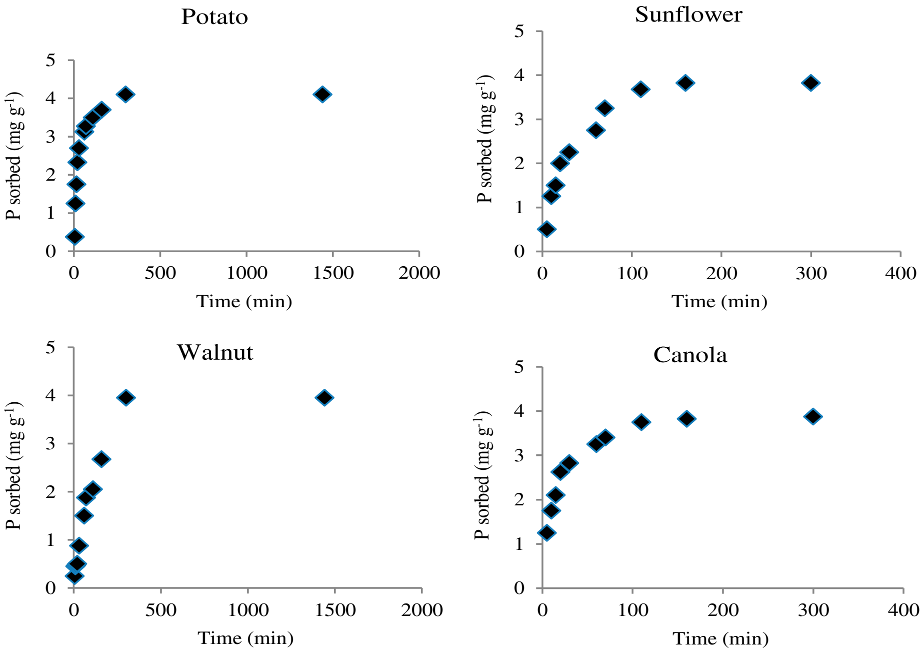

Fig. 5. The effect of time on sorption of P.

equilibrium time of P sorption by coir pith was found to be 12 h, while this time for P sorption by cotton residue [18] was obtained to be 15 min. It is suggesting that different sorbents have different behavior in sorption of P on basis of their nature and properties.

3.4. Sorption isotherms

The results of P sorption isotherms by native and modified sorbents are shown in Fig. 6. Phosphorus sorption isotherms indicated that the amount of P sorption by modified sorbents was more than native ones. In order to describe and model the equilibrium sorption, Langmuir and Freundlich equations were used. The parameters of these equations obtained from fitting to sorption data are given in Table 2.

Langmuir equation described the sorption of P onto native and modified sunflower residues with R^2 values in the range of 0.93–0.99. Maximum sorption capacity ($Q_{\max}$) of native sunflower residue for P was

