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A novel nanopore biopolymer multi adsorbent for simultaneous removal of anionic and cationic mixtures

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ABSTRACT

A novel nanopore biopolymer alginate gel bead impregnated with surfactant-modified zeolite (SMZ) and powdered activated carbon (PAC) is developed for simultaneous removal of anionic and cationic compounds from wastewaters. Cadmium and nitrate were used as a representative of cationic and anionic compounds, respectively. Testing different aspect ratio of alginate, SMZ and PAC showed that 3:4:1 (alginate:SMZ:PAC) is the best aspect ratio. The removal percent of (99.8%) cadmium is more powerful in cationic removal than the removal percent of (56%) nitrate in anionic removal. Isothermal study showed that Temkin is the governing equation for nitrate sorption, and Freundlich is the governing equation for cadmium sorption. Pseudo-second-order model is the governing equation for both nitrate and cadmium sorption. Although nitrate presence in the solution with different concentrations has no significant effect on cadmium sorption, but the cadmium presence will enhanced the nitrate sorption which is related to nitrate-cadmium clates. Because of activated carbon ability for organic pollutant removal, this sorbent can also be used for treating organic pollutants.

Keywords: Multisorbent; Alginate; Zeolite; Activated carbon; Cadmium; Nitrate; Organic; Pollutants

1. Introduction

Industrial and agricultural wastewaters are important source of groundwater and river pollution. They often contain both anionic and cationic compounds such as nitrate, phosphate, and heavy metals [1]. Among cationic pollutants, heavy metal ions are sources of great concern in aquatic environments, because they are nondegradable and therefore persistent and should be removed from wastewaters before injected to water resources. One of heavy metals, which pose risks to human, plants, and animals health, is cadmium. Cadmium enters water resources through wastewaters from industries such as electroplating, alloy manufacturing, smelting, plastic, pigments, fertilizers, pesticides, cadmium-nickel

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batteries, mining, pigments and dyes, textile operations, and refining [2–7]. A major past disaster "Itai-Itai" due to cadmium contamination in Jintsu river of Japan is well known [8].

Anionic compounds such as nitrate and phosphate are used as raw materials in compost that is essential for the plants growth. These compounds are carcinogenic, and their presence in rivers and groundwater poses significant risks to the environment. Among them, nitrate has more concern on a global scale [9]. High nitrate concentration increases the growth of aquatic plants and algae growth leading to dissolved oxygen depletion that is well known as eutrophication phenomenon [10]. NO_3 can also be dangerous for human in two ways: nitrosamines formation which is carcinogenic and "blue-baby syndrome" (methemoglobinemia), that is inducted especially in infants [11,12].

So far considerable efforts have been made for the removal of these compounds. For instance, the removal of heavy metals was made using membrane filtration, chemical precipitation, ion exchange, and adsorption [13,14]. Although precipitation methods are reliable but usually require a subsequent treatment and also large settling tanks for the precipitation leading to be expensive. Adsorption ion exchange, a more sophisticated technique, which is more expensive, has the advantage of metallic ions recovery. Studies on the treatment of effluents containing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from wastewater [15–18]. Various adsorbents such as chitosan [19,20] zeolite [21–23], clay [24] and activated carbon [6,8] are used for heavy metal removal. The most efficient adsorbent was found to be activated carbon.

Different methods have been used for nitrate removal, such as autotrophic and heterotrophic denitrification [25,26], chemical reduction [25], adsorption [27], ion exchange [28], electrodialysis [29], or reverse osmosis [30]. The biological methods are often used in industrial plants but need addition of specific bacteria, able to reduce NO_3^- into N_2 (e.g. *Bacillus* or *Thiobacillus denitrificans*) [31]. Low initial cost, simplicity of design, and ease of operation are the advantages of sorption methods. For the removal of anionic compounds, many attempts have carried out using various adsorbents [32–34]. To date, the most widely used adsorbent is modified zeolite for the removal of anionic compounds, such as nitrate, phosphate, and chromate [35–37].

Recently, most developed sorbents are useful for only one kind of pollutant removal. So treating wastewaters, containing different pollutants need several treatment cycles leading to be hard and cost-effective. Therefore, since 2003, researchers have tried to introduce new complex sorbents for the simultaneous removal of different kind of pollutants [38,39]. Alginate–chitosan hybrid gel beads, prepared from alginic acid, and chitosan were used for the simultaneous removal of Cu (II), Co (II), and Cd (II) [40]. Simultaneous removal of Cu and phenol were also performed by Kim et al. [41] using alginate-powder-activated carbon beads. In another study, Choi et al. [1] tried to remove zinc and toluene simultaneously using alginate complex impregnated with zeolite and activated carbon.

However, best multi-sorbents which have been used so far, cannot remove anionic, cationic, and organic compounds, simultaneously. Therefore, in this study, it is tried to develop a novel nanopore biopolymer alginate gel bead impregnated with surfactant-modified zeolite (SMZ) and powdered activated carbon (PAC) for the removal of mixed contaminants. In order to examine the adsorption rate and capacity of this multi-sorbent, both equilibrium and kinetic batch studies were performed. Cadmium and nitrate were used as a representative of cationic and anionic compounds, respectively. Effect of different sorbent dose, diameter and aspect ratio of alginate, SMZ and PAC on sorption was investigated. The effect of simultaneous presence of nitrate and cadmium on sorption was also investigated. Because of activated carbon that is used in this sorbent, it can also be used for organic pollutant removal.

2. Materials and methods

All chemicals of cadmium titrasol, nitrate saline solution, calcium chloride anhydrate, and surfactant HDTMA-Br (Merck chemical Co., German) were reagent grade.

Sodium alginate which is used was extracted from brown algae (Sargassum hystrix) which are native to southern coast of Iran (molecular weight of 50,000). Sodium alginate with chemical formula of $(C_6H_7NaO_6)_m$ has a formula unit weight of 198.11 and its macromolecular is in the range of 10,000–60,000 depending on the number of units (m). Physicochemical structure of sodium alginate was discussed elsewhere [42–44]. Used activated carbon was made of lemon tree wood by two-step physical method [45–47].

The type of natural zeolite which was extracted from mines of Semnan province in Iran was clinoptilolite. For X-ray diffraction pattern recording of raw zeolite, a Philips PW1800 diffractometer operating with Cu K_α radiation ($\lambda = 0.1542$ nm) in the 2θ range 4–90° and equipped with an X′Celerator real-time multiple strip detector were used. The powder X-ray diffraction pattern is shown in Fig. 1. Table 1 shows overall chemical composition.

