Adsorption of Cd^{2+} ions onto magnetic Bentonite/Fe$_3$O$_4$ nanoparticles loaded on Alginate beads in simulated wastewater to protect the environment

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ABSTRACT

Bentonite/Fe$_3$O$_4$ nanoparticles and sodium alginate have high efficiency for adsorption of heavy metal ions. For the purpose, four groups of bentonite magnetic nanoparticles were synthesized at different weight ratios and the prepared magnetic nanoparticles were immobilized on alginate to form calcium alginate beads for elimination of cadmium ions in the synthetic pollutant solution in different condition of adsorbent dosage, pH, stirring rate, pollutant concentration and time of adsorption. The results show that the optimum condition for removal of Cd^{2+} was using 0.15 g of the prepared magnetic alginate/bentonite beads containing 0.4 g magnetic nano bentonite, duration of 8 h for adsorption time and stirring rate of 200 rpm. Furthermore, adsorption efficiency of the beads for adsorption of 100 ppm of Cd^{2+} solution was achieved about 98% and the adsorption of Cd^{2+} by using alginate magnetic beads following Freundlich isotherm model.

Keywords: Alginate beads; Bentonite; Cd^{2+}ions; Isotherm models; Adsorption

1. INTRODUCTION

One of the current concerns of researchers and industry owners is to protect the environment from the pollution created by modern technology and industries. Today pollutants and heavy metals have caused many problems for humans and environment, so, it is important to know and correct the methods of eliminating these pollutants [1]. These heavy metals including lead, zinc, cadmium, copper, nickel and chromium that are soluble in seas, water etc. and cause some problems to health. Among the most important environmental pollutants are cadmium and lead [2, 3].

Cadmium combines with many heavy metals to yield alloys; the most important are bearing alloys and low-melting alloys used for brazing. The small quantities of cadmium added to the heavy metals but cadmium are toxic elements for human and can be very dangerous. Cadmium (Cd) is a toxic metal present in food, tobacco smoke, air, water and other medium, and it

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can enter human bodies through inhalation, ingestion and dermal contact [4]. Cadmium can accumulate in various organs and tissues, but mostly in kidney cortex [5]. In fact, kidney has been considered as the most sensitive target organ in front of cadmium effects [6]. Studies have evaluated population health risks due to cadmium exposure through various pathways, e.g. direct ingestion of water and accidentally soil, consumption of food grown in contaminated fields, inhalation of dust, and dermal contact of soil and water [7–9]. Magnetic nanoparticles are particles that have at least one dimension in the nano scale and their behavior depends on their size. One of the advantages of magnetic nanoparticles is their high efficiency in removing alloys that distinguishes them from other adsorbents [10, 11]. Bentonite is a kind of quasi-clay minerals formed from swollen minerals and generally contains montmorillonite and a small amount of biolith [12, 13]. It is essentially composed of montmorillonite or smectite group minerals and contains Na^+ and Ca^{2+} as exchangeable cations [14, 15]. Bentonite that modified magnetic iron oxide has been used previously. These nanoparticles were used to purify water after producing contamination with cadmium (II) and lead (II) ions [16]. The clay surface was loaded by loading the nanoparticles as activator to remove lead and cadmium ions. Bentonite was used for removal of Cr (VI) [17], Pb^{2+} [18], Co^{2+} [19], Ni^{2+} [20], Cd^{2+} [20] as well.

Sodium alginate is a linear polysaccharide and is a cheap biopolymer that has received much attention because of its biodegradability, hydrophilic properties, pH sensitivity and natural nature. It has also been used in recent years for applications in biotechnology, medical, pharmaceutical and especially food industries [21]. Furthermore, sodium alginate can be cross-linked by using

calcium ions and make beads [22, 23].

Alginate beads were used for elimination of Cu^{2+} [24], La^{3+} [22], As (V) [25] and Cr (VI) [26] as well.

Bentonite/alginate composition has previously been used to remove Cu (II) as an alternative to reduce pollution problems [27]. Alginate / Bentonite was used for absorption of Cd (II) [28], Cr (V) [29], Ni^{2+} [30] and Cs^+ [31] by researchers.