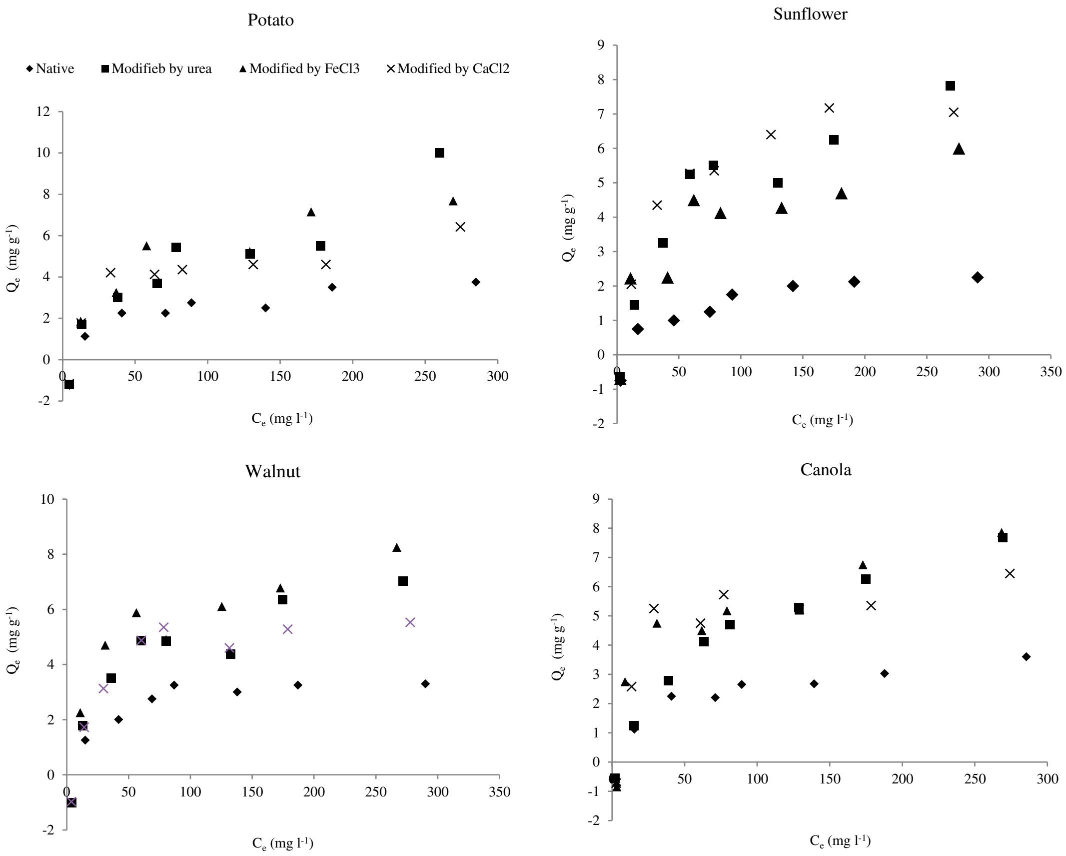

Fig. 6. Sorption isotherms of P by native and modified sorbents.

2.8 mg g^{-1}, while in modified sunflower residues by urea, $CaCl_2$, and $FeCl_3$, it was 9.3, 6.6, and 8.0 mg g^{-1}, respectively. The Q_{max} of native potato, canola, and walnut residues was 4.3, 4, and 3.7 mg g^{-1}, while Q_{max} of modified ones was more than that of natives (Table 2).

The K_L indicating bonding energy in sorption process was less for most native sorbents compared to modified ones indicating that the modified sorbents have high affinity for P adsorption in comparison with native ones. The R^2 and SE values in Langmuir equation used for describing P sorption by all sorbents were more than Freundlich model.

The comparison of means for P sorption by native and modified sorbents (as mean) was statistically carried out using Duncan test and results showed that P sorption by four native sorbents was significantly less than P sorption by modified ones by urea, $CaCl_2$, and $FeCl_3$ (Table 3). The mean sorption of P by native sorbents and those modified by urea, $CaCl_2$, $FeCl_3$ was 3.70, 9.08, 8.24, and 6.78 mg g^{-1}, respectively. The results indicated that the modification of sorbents by urea enhanced significantly the sorption capacity of sorbents. Overall, the capability of native plant residue for P sorption was low, but their chemical modification increased the sorption capacity. Among native sorbents, potato residue had the maximum capacity for P sorption (4.3 mg g^{-1}), while among modified ones the canola residue modified by urea had the maximum P sorption capacity (10.5 mg g^{-1}) in comparison with other modified sorbents. Riahi et al. [19] indicated that the maximum P sorption capacity by Date palm fibers was 1.4 mg g^{-1}. The maximum P sorption by modified Aleppo pine [12] and by a sea weed [20] was 38 and 0.09 mg g^{-1}, respectively. In another study, Xu et al. [18] reported that the Q_{max} of P sorption by cotton residue and corn stalk modified by Diethylene triamine was 16.8 and 19.4 mg g^{-1}, respectively. The modified coir pith by $FeNO_3$ sorbed 22.7 mg P g^{-1} [16]. The value of n parameter for P sorption obtained from this study was more than 1. Benyoucef and Amrani [12] reported that the value of $n > 1$ indicates desirable sorption. The results of P sorption by different sorbents show that the nature and chemical and physical properties of sorbents affect their capability for P sorption.