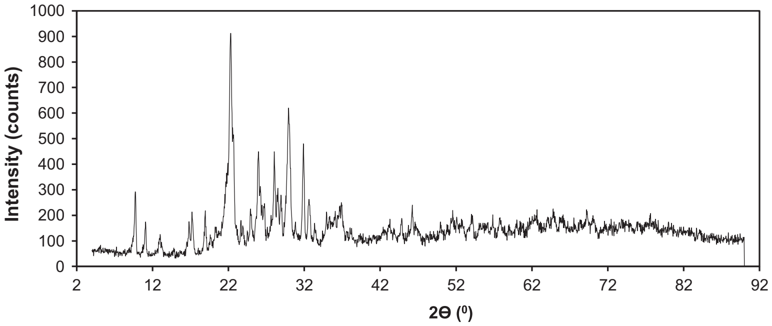

Fig. 1. Results of XRD of Semnan Clinoptilolite.

The resulting Si/Al molar ratio is close to 6.5 and is thus higher than the usual Si/Al framework molar ratio of clinoptilolite samples, resulting to zeolite with more negative structure.

The external cationic exchange capacity (ECEC) was determined by a method which is adapted from proposed method by Ming and Dixon [48] and Haggerty and Bowman [49]. The determination of the mineral ECEC was carried out in triplicate, and the calculated ECEC is 120 meq/kg.

2.1. Preparation of the SMZ sample

The zeolite should be modified for nitrate removal. The SMZ sample was prepared according to a usual procedure proposed by Bowman [50] using HDTM-Br. Clinoptilolite which was extracted from mines of Semnan was powdered and sieved. About 200 g of raw clinoptilolite materials which was passed from 88-micrometer sieve and retained on 74-micrometer sieve (mean diameter of 81 micrometer) was treated by 1,000 mL of a 0.052 M surfactant solution at 25˚C in shaking speed of 120 rpm for 72 h. After filtration, to remove the excess of HDTMA, the sample was washed with 1,000 mL distilled water and was dried at room temperature overnight. A complete exchange of HDTMA would have led to a sorbed amount of 240 meq/kg (200% ECEC). But in the experiment, only 115 meq/kg of HDTMA is sorbed to zeolite (~100% ECEC).

2.2. Alginate bead preparation

Sodium alginate which is a natural biopolymer was used as a base for this sorbent. Other sorbents (PAC and SMZ) were impregnated in sodium alginate by the following procedure. Solutions of 3% w/v of sodium alginate were prepared with ultrapure water by mixing 12 g of sodium alginate powder with 400 mL distilled water. After adding 4 g of PAC and 20 g of SMZ into 400 mL alginate solution, homogeneous mixing was performed for 3 h to yield 3% (w/v) alginate solution mixed with PAC and SMZ. Then, because of degassing, the solution was remained stationary for 1 h, and this solution was used to make final sorbent as beads with 4 different diameters. Following procedure was used for 3 of them. The prepared 3% alginate solution was poured in a burette and syringe with two different needles and then allowed to drop into a solution of 4% $CaCl_2$ (500 mL) to form alginate-SMZ-PAC beads with 3 different diameters. Calcium alginate complex gel beads were formed upon contact with the cross linker solution and were left overnight to stabilize. The remaining $CaCl_2$ solution was removed by filtration, and the resulting beads were washed with distilled water several times. The beads were dried at room temperature for three days (diameters of 2.1, 1.35, and 1.23 mm). Beads with diameter of 0.68 mm were prepared using smaller needle and a vacuum pump.

The beads which were prepared in this procedure have the aspect ratio of 3:4:1 (Alginate:SMZ:PAC). In order to compare two different aspect ratios, the same procedure was used to form 3:5:1 aspect ratio beads by adding 20 g of zeolite instead of 16 g. Aspect ratios were selected on the base of Choi et al. [1] and Kim et al. [41]. Choi et al. used aspect ratio of 5:1:1 (sodium alginate:zeolite:activated carbon). Kim et al. used 3:3 (sodium alginate:activated carbon) aspect ratio. Regarding to initial experiments, more SMZ were used than PAC, to balance sorption ability of PAC and SMZ. The physical properties of the complex bead were measured using a BET (Belsorp mini II, BelJapan). Other physical properties like porosity, density, and hydraulic conductivity were measured in the laboratory. The physical properties of the nanopore biopolymer are listed in Table 2 for the diameter of 0.68 mm which was selected as the best diameter.

Although the average particle size was about 0.68 mm, but the distribution size of the beads is in

Table 1
Results of XRF of Semnan Clinoptilolite

SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	CaO (%)	Fe_2O_3 (%)	MgO (%)	L.O.I (%)	$\frac{SiO_2}{Al_2O_3}$	TiO_2 (%)	P_2O_5 (%)	MnO (%)	SO_3 (%)	Cl (ppm)	Ba (ppm)	Sr (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	Ni (ppm)	Cr (ppm)
69.1	10.76	2.41	1.69	1.44	0.86	0.86	12.37	6.42	0.159	0.012	0.001	0.003	69	133	1,340	57	25	36	33	8

the range of 0.2 to 1.2 mm. Gradation curve is shown in Fig. 2.

The SEM (Philips, XL30) pore structure of the novel alginate complex bead by air drying is shown in Fig. 3. As shown in these figures, the porous structure of the novel complex bead can clearly be seen.

2.3. Adsorption kinetics

Kinetic studies were performed to determine the rate of cadmium and nitrate sorption. It was examined in a batch mode using 30-mL flasks. A number of flasks were used during each kinetic experiment. A solution with desired cadmium (500 ppm) or nitrate (25 ppm) concentration was prepared. Nitrate solution was prepared according to ASTM standard (4500–NO_3–B). According to 4500–NO_3–A standard, concentration measurements were started promptly after sampling. To ensure that there is no concentration change during experiment (maximum 7 h), some initial tests also have done. No changes were observed. The pH value was then adjusted to 6.5. After that, 10 mL of the solution together with 3 g of the beads (0.68 mm) was poured in each flask, and the samples were shaken with the speed of 120 rpm for 5, 15, 30, 45, 60, 120, 180, 240, and 300 min. For each time, two flasks were considered for duplication. Cadmium concentrations were measured by using atomic absorption spectroscopy (Varian AA-240), and nitrate solutions were analyzed by UV–Vi JENWAY-6705 spectrophotometer at 200 nm.

Pseudo-first-order model

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \tag{1}$$

and pseudo-second-order kinetic equation

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

were fitted to the data [51].

Here, k_1 is the pseudo-first-order rate constant, k_2 is the pseudo-second-order rate constant, q_t and q_e are the amounts of adsorbed Cd/Ni at time t and the equilibrium time, respectively.

The parameters were estimated by plotting ln $[(q_e - q_t)/q_e]$ vs. t for pseudo-first-order model and t/q_t vs. t for pseudo-second-order model. The parameters were calculated from the slope and intercept of the fitted line.