At the first step of this research, magnetic bentonite nanoparticles with different mass ratios of bentonite were prepared and the samples characterized by Fourier-transform infrared spectroscopy (FT-IR), Vibrating-sample magnetometer (VSM) and Field Emission Scanning Electron Microscopy (FE-SEM). Then, magnetic beads of calcium alginate were prepared using magnetic bentonite nanoparticles and sodium alginate biopolymer. The prepared beads were used for adsorption of Cd^{2+} ions in different conditions for obtaining the optimum condition for adsorption of Cd^{2+} ions. Furthermore, the adsorption isotherms were investigated as well.

2. EXPERIMENTAL
2.1 Materials and Methods
Natural bentonite clay was prepared from Bentonite mines of Zanjan province, $FeCl_3.3H_2O$, ethylene diamine (99%), ethylene glycol (99.8%), sodium alginate, $Cd(NO_3)_2$ (98%), Sodium acetate trihydrate (99%), HCl (37%), NaOH (98%) were all from Merck chemical company.

2.2 Instrumentation
Fourier-transform infrared spectroscopy (FT-IR) spectra was obtained by using PERKING ELEMER spectrometer. VSM analyses performed using an apparatus model MDKM. The surface morphology of the synthesized adsorbent has been studied using Field Emission Scanning Electron Microscopy (FE-SEM) model SIGMA VP

(ZEISS, Germany) equipped with Energy-dispersive X-ray spectroscopy (EDX) analyses. Atomic absorption spectroscopy model Varian (AA 240) with the wavelength and current of the lamp for cadmium (228.8 nm and 4 mA respectively) measured the atomic absorption of the contaminant.

2.3 Preparation of Fe₃O₄/Bentonite nanoparticles immobilized on Alginate beads

Fe$_3$O$_4$/Bentonite was prepared using the method described by Yan et al [18]. For this purpose, 2 g of three-valent iron chloride was dissolved in 40 ml ethylene glycol to create a brownish solution and shacked for 30 min using a shaker. Then 6 g sodium acetate trihydrate and 20 ml ethylene diamine were added to the solution. After that natural bentonite in different weights of (0.2, 0.4, 1 and 2 g) was distributed evenly in the solution and stirred for 30 min. Then the solution poured in stainless high-pressure autoclave and heated for 8 h at 200 ^{0}C. The resulting solid is separated by a magnet and washed with deionized water several times, then dried for 12 h in an oven at 80 ^{o}C and passed through a 100-mesh sieve. The prepared samples put in a desiccator for further usage. The prepared samples put in a desiccator for further usage. These samples coded as Table 1 and coded as M1, M2, M3 and M4. For preparation of magnetic beads, method described by Kanakaruju et al. was used with some modification [32]. At the next step, 1 g of sodium alginate was dissolved in 25 ml of distilled water and stirred for 1 hr. at 60 °C. then 1 g of magnetic bentonite which had dispersed in 25 ml of distilled water was poured slowly into sodium alginate solution drop by drop and stirred vigorously for 2 h at 60 °C. Then it was putted in a stainless high-pressure autoclave for 20 min. at 120 °C. The

mixture of sodium alginate and bentonite was poured into the borate and added drop by drops into the calcium chloride mixture (3% wt. in distilled water) which was stirred vigorously in the container. The prepared beads were kept for 24 h rest in calcium chloride solution. Then the magnetic beads (sorbents) were separated and washed with distilled water for several times. Then dried for 10 h at 40 °C in an oven. These samples coded as Table 1.

Table1. Prepared magnetic sample of Fe$_3$O$_4$ / Bentonite

Sample code	Description
B$_1$	2g FeCl$_3$. 6H$_2$O + 0.2 g Bentonite
B$_2$	2g FeCl$_3$. 6H$_2$O + 0.4 g Bentonite
B$_3$	2g FeCl$_3$. 6H$_2$O + 1g Bentonite
B$_4$	2g FeCl$_3$. 6H$_2$O +2 g Bentonite

2.4 Adsorption efficiency of the prepared magnetic beads

For investigate of adsorption process, 0.1 g of adsorbent was added to 50 mL contaminant solution of 3 mg / L Cadmium nitrate salt. The solution was stirred for 12 h. After that, the residual concentration of the pollutant solution was measured using atomic absorption spectrophotometer. To achieve the optimum condition, different amounts of adsorbent (0.05 , 0.1, 0.15 and 0.25 g), different contacting time (2, 4, 8, 12 and 24 h), different concentrations of pollutant (30 , 100 , 200 , 400 , 500 mg/l), different stirring rate (50, 100, 150 and 200 rpm) and different pH of the solution (2 , 4, 7, 10 and 12) were examined and the adsorption percentage of Cd^{2+} ions was calculated using equation 1.

$$Adsorption\ (\%) = \frac{C_i - C_f}{C_i} * 100 \qquad (eq.\ 1)$$

Where, C_i and C_f are the initial and final metal ion concentrations, respectively.