Table 2
Model parameters of sorption isotherm of P

		Langmuir				Fruendlich			
	Sorbent type	$Q_{\max}$ (mg g^{-1})	K_L (l mg^{-1})	R^2	SE	n	K_{Fr}	R^2	SE
Sunflower	Native	2.8	0.015	0.97	6.45	2.3	0.22	0.94	0.11
	Urea[a]	9.3	0.014	0.94	2.74	1.9	0.46	0.87	0.21
	$FeCl_3$[b]	6.6	0.020	0.93	4.08	3.2	0.97	0.79	0.89
	$CaCl_2$[c]	8.0	0.031	0.99	0.87	2.5	0.96	0.90	0.15
Potato	Native	4.3	0.018	0.95	5.67	2.6	0.45	0.90	0.14
	Urea	8.5	0.014	0.95	5.07	2.1	0.55	0.94	0.17
	$FeCl_3$	9.0	0.017	0.96	2.29	2.2	0.65	0.90	0.16
	$CaCl_2$	6.6	0.025	0.94	3.92	3.0	0.95	0.79	0.19
Canola	Native	4.0	0.021	0.98	4.03	2.8	0.48	0.90	0.12
	Urea	10.5	0.009	0.98	1.16	1.6	0.28	0.96	0.13
	$FeCl_3$	8.4	0.025	0.94	2.92	3.6	1.55	0.90	0.11
	$CaCl_2$	6.5	0.055	0.98	2.23	4.4	1.82	0.65	0.19
Walnut shell	Native	3.7	0.039	0.95	2.36	3.6	0.73	0.63	0.15
	Urea	8.0	0.018	0.93	3.45	2.4	0.71	0.88	0.16
	$FeCl_3$	9.0	0.023	0.96	2.15	1.9	0.66	0.59	0.15
	$CaCl_2$	6.0	0.039	0.99	1.96	2.8	0.85	0.78	0.22

[a] Modified by urea.
[b] Modified by $FeCl_3$.
[c] Modified by $CaCl_2$.

Table 3
Comparison of means of maximum P sorption capacity of sorbents

Sorbent	The mean of P sorption (mg g^{-1})	Difference indicator
Native	3.70	C[a]
Modified by urea	9.08	A
Modified by $FeCl_3$	8.24	AB
Modified by $CaCl_2$	6.78	B

[a] The letters indicate significant or insignificant differences of means.

The sorption of P ions on heterogeneous surfaces of sorbents used in this study was described well with Langmuir equation. The similar result was reported by Krishnan and Haridas [16]. Increase in P sorption by sorbents modified by $FeCl_3$ may be attributed to cation bridge effect of Fe ions on sorbent surface [16].

In order to explicit the P sorption, SEM micrographs of native and modified sorbents after P sorption were utilized (Fig. 7). These images show the changes of sorbents surface after modification. The sorption of P has been caused to fill the pores. SEM images revealed that modification of the sorbents resulted in the development of the porous surface with coarse fibrous texture making the surface more suitable for the attachment of reactive functional groups.

Sorption of P may occur due to the different mechanisms. Electrostatic sorption of P is related to the amount of positive charges on sorbent surface. Increase in positive charges on surface enhanced P sorption. The pH_{zpc} of sorbents used in this study before and after modification is shown in Table 4. The pH_{zpc} of the native sunflower, potato, canola, and walnut shell residues was 6.06, 6.80, 6.15, and 5.85, respectively. The elevated pH_{zpc} of all modified sorbents indicated that the amounts of positive charges in modified sorbents increased. In other word, it can be concluded that the sorbents are positively charged in more extended range of pH, and consequently the condition for electrostatically P sorption is favored. If the increase in pH_{zpc} is attributed to P sorption,