The change in the adsorbed concentration on to adsorbent with time is tested by parabolic diffusion equation [52] as follows:

Table 2
Physical properties of the adsorbents used in this study

Property	Amount
Mean diameter (mm)	0.68
BET surface area (m^2/g)	210
Pore radius (nm)	4.88
Pore volume (cm3/g)	0.21
Porosity	0.819
Density (g/cm^3)	2.13
Hydraulic conductivity (cm/s)	0.21

$$q_t = K_{\text{id}} t^{1/2} \tag{3}$$

where K_{id} is the rate constant of intraparticle transport (μg g^{-1} $min^{-1/2}$).

2.4. Adsorption equilibrium

These experiments were carried out for investigating the effect of initial cadmium and nitrate concentration, sorbent dose, beads diameter, and sorbent aspect ratio on removal. The effect of cadmium and nitrate presence on each other and determining the governing isotherm is also investigated. Same flasks were used for adsorption equilibrium tests. In this case, flasks were shaken for 5 h (determined from kinetic experiments) to provide enough time and contact for equilibrium between the solid and liquid phase. The initial concentrations of the solutions were in the range of 10 to 125 ppm for nitrate and 100 to 1,000 ppm for cadmium.

The samples which were taken from flasks after certain time in kinetic experiments or after equilibrium for equilibrium tests were centrifuged on 8,000 rpm

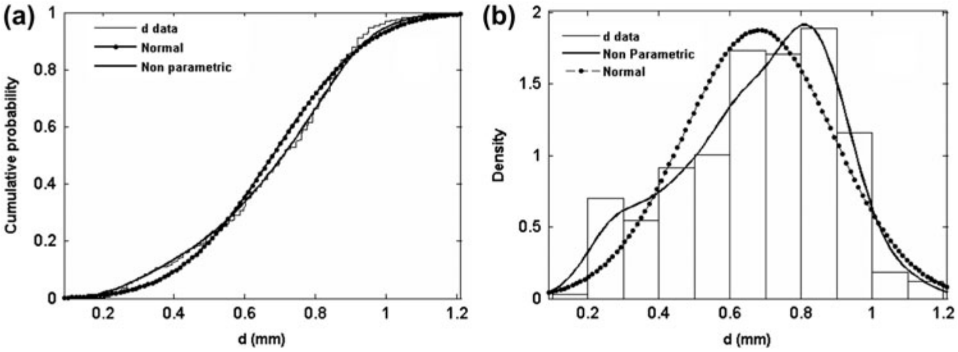

Fig. 2. Gradation curve in diameter of 0.68 mm adsorbents.

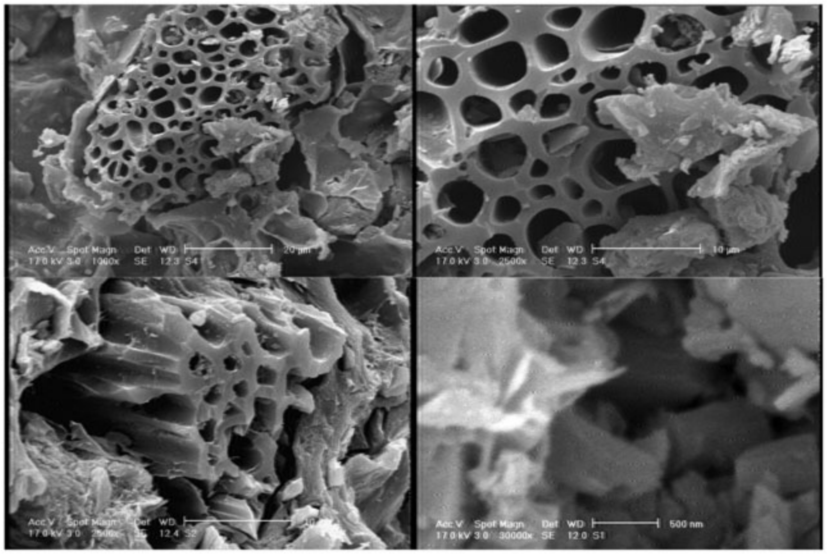

Fig. 3. SEM photograph of cross-sectional view of complex bead.

(to ensure that all impurities are deposited), and then the clear supernatant was used for cadmium or nitrate concentration measurements. The centrifuge had refrigerator to fix temperature. The amounts of ions adsorbed on the beads, q (mg/g wet beads), were determined from the measured bulk concentrations, using the following equation:

$$q_t \text{ or } q_e = \frac{(C_0 - C_{e\,\text{or}\,t})\forall}{W} \tag{4}$$

where ∀ (l) is the solution volume, W (g) is the weight of wet beads, C_0 (ppm) is the initial metal concentration, and $C_{e \text{ or } t}$ (ppm) is the bulk concentration at indicated time or is the equilibrium concentration of the solution.

Isotherm models of Langmuir

$$q_e = \frac{Kq_m C_e}{1 + KC_e} \tag{5}$$

Freundlich

$$q_e = kC_e^n \tag{6}$$

and Temkin

$$q_e = \frac{\text{RT}}{b_T} \ln\,(A_T C_e) \tag{7}$$

were fitted to describe equilibrium adsorption [53]. Where C_e is the supernatant concentration at the equilibrium state of the system (mg/L), K is the Langmuir affinity constant, q_m is the maximum adsorption capacity of the sorbent (mg/g), k is the Freundlich constant related with adsorption capacity, and n is the Freundlich exponent. Also, R is Universal gas constant, T is Absolute temperature, b_T is Temkin isotherm constant, and A_T is Temkin isotherm constant. To estimate parameters from experimental data, linear form of the Eqs. (5–7) were used. The linear forms are as follows:

$$q_e = q_m - \left(\frac{1}{K}\right)\frac{q_e}{C_e} \tag{8}$$

$$\log(q_e) = \log(k) + n\log(C_e) \tag{9}$$

$$q_e = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(C_e) \tag{10}$$

2.5. Model evaluation

As described in Sections 2.3 and 2.4, the parameters of the kinetic and equilibrium models were determined using linear form of the models. Sum of square error (SSE),

$$\text{SSE} = \sum_{i=1}^{N} (O_i - P_i)^2 \tag{11}$$

modeling efficiency (EF) [54],

$$\text{EF} = 1 - \frac{\sum_{i=1}^{N} (O_i - P_i)^2}{\sum_{i=1}^{N} (O_i - \overline{O})^2} \tag{12}$$

and coefficient of residual mass (CRM) [55,56],

$$\text{CRM} = \frac{\sum_{i=1}^{N} O_i - \sum_{i=1}^{N} P_i}{\sum_{i=1}^{N} O_i} \tag{13}$$

are used along with R^2, to evaluate models. P_i and O_i are the calculated and measured amounts of adsorbed cadmium or nitrate. EF changes between 1.0 for perfect fit and $-\infty$. The values lower than zero indicate that the mean value of the observed data would have been a better estimation than the model. The CRM is a measure to show the model tendency to overestimate or underestimate the measurements. CRM with positive values indicate that the model underestimates the measurements. Negative values for CRM show the model tendency to overestimate.