2.5 Adsorption Isotherms

In this study, Langmuir or *FREUNDLICH* equations models were

applied to analyze the experimental result of the optimum condition.

Equation 2 and 3 show Freundlich adsorption isotherms:

$$q_e = K_f . C e^{1/n} \qquad \text{(eq. 2)}$$

$$\text{Log } q_e = \log K_f + 1/n . \log C_e \qquad \text{(eq. 3)}$$

Where:

C_e: equilibrium concentration of species absorbed in solution (mg/L)

q_e (mg /g): amount of adsorbate which adsorbed per unit of adsorbent.

K_f (mg/L) and n are Freundlich constants of absorption capacity and non-uniformity of bond strength, if n less than one, indicates the suitability of the adsorption conditions. The following equation is used to obtain the amount of material adsorbed at each desired point and moment of equilibrium [33-35].

$$q_e = (C_0 - C_1) \, V / m \qquad \text{(eq. 4)}$$

In which, q_e: is adsorbed amount at time (mg/g), C_0: is initial concentration of Cd^{2+} (mg/L) at time, C_1: is final concentration of Cd^{2+} (mg/L), m: is mass of adsorbent (g) and V: is volume of the adsorbate solution (L).

Equation 5 shows Langmuir adsorption isotherm:

$$1 / q_e = 1 / C_e \, q_{max} \, k_L + 1 / q_{max} \qquad \text{(eq. 5)}$$

Where, k_L: constant related to the bonding energy of the adsorbent for adsorbate (Lmg^{-1}),

q_{max}: maximum uptake of adsorbate (mg / g) and C_e: equilibrium concentration of species absorbed in solution (mg/L).

Dimension separation factor RL (eq. 6), indicates the type of isotherm to be unfavorable (RL> 1), favorable (0 < RL< 1) or irreversible (RL= 0) and defined as [33, 34]:

$$RL = \frac{1}{1 + k_l \, C_0} \qquad \text{(eq. 6)}$$

Where, k_L (L/mg) is the Langmuir constant and Co (mg/L) is the initial concentration of Cd^{2+}.

3. RESULTS AND DISCUSSION
3.1 VSM analyses of the nano particles

Fig. 1 shows hysteresis curve of the samples at room temperature in the magnetic field of -15000 to 15000 Oe. Based on the theory of ferromagnetism (Neel Theory), in the spinel structure cations under different structures of (quadrilateral and octahedral position) have antiparallel torque. Therefore, according to this theory and awareness of the amounts of magnetic moments, the magnetic behavior of the specimens can be justified [20].
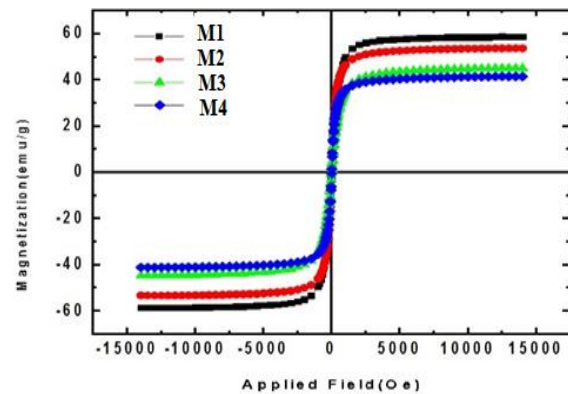

Fig. 1 VSM curves of the prepared magnetic samples

As it can be seen, the particles magnetization curve passes through the source, with no forcing field and residual magnetization. Therefore, it can be concluded that the synthesized particles are all at superparamagnetic room temperature.

Such a high magnetization was related to the synthesis of Fe_3O_4 nanoparticles on the bentonite surface during the solvothermal process [20], thus, separation of the samples from the solution are quickly by using a magnet.