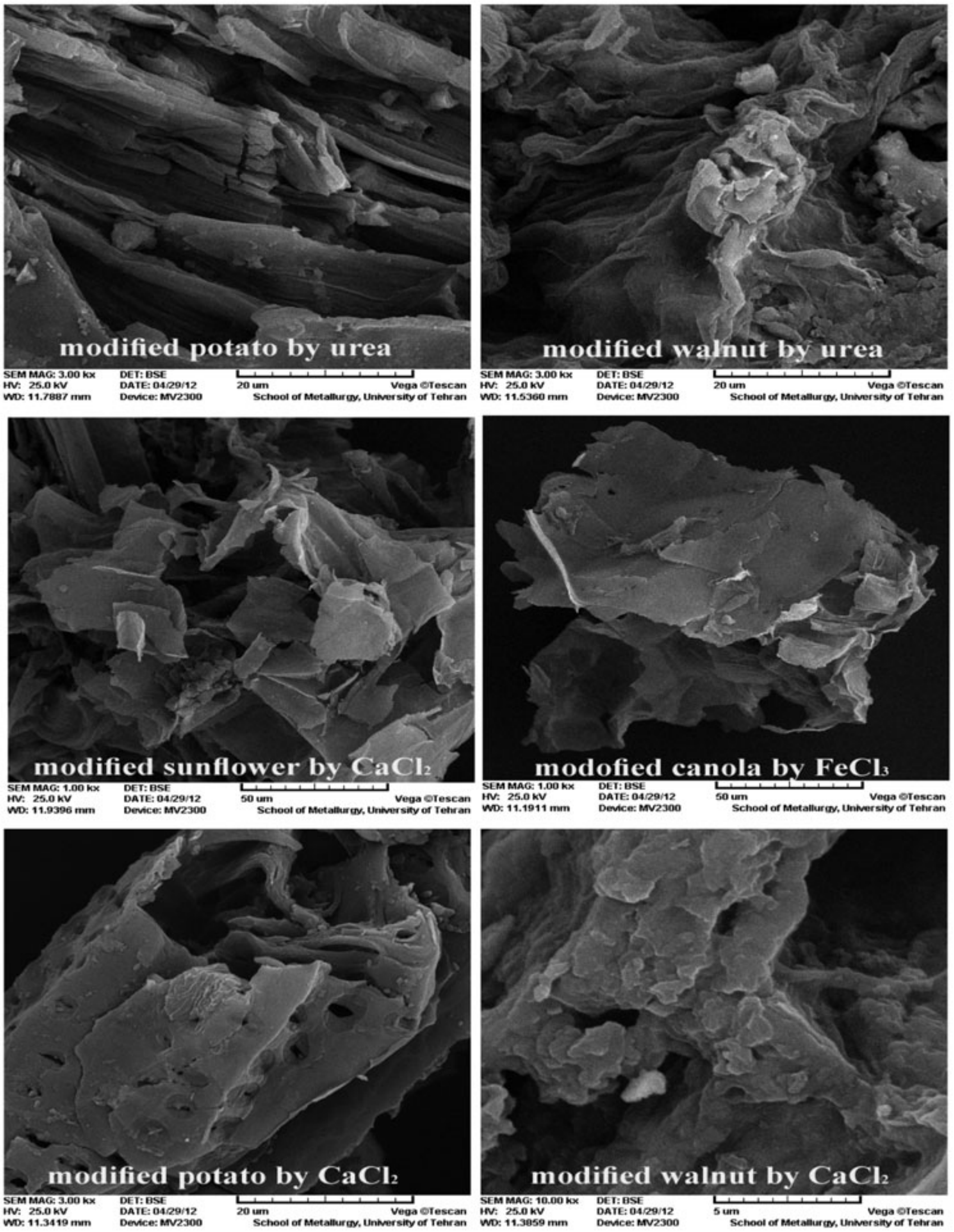

Fig. 7. SEM images of modified sorbents after sorption of P.

Table 4
pH_{ZPC} of native and modified sorbents

	pH_{ZPC}		
Sorbent	Native	Modified by	
Sunflower residue	6.06	urea	6.70
Potato residue	6.80	$CaCl_2$	6.85
Canola residue	6.15	urea	6.72
Walnut shell	5.85	$FeCl_3$	6.35

accordingly, it can be said that P sorption was quite electrostatical. However, the results showed that the enhancement quantity of pH_{zpc} in different sorbents did not correlate with increased amounts of P sorption, e.g., increase in pH_{zpc} at the rate of 0.05 unit in potato residue affected by modification, by $CaCl_2$ elevated P sorption 1.5 times more than native one, while this value of increased pH_{zpc} (0.05 unit) in other modified sorbents did not increase P sorption with this rate. Therefore, it can be concluded that P removal does not merely occur through electrostatic sorption mechanism but other mechanisms such as complexation and precipitation may be involved in sorption of P.