3. Results and discussion

3.1. Kinetic study

Kinetic studies were performed to determine the sorption rate of cadmium and nitrate. The cumulative adsorption of cadmium and nitrate against time were plotted for each experiment as shown in Fig. 4(a) and (b). The kinetics studies of cadmium and nitrate sorption shows a two-stage time depended behavior with an initially rapid reaction followed by a slower phase. It is clear from Fig. 4 that cadmium sorption is more rapid than nitrate sorption. The time needed for nitrate and cadmium to reach equilibrium is 250 and 50 min, respectively. So 300 min (=5 h) is considered for equilibrium experiments.

Pseudo-first-order model and pseudo-second-order kinetic equation were fitted to the data (Eqs. (1) and (2)). The parameters were calculated from the slope

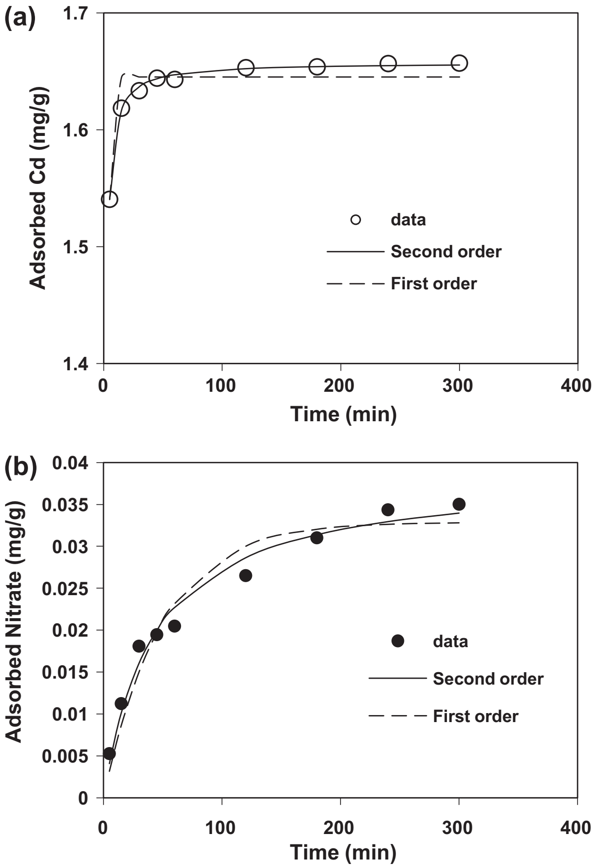

Fig. 4. Adsorbed cadmium (a) and nitrate (b) vs. time.

and intercept of the fitted line. The R^2 of fitted lines are listed in Table 3. The SSE, CRM, and EF for pseudo-first and pseudo-second order and the rate constants derived from these equations are also shown in Table 3.

Considering SSE, CRM, R^2, and EF in Table 3, the pseudo-second-order model is the governing equation for both cadmium and nitrate kinetic sorption. This is also clear in Fig. 4. EF values of 0.98 and 0.96 for nitrate and cadmium sorption shows that pseudo-second-order equation has a very good ability in kinetic sorption modeling. And CRM values show a very low tendency to overestimate nitrate (−0.004) and underestimate cadmium (0.001) kinetic sorption.

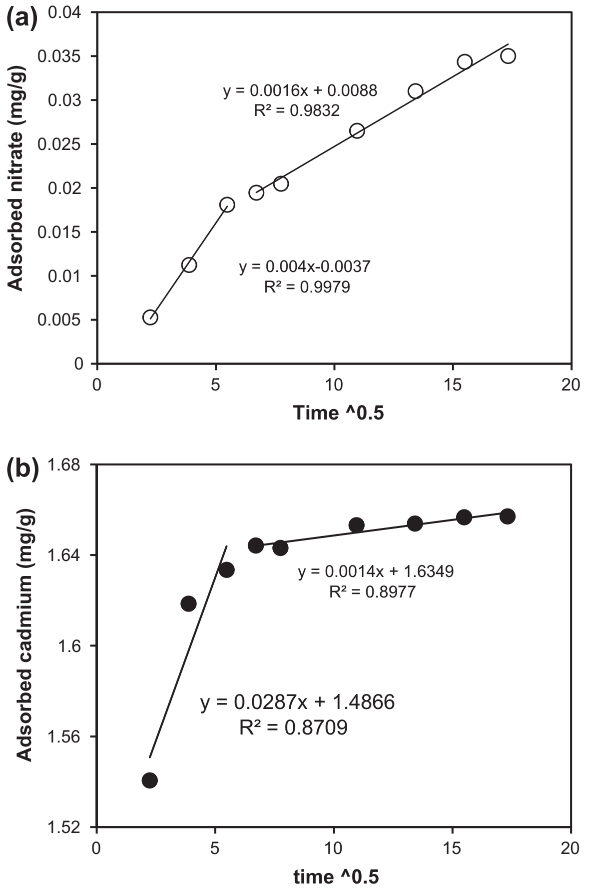

Fig. 5. Adsorbed nitrate (a) and cadmium (b) vs. *t*^0.5.

The changes in amount of adsorbed Cd/Ni vs. time were tested by parabolic diffusion equation. The assumption of a parabolic diffusion is not supported well by the results of fitting this equation to the cadmium experimental data. This is also shown in Fig. 5. As shown in Fig. 5(a) and (b), the plot of q_t vs. $t^{1/2}$ in nitrate experiments is more close to a line with

Table 3
Estimated parameters, R^2, rate constants, q_e, SSE, EF and CRM

Pollutant	Model	$k_1/k_2/k_{id}$	q_e	SSE	R^2	EF	CRM
	Pseudo-first order	0.0073	–	0.0003	0.98	0.62	0.2262
Nitrate	Pseudo-second order	0.5886	0.039	2.08E-05	0.99	0.98	−0.0043
	Parabolic diffusion	0.0023	–	8.57E-05	0.90	0.90	0.0499
	Pseudo-first order	0.0168	–	5.481	0.94	−499.11	0.3619
Cadmium	Pseudo-second order	1.3330	1.659	0.0004	1	0.96	0.0016
	Parabolic diffusion	0.0051	–	0.0052	0.53	0.53	−0.0002

a constant slope in the time span of the experiments. But in the case of the cadmium experiments, a two-step sorption behavior was obviously observed. For cadmium sorption, if we consider Eq. (3) as $q = k_{\mathrm{id}}t^{1/2}$ + constant, this problem will be solved. The values of k_{id}, R^2, and SSE of cadmium sorption data with modified equation are listed in Table 3.