Table 2 shows the magnetization saturation values (M) of the samples. As expected, by increasing the amount of bentonite in the structure, a decreasing trend is observed.

Table 2. Magnetization value of the magnetic bentonite nano particles

M (emu/g)	M1	M2	M3	M4
	60	56	42	40

Curves M_1, M_2, M_3 and M_4 justify the magnetic behavior of the samples, which, as we expect, decreases with increasing bentonite content in the nanoparticle structure. All samples pass through the origin, and all of them are super-magnetic, and the higher the height of the graphs, they are the more magnetic.

3.2 FE-SEM images of the magnetic beads

Fig. 2 shows FE-SEM images of the prepared magnetic nano particles and the beads. As it can be seen from the images (Fig. 2a), Fe_3O_4/Bentonite nanoparticles are spherical shapes and uniform size of about 15-32 nm. Furthermore, magnetic nanoparticles of Fe_3O_4 covered the surface of bentonite. During the reaction, at first Fe^{3+} ions formed by dissolving and cross-linked to the surface of bentonite. Fig. 2b shows the morphology of the prepared magnetic bentonite/alginate beads befor

using as an adsorbent. Dehydration process make the surface of alginate beads ridge-like structure, but because of the presence of Fe_3O_4/ Bentonite nanoparticles and cross linking process between bentonite and alginate, the surface of the beads varied [18].

The morphology of the beads revealed in Fig. 2 which indicated the presence of pores on the surface of the prepared alginate/ bentonite bead.

3.3 FT-IR analyses of the magnetic nanoparticles

Fig. 3 shows the FT-IR spectra of magnetic bentonite/alginate beads. A peak at 1420 cm^{-1} belongs to CH_2 bending vibration and C-OH in plane bond, the peak around 3300 cm^{-1} shows O-H stretching vibration, a peak at around 1600 cm^{-1} shows COO^- asymmetric and symmetric stretching vibration which all belongs to the presence of alginate in the composite. A peak at 575 cm^{-1} shows C-O-C, C-C-H bending C-H group out of plane and C-C bending out of plane vibration. A peak at 1055 cm^{-1} shows C-O-C, CO stretching vibration and O-H vibration of saccharide structure. A peak at 817 cm^{-1} shows the torsion of –CH_3 [36].

Furthermore, the existence of the peak around 560 cm^{-1} shows the presence of Fe-O vibration of iron oxide.
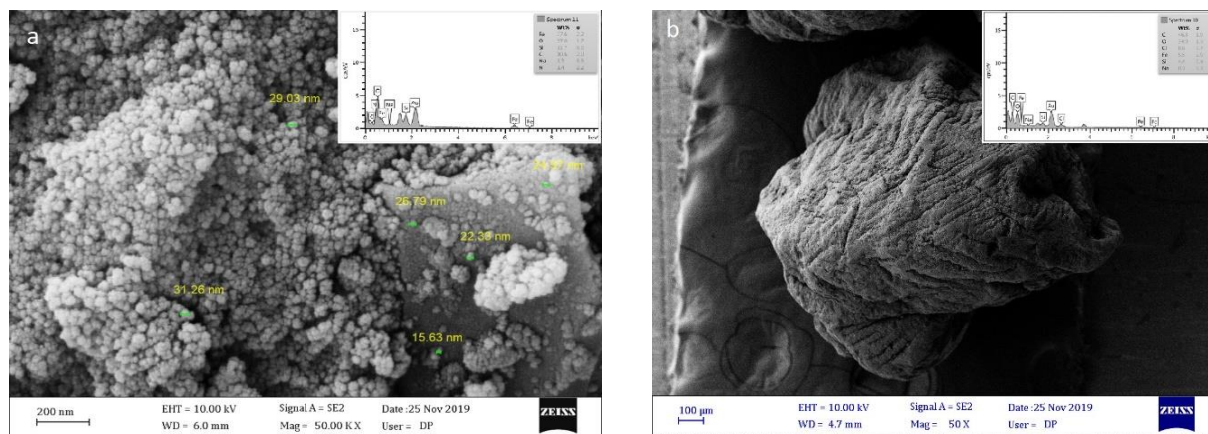