3.5. Speciation of P and calculation of saturation indices (SI) of P minerals in solution

The results of speciation of P and calculation of SI of minerals in some solutions used in sorption isotherm studies were shown in Tables 5 and 6, respectively. The dominant species of P in solution of all sorbents was $H_2PO_4^-$. The abundance of other species followed this order: $FeHPO_4$ (aq) > $MgHPO_4$ (aq) > HPO_4^{2-} > $MgHPO_4$ (aq) > $CaHPO^4$ (aq) > $CaH_2PO_4^+$. The results of SI of minerals indicated that all solutions were supersaturated with respect to hydroxyapatite revealing that this mineral controls P concentration in solution. Moreover, the SI of $Ca_3(PO_4)_2$ (am_2), $Ca_3(PO_4)_2$ (beta), and $Ca_4H(PO_4)_3{:}3H_2O(s)$ was more than zero. It is concluded that in addition to adsorption of P, precipitation was involved in P removal from aqueous solutions.

3.6. Kinetics of P sorption

Sorption kinetic which represents relationship between adsorbate and time is one of the important characteristics that define the sorption performance [16]. Mathematical models which describe the behavior of sorption process under experimental conditions are useful for sorption studies in large scales, or optimization of sorption process [12]. In present study, in order to describe the sorption kinetic, the empirical equations (pseudo-first-order and pseudo-second-order) were used and according to R^2 and SE, the better model was proposed.

The parameters of different models resulting from fitting to the kinetic data are given in Table 7. Pseudo-first-order model with R^2 0.94 (as mean for 4 sorbents) described the kinetic of P sorption. The constant of pseudo-first-order model related to sorption rate ($K_{1,}$) was in the range of 0.005–0.027 min^{-1} with the mean of 0.018 min^{-1}. The maximum and minimum values were obtained for sunflower and walnut shell residues, respectively. The Q_f (Table 7) parameter as the predicted value of equilibrium sorption of P by model ranged from 2.7 to 3.6 $mg\,g^{-1}$ indicating this model did not well predict the equilibrium sorption of P. SE of this model was found to be in range of 0.06–0.22. The second-order model well described the sorption kinetic of P with R^2 in range of 0.95–0.99 (mean, 0.97). The rate constant (K_2) of this model was found to be in range of 0.002–0.020 $mg\,g^{-1}\,min^{-1}$ and the maximum and minimum were observed in canola and walnut shell residues. The calculated Q_f by second-order model for different sorbents was obtained in the range of 4.1–4.7 $mg\,g^{-1}$. The second-order model could well describe the sorption kinetic of P sorption. Benyoucef and Amrani [12] reported that second-order model well described the kinetics of P sorption by Aleppo pine residues.

Table 5
Speciation of P in solutions of isotherm experiments for some adsorbents

Sorbent	Potato[a]–urea (%)	Walnut–urea (%)	Sunflower–$CaCl_2$ (%)	Canola–$FeCl_3$ (%)	Potato–$CaCl_2$ (%)	Walnut–$CaCl_2$ (%)
Species						
HPO_4^{-2}	11.13	6.55	1.58	0.83	0.39	0.08
$H_2PO_4^-$	43.45	58.56	87.37	89.47	86.94	89.39
H_3PO4	0.02	–	0.05	0.09	0.19	0.92
$FeH2PO_4^+$	0.04	0.02	0.07	0.47	0.37	0.30
$FeHPO_4$ (aq)	27.33	0.02	–	0.03	0.01	–
$MgHPO_4$ (aq)	12.40	16.10	3.53	1.73	0.77	0.14
$CaHPO_4$ (aq)	0.12	11.41	0.93	0.68	0.45	0.10
$CaPO_4^-$	2.74	0.05	–	–	–	–
$CaH2PO_4^+$	0.23	5.76	2.90	4.11	5.71	6.03
$NaHPO_4^-$	0.26	0.15	0.02	–	–	–
$KHPO_4^-$	1.82	0.11	0.03	0.03	–	–
$AlHPO_4^+$	0.28	0.74	2.89	1.92	4.44	2.41
KH_2PO_4 (aq)	0.18	0.28	0.40	0.46	0.49	0.41
$NaH2PO_4$ (aq)	–	0.25	0.23	0.18	0.23	0.22
$Al_2PO_4^{+3}$	–	–	–	–	0.01	–

[a] The solution of last concentration of isotherm (300 $mg\,l^{-1}$) of sorption of P by potato residue modified by urea.