3.2. Equilibrium study

Equilibrium batch experiments were performed to investigate the effect of initial cadmium and nitrate concentration, isotherm modeling, beads diameter, sorbent dose, sorbent aspect ratio and also to investigate the effect of cadmium and nitrate presence on each other.

The initial pollutant concentration has pronounced effect on all of the adsorptive removal processes. In the present study, the effect of initial nitrate (10, 15, 25, 40, 50, 65, 75, 100, and 125 ppm) and cadmium (100, 300, 500, 700, and 1,000 ppm) concentration was investigated. In these experiments, sorbent dose, temperature, and pH were 300 g/l, 25˚C, and 7.2 ± 0.2, respectively.

The adsorbed amount and removal percent of cadmium and nitrate vs. C_o is shown in Figs. 6 and 7. By increasing the initial concentration, the amount of adsorbed pollutant increased from 0.33 to 3.31 mg/g for cadmium and from 0.019 to 0.102 mg/g for nitrate.

From Fig. 7, it is clear that cadmium and nitrate sorption does not show a same trend in the removal percent. Although initial concentration increasing reduces removal percent of the nitrate from the solutions, obviously (from 56.0 to 21.2%), but this effect is very low for cadmium removal (from 99.78 to 99.25%). It can be related to the initial concentration ranges and the maximum capacity of the beads. The ranges of cadmium initial concentration which are used here are very low respect to maximum capacity of the beads. So the sorption increases with the same rate as the initial concentration increases (Figs. 6(b) and 8(b)). But about nitrate it is near maximum capacity, and the sorption increasing rate is lower than initial concentration increasing rate (Figs. 6(a) and 8 (a)). In the other words, the concentrations which were used for cadmium sorption experiments only spread over linear part of the isotherm (Fig. 8(b)), while

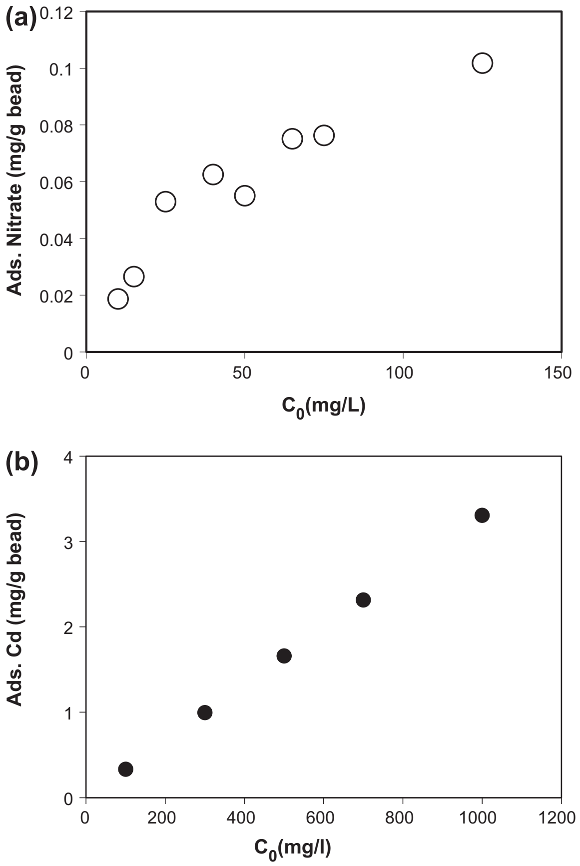

Fig. 6. The adsorbed amount of nitrate (a) and cadmium (b) vs. C_{o}.

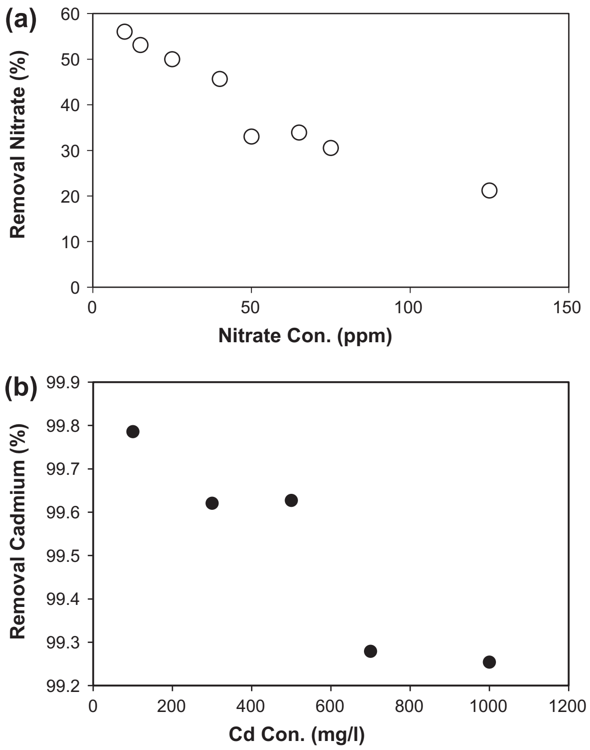

Fig. 7. Removal percent changes vs. initial concentration of nitrate (a) and cadmium (b).

nitrate ones spread over linear and nonlinear part of the isotherm (Fig. 8(a)).

3.3. Effect of diameter

The beads with 3:5:1 aspect ratio was used to investigate the effect of different bead diameters (0.68, 1.23, 1.35, and 2.1 mm) on sorption process. In these experiments, initial nitrate and cadmium concentration, shake speed, and sorbent dose was 10 ppm, 50 ppm, 150 rpm, and 9 g/L (for nitrate: 36 g/L), respectively. Nitrate and cadmium removal vs. diameter is shown in Fig. 9. As it is shown by increasing diameter from 0.68 to 2.1 mm, the removal percent will decrease for nitrate from 18.6 to 16.4% and for cadmium from 98.4 to 75.7%. The rate of decreasing for cadmium is constant and also higher than nitrate.

3.4. Effect of sorbent dose and different aspect ratio

Beads with diameters of 2.1 mm were used to investigate the effect of sorbent dose and different aspect ratio of sodium alginate, PAC, and SMZ on cadmium and nitrate sorption. In these experiments, the initial nitrate and cadmium concentration, temperature, and pH was 10 ppm, 50 ppm, 25℃, and 7.2 ± 0.2, respectively.