Table 6
Saturation indices of P minerals in aqueous solutions

Adsorbent	Potato[a]–urea	Walnut–urea	Sunflower–$CaCl_2$	Canola–$FeCl_3$	Potato–$CaCl_2$	Walnut–$CaCl_2$
Species						
$Ca_3(PO_4)_2$ (am1)	−0.94	−1.50	−5.72	6.45	−7.28	−9.92
$Ca_3(PO_4)_2$ (am2)	1.81	1.25	−2.98	−3.71	−4.53	−7.17
$Ca_3(PO_4)_2$ (beta)	2.48	1.92	−2.31	−3.04	−3.86	−6.50
$Ca_4H(PO_4)_3$:$3H_2O$(s)	3.01	2.43	−2.89	−3.76	−4.75	−8.05
$CaCO_3 \times H_2O$(s)	−1.82	−1.80	−3.06	−3.02	−3.27	−4.03
$CaHPO_4$(s)	0.77	0.75	−0.34	−0.48	−0.65	−1.30
$CaHPO_4$:$2H_2O$(s)	0.49	0.47	−0.61	−0.76	−0.93	−1.58
Hydroxyapatite	9.96	8.86	1.49	0.18	1.30	6.00
$Mg_3(PO_4)_2$(s)	−2.55	−3.68	−6.63	−7.87	−9.21	−12.07
$MgHPO_4$:$3H_2O$(s)	−0.13	−0.34	−0.99	−1.31	−1.65	−2.37
Vivianite	0.92	−0.43	−2.33	−1.06	−2.64	−5.62

[a]The solution of last concentration of isotherm (300 mg l^{-1}) of sorption of P by potato residue modified by urea.

Table 7
The parameters obtained from fit of kinetic models to the experimental data

	Pseudo-first order				Pseudo-second order			
Sorbent (native plant residues)	K_1 (min^{-1})	Q_f (mg g^{-1})	R^2	SE	K_2 (mg g^{-1} min^{-1})	Q_f (mg g^{-1})	R^2	SE
Sunflower	0.027	3.6	0.966	0.20	0.006	4.7	0.974	0.11
Potato	0.013	2.7	0.900	0.22	0.008	4.5	0.987	2.42
Canola	0.027	2.7	0.979	0.15	0.020	4.2	0.998	0.52
Walnut shell	0.005	3.5	0.929	0.06	0.002	4.1	0.953	6.08

4. Conclusion

Sorption of P is mostly dependent upon sorbent type, solution, pH, and contact time. Organic materials usually adsorb the positively charged ions more than anions such as P due to the net negative charge of their surfaces. In present research, the native sorbents showed low ability for sorption of P, so that the maximum sorption capacity of P was found to be in the range of 2.8–4.3 mg g^{-1}, while that of P by modified sorbents was obtained in the range of 6–10.5 mg g^{-1} (4 sorbents modified by 3 procedures). Chemical modification of sorbents enhanced their efficiency for P removal from aqueous solutions. The cation bridge is the possible mechanism for P sorption. Langmuir model well described the P sorption isotherm. Sorption kinetic studies revealed that P sorption rate was initially high, but decreased over time. The description of P sorption kinetic by second-order model was better than the first-order one. Overall, increase in sorbent capacity for P sorption affected by modification process depends on chemical agent and modification method. Any procedure which causes to increase the positively charged functional groups on sorbent surfaces is a stimulus factor for electrostatic sorption of anions such as P. In addition to electrostatic sorption, specific adsorption, ligand exchange, and precipitation are the likely mechanisms involved in removal of P by used sorbents from aqueous solutions.