Figs. 10 and 11 show amount of adsorbed cadmium and nitrate vs. sorbent dose for two different (Al:SMZ:PAC) aspect ratios. Figs. 10(a) and 11(a) show that the adsorbed amount of both cadmium and nitrate decreases by sorbent dose increasing. The rate of this decreasing is more for cadmium in comparison with nitrate. On the other hand, as depicted in Figs. 10 (b) and 11(b), the removal percent of both nitrate and cadmium will increase by sorbent dose increasing.

By comparing different aspect ratios in Fig. 10 for cadmium removal, one can conclude that 3:5:1 has a better result in removal. On the other hand Fig. 11 shows that 3:4:1 is removed nitrate more effective than 3:5:1.

Comparison of Fig. 10 with Fig. 11 shows that the synthesized beads remove cadmium better than nitrate. So, finally, 3:4:1 aspect ratio is selected for remained experiments.

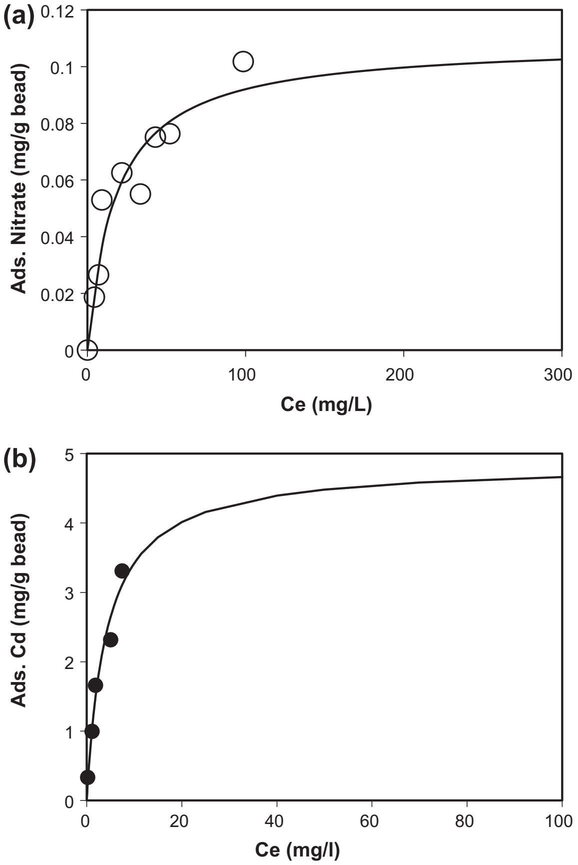

Fig. 8. The adsorbed amount of nitrate (a) and cadmium (b) vs C_e.

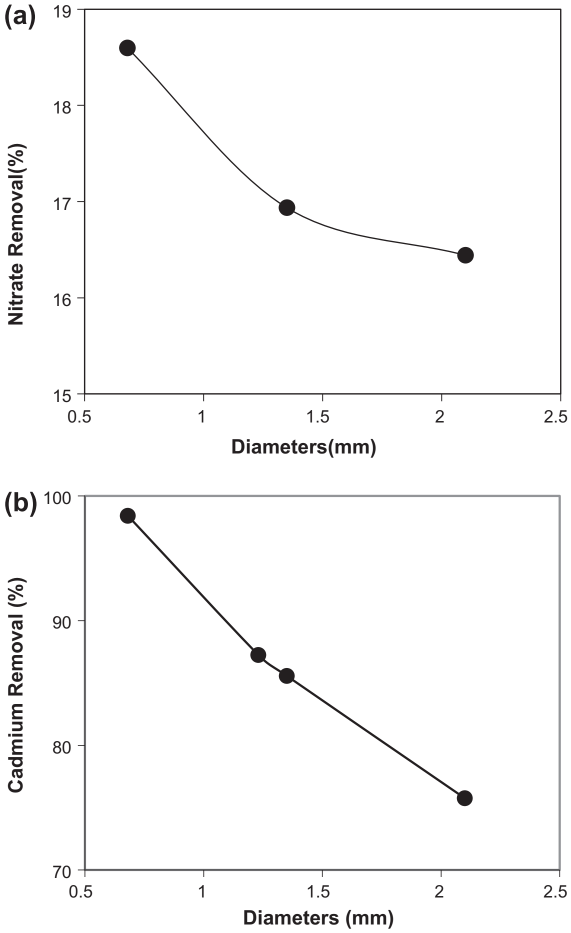

Fig. 9. Nitrate (a) and cadmium (b) removal vs. diameter.

3.5. Effect of nitrate and cadmium presence on each other

This sorbent should be used for the simultaneos removal of anionic and cationic compounds.

So their effect on each other was investigated through equlibrium test. In this sorbent, sodium alginate and activated carbon is used for cationic pollutant removal, and modified zeolite is used for anionic pollutant removal. Schick et al. [31] studied the effect of HCO_3^-, SO_4^{2-} and Cl^- on nitarte sorption to SMZ. Their results showed that although the presence of compiting ions have no effect on equilibrium sorption of nitarte, but they slow down nitate sorption kinetics. Although the affinity of bicarbonate, sulfate, and nitare ions toward the SMZ are the same, but chloride ions is very different with no affinity for the SMZ. These observations had been related to steric or morphological effects [31]. Competitive sorption of simultaneous presence of anionic pollutants is also examined by [57,58]. Papageorgiou et al. [43,59] were studied the competitve sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} on calcium alginate beads. Their study showed that the presence of other metals in the solutions affects, the shape of the isotherm curve, due to changes in apparent metal affinity for the active sites (carboxylic group). Also, the maximum sorption of each heavy metal decreases. Competitive sorption of simultaneous presence of cationic compounds to activated carbon is also examined by [60–62]. In this study existance of two kind of pollutant (anionic and cationic pollutant) were studied experimentally.