Symbols

Q_e — the amount of P sorbed (mg g^{-1})
C_i — initial concentrations of P (mg l^{-1})
C_e — equilibrium concentrations of P (mg l^{-1})
V — volume of aqueous phase (l) and M is the sorbent dose (g)
K_{Fr} and n — Freundlich equation constants
K_L — Langmuir constant related to the energy of sorption (l mg^{-1})
Q_{max} — maximum sorption capacity of sorbent for P
Q_t — the amount of P adsorbed on the sorbent at time t (mg g^{-1}) in kinetic experiments
Q_f — the amount of P adsorbed on the sorbent at equilibrium time (mg g^{-1}) in the kinetic experiments
K_1 — the rate constant of sorption in the pseudo-first-order equation (min^{-1})
K_2 — the rate constant of sorption in the pseudo-second-order equation (g mg^{-1} min^{-1})
R^2 — coefficient of determination
SE — standard error

References

[1] G.L. Song, W.H. Hou, Q. Wang, J.L. Wang, Effect of low temperature on eutrophicated waterbody restoration by *Spirodela polyrhiza*, Bioresour. Technol. 97 (2006) 1865–1869.

[2] E.N. Peleka, E.A. Deliyanni, Adsorptive removal of phosphates from aqueous solutions, Desalination 245 (2009) 357–371.

[3] J.F. Duenas, J.R. Alonso, A.F. Rey, A.S. Ferrer, Characterisation of phosphorous forms in wastewater treatment plants, J. Hazard. Mater. 97 (2003) 1–3.

[4] R.G. Penetra, M.A.P. Reali, E. Foresti, J.R. Campos, Post-treatment of effluents from anaerobic reactor treating domestic sewage by dissolved-air flotation, Water Sci. Technol. 40 (1999) 137–143.

[5] L. Ruixia, G. Jinlong, T.J. Hongxiao, Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber, J. Colloid Interface Sci. 248(2) (2002) 268–274.

[6] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, K. Ooi, T. Hirotsu, Selective adsorption of phosphate from seawater and wastewater by amorphous zirconium hydroxide, J. Colloid Interface Sci. 297 (2006) 426–433.

[7] A. Gieseke, P. Arnz, R. Amann, A. Schramm, Simultaneous P and N removal in a sequencing batch biofilm reactor: Insights from reactor and microscale investigations, Water Res. 36(2) (2002) 501–509.

[8] E. Eggers, A.H. Dirkzwager, H. Van der Honing, Full-scale experiences with phosphate crystallization in a crystalactor, Water Sci. Technol. 24 (1991) 333–334.

[9] S. Farag, E.I. Al-Afaleq, Preparation and characterization of saponified delignified cellulose polyacrylonitrile-graft copolymer, Carbohydr. Polym. 48 (2002) 1–5.

[10] M.C. Basso, E.G. Cerrella, A.L. Cukierman, Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater, Ind. Eng. Chem. Res. 41 (2002) 3580–3585.

[11] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[12] S. Benyoucef, M. Amrani, Adsorption of phosphate ions onto low cost Aleppo pine adsorbent, Desalination 275 (2011) 231–236.

[13] G.M. Sakala, D.L. Rowell, C.J. Pilbeam, Acid–base reactions between an acidic soil and plant residues, Geoderma 123 (2004) 219–232.

[14] D.L. Rowell, Soil Science, Methods and Applications, Longman Group, Harlow, 1994, p. 345.

[15] J. Murphey, J.P. Riley, A modified single solution method for the determination of phosphate in natural waters, Anal. Chim. Acta 27 (1962) 31–36.

[16] 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.

[17] J. Rivera-Utrilla, I. Bautista-Toledo, M. Ferro-Garcy, C. Moreno-Castilla, Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption, J. Chem. Technol. Biotechnol. 76 (2001) 1209–1215.

[18] X. Xu, Y. Gao, B. Gao, X. Tan, Y.Q. Zhao, Q. Yue, Y. Wang, Characteristics of diethylenetriamine-cross-linked cotton stalk/wheat stalk and their biosorption capacities for phosphate, J. Hazard. Mater. 192 (2011) 1690–1696.

[19] K.H. Riahi, B.B. Thayer, A.B. Mammou, A.B. Ammar, M.H. Jaafoura, Biosorption characteristics of phosphates from aqueous solution onto *Phoenix dactylifera* L. date palm fibers, J. Hazard. Mater. 170 (2009) 511–519.

[20] S. Wang, X. Jin, H. Zhao, F. Wu, Phosphate biosorption characteristics of a submerged macrophyte *Hydrilla verticillata*, Aquat. Bot. 89 (2008) 23–26.