Effect of nitarte on cadmium sorption was investigated in cadmium concetration of 300 ppm, temprature of 25°C, and sorbent dose of 5 g/L. Five flasks with cadmium concentration of 300 ppm were considered. The nitrate concentration in each flask was 0, 12.5, 37.5, 75, and 100 ppm. After 5 h shaking, the cadmium concentrations in the samples were measured. This experiment was carried out in duplicate. *T*-test at 5% level of significance shows that there is no significant difference between cadmium concentration of the

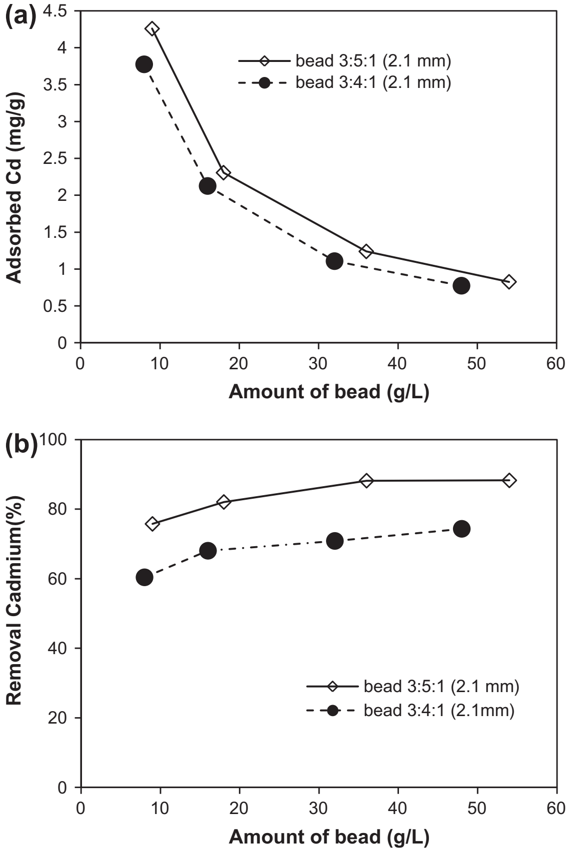

Fig. 10. Effect of sorbent dose and aspect ratio on cadmium sorption (a) and removal (b).

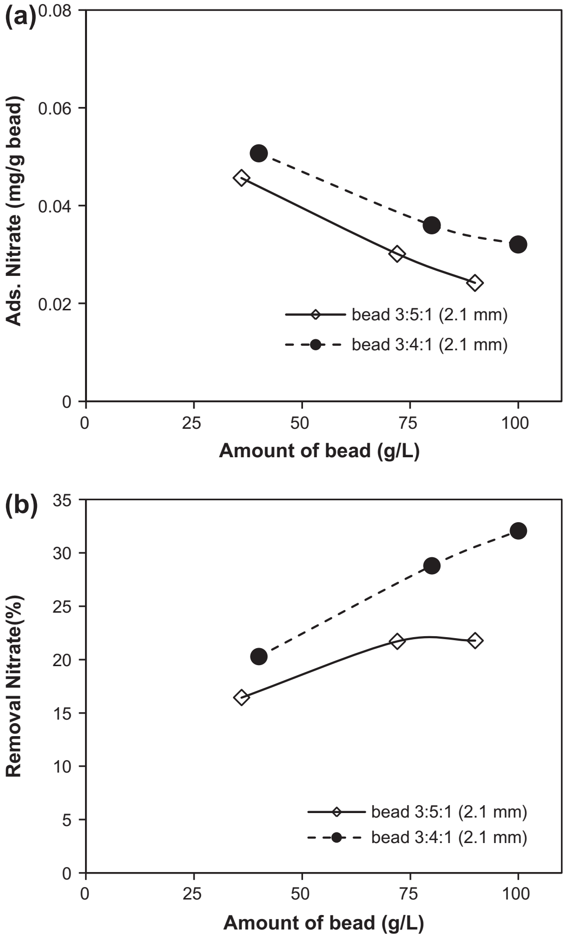

Fig. 11. Effect of sorbent dose and aspect ratio on Nitrate sorption (a) and removal (b).

flasks after 5 h shaking. This is also shown in Fig. 12. Fig. 12(a) and (b) show equlibrium concentration of cadmium and removal percent vs. nitrate concentration. From this figure, as the nitrate concentration increases, the removal percent changes from 38.8 to 37 and equilibrium concentration increases from 183 to 188 which is not statistically significant.

Effect of cadmium on nitrate sorption was investigated in temperature of 25°C and sorbent dose of 100 g/L. Five flasks with nitrate concentration of 25 ppm were considered. The cadmium concentration in each flask was 0, 50, 100, 300, and 500 ppm. After 5 h shaking, the nitrate concentration in the samples were measured. This experiment was carried out in duplicate. *T*-test at 5% level of significance shows that there is significant diffrence between nitrate concentration of the flasks after 5 h shaking. This is also shown in Fig. 13. Fig. 13(a) and (b) show equlibrium concentration of nitrate and removal percent vs. cadmium concentration. From this figure as the cadmium concentration increases, the removal percent increases from 18 to 22 and equlibrium nitrate concentration decreases from from 20 to 18 which is statistically significant. Although nitrate has not significant effect on cadmuium sorption, but cadmium slightly increases nitarte sorption. It can be related to physical sorption of cadmium to activated carbon which can sorbe nitrate to itself and made a Cd–NO_3 clate.

3.6. Isotherm modeling

Isotherm models of Langmuir, Freundlich and Temkin were fitted to describe equilibrium adsorption (Eqs. (5–7)). The parameters were calculated using linear form of the models (Eqs. (8–10)) by plotting q_e vs. q_e/C_e for Langmuir, log (q_e) vs. log (C_e) for Freundlich and q_e vs. ln (C_e) for Temkin. The calculated parameters, CRM, EF, and SSE, for each model are listed in Table 4. According to Table 4, although all 3 models have a relatively good fitting statistics for cadmium,

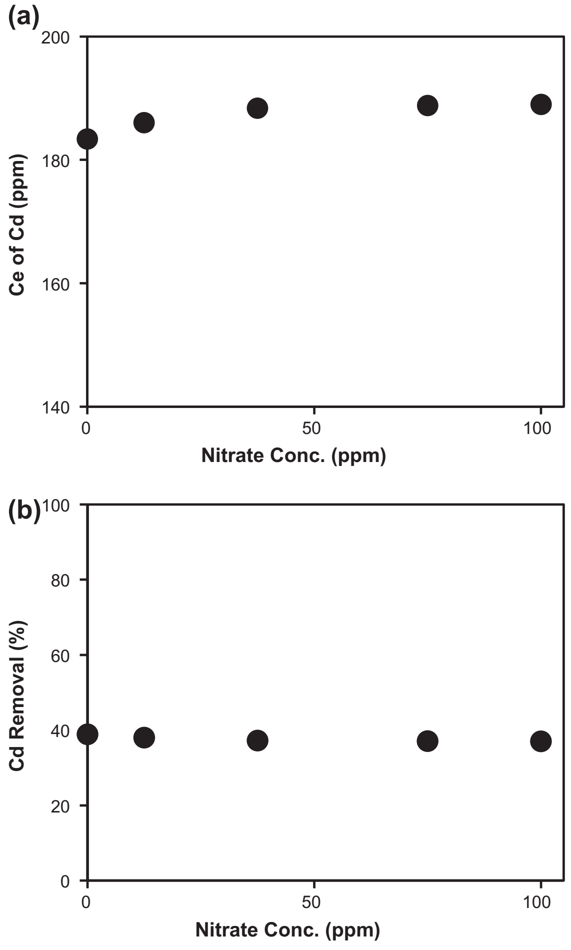

Fig. 12. Equlibrium cadmium concentration (a) and removal percent (b) vs. nitrate concentration.

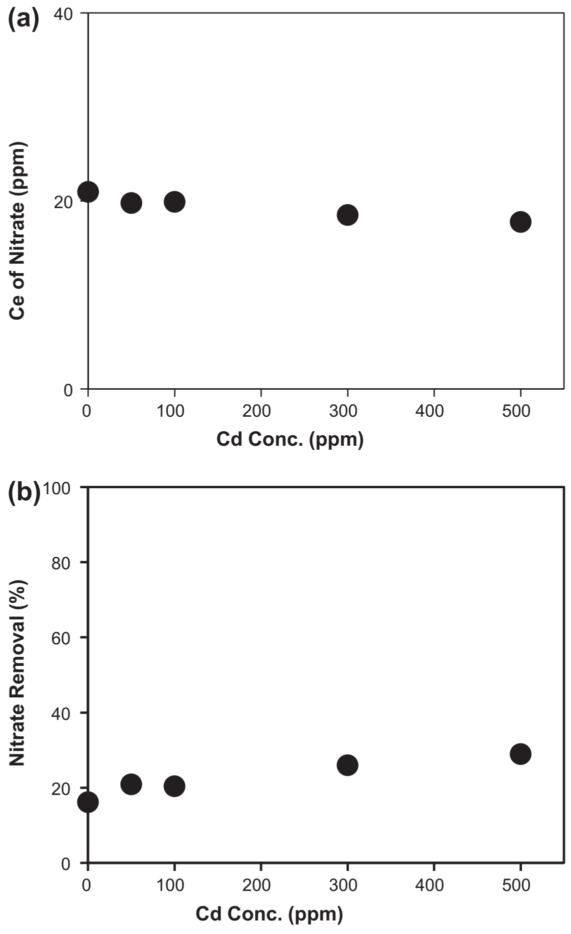

Fig. 13. Equlibrium nitrate concentration (a) and removal percent (b) vs. cadmium concentration.

Table 4
Estimated parameters, SSE, EF, CRM, and R^2 of Langmuir, Freundlich, Temkin for nitrate and cadmium experiments

Pollutant	Isotherm	$q_m/F/b_T$	$K/n/a_T$	SSE	R^2	EF	CRM
Nitrate	Langmuir	0.0904	0.0889	0.00088	0.48	0.89	0.0299
	Freundlich	0.0118	0.4836	0.00064	0.85	0.92	0.0064
	Temkin	1036.69	0.5596	0.00052	0.89	0.94	−0.0006
Cadmium	Langmuir	3.6660	0.4344	0.3451	0.81	0.9353	0.01494
	Freundlich	0.9304	0.6337	0.1567	0.98	0.9706	−0.0053
	Temkin	31.0953	5.0626	0.4873	0.91	0.9086	1.576E-05

but Freundlich with Less SSE and Better EF and R^2 is selected for the governing equation for cadmium sorption. The CRM value of −0.0053 shows a little tendency to overestimate the results.

Table 4 shows that best fit for the nitrate sorption is Temkin with EF = 0.94 and CRM = −0.00063. It shows that this sorbent is more powerful in cadmium sorption than nitrate sorption. Because Freundlich isotherm shows that it is far from its maximum capacity in cadmium sorption.

4. Conclusion

A novel nanopore biopolymer alginate gel bead impregnated with SMZ and PAC was developed for the removal of mixed agricultural and industrial contaminants. Zeolite was modified using HDTMA-Br to remove anions. To remove cationic and organic compounds, lemon-activated carbon was used in this sorbent. In order to examine the adsorption capacity of the alginate complex, both equilibrium and kinetic batch studies were performed. Cadmium and nitrate were used as a representative of cationic and anionic compounds, respectively. Because of the activated carbon used in this sorbent, it has the ability to remove organic and microbial pollutant. The results showed that:

- Pseudo-second-order model is the governing equation for both nitrate and cadmium sorption.
- Parabolic diffusion equation test showed that the plot of q_t vs. $t^{1/2}$ in nitrate experiments is more close to a line with a constant slope in the time span of the experiments. But in the case of the cadmium experiments, a two-step sorption behavior was observed.
- By increasing the initial concentration of cadmium, the amount of the adsorbed Cd increased from 0.33 to 3.31 mg/g, while the removal of Cd from the solutions did not changed significantly (from 99.78 to 99.25%).
- Although the amount of adsorbed nitrate was increased from 0.019 to 0.102 mg/g by increasing initial concentration of nitrate, but the removal percent of nitrate from the solutions was decreased significantly from 56.0 to 21.2%.
- Diameter changes have more effect on cadmium sorption than nitrate sorption. As it was shown in the experiments by diameter increasing from 0.68 to 2.1 mm, the removal percent will decrease for nitrate from 18.6 to 16.4% and for cadmium from 98.4 to 75.7%.
- Comparing different aspect ratios showed that 3:4:1 aspect ratio is the best one.
- Although nitrate presence in the solution with different concentrations has no significant effect on cadmium sorption, but the cadmium presence will enhanced the nitrate sorption which is related to nitrate-cadmium clates.
- Isothermal study showed that Temkin is the governing equation for nitrate sorption and Freundlich is the governing equation for cadmium sorption.
- It shows that this sorbent is more powerful in cadmium sorption than nitrate sorption. Because Freundlich isotherm shows that it is far from its maximum capacity in cadmium sorption.

List of symbols

$\forall$ — the solution volume (l)
W — the weight of wet beads (g)
C_0 — the initial metal concentration (ppm)
t — time
$C_{e \text{ or } t}$ — the bulk metal concentration at indicated time or the equilibrium concentration of the solution (ppm)
k_1 — the pseudo-first-order rate constant
k_2 — the pseudo-second-order rate constant
q_t — the amounts of adsorbed pollutant at time t
q_e — the amounts of adsorbed pollutant at equilibrium time

K_{id} — the rate constant of intra-particle transport (μg g^{-1} min$^{-1/2}$)
C_{e} — the supernatant concentration at the equilibrium state of the system (mg/L)
K — the Langmuir affinity constant
q_{m} — the maximum adsorption capacity of the material (mg/g)
k — the Freundlich constant related with adsorption capacity
n — the Freundlich exponent
R — universal gas constant
T — absolute temperature
b_{T} — temkin isotherm constant
A_{T} — temkin isotherm constant
N — number of data
O_{i} — measured data
$\bar{O}$ — average of measured data
P_{i} — predicted or calculated data
m — number of units in sodium alginate macromolecule
R^2 — statistical linear coefficient of determination (the square of the correlation coefficient, R)

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