Fig. 2 FE-SEM images of a) Fe_3O_4/Bentonite nanoparticles (sample M3), b) Magnetic Bentonite/Alginate beads with EDX analyses
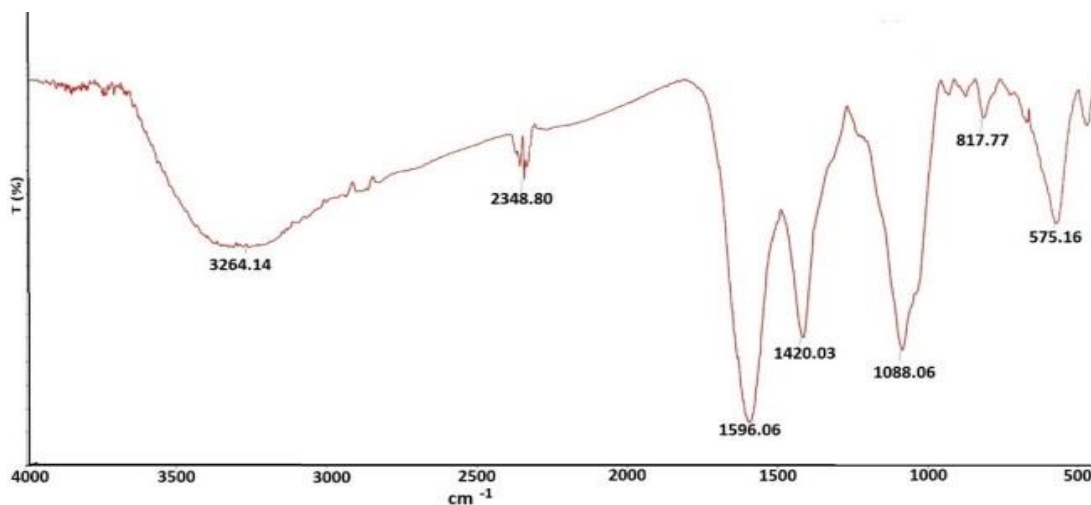
Fig. 3 FT-IR spectra of the magnetic alginate/bentonite beads

3.4 Adsorption efficiency
3.4.1 Effect of bentonite amount of the nanoparticles on the adsorption efficiency

To determine the optimum amount of bentonite in the beads structure for the adsorption experiments, 0.1 g of each nano magnetic beads of the samples (M1, M2, M3 and M4) was added to 50 ml of Cd^{2+} solution (3 ppm) at absorption time of 24 h, pH =7 and stirring rate of 100 rpm at room temperature. Fig. 4a shows the results of the adsorption of Cd^{2+} ions in the presence of different sorbents. The results showed that the weight of 0.4 g bentonite (composition of sample M2) in the bead structure for Cd^{2+} removal had the best performance, which was 49.4% adsorption efficiency. The composition of this sample used for making extra magnetic alginate/bentonite beads for further experiments.

3.4.2 Effect of the beads amount on the adsorption efficiency

The adsorbent of Fe_3O_4/bentonite on alginate beads (prepared by 0.4 g bentonite) were used in the amount of (0.05, 0.1, 0.15 and 0.25 g) at condition of adsorption time = 24 h, pH =7, stirring rate of 100 rpm and contaminated concentration of 3 mg/L of cadmium

solution (50 ml). The results were illustrated in Fig. 4b. As it can be seen, by using 0.15 g of the beads, the level of contaminate was decreased from 3 mg/L to 0.69 mg /L, which was 77% efficiency. Therefore, using 0.15 g of the beads in the first step had better adsorption performance.

3.4.3 Effect of contact time on the adsorption efficiency

0.15 g of the prepared beads were put in 50 ml of water containing 3 mg/L Cd^{2+} at the condition of pH =7, stirring rate =100 rpm and adsorption time of 2, 4, 8, 12 and 24 h. The atomic adsorption results showed that at duration of 8 h the adsorption for cadmium contaminate reached to maximum level and after that, adsorption efficiency does not improve (Fig. 4c). Therefore, 8 h of contact time was choose as the best time that shows about 77% adsorption efficiency.

At the contact time of less than 8 h, there was still empty space in the beads to adsorb the cadmium ions, which in 8 h, these spaces were minimized by adsorption. After 8 h of contact time, desorption of Cd^{2+} ions from the adsorbent surface into the solution increase the amount of cadmium ions of the solution, so

the efficiency was decreased by decreasing the adsorption amount and increasing the cadmium ions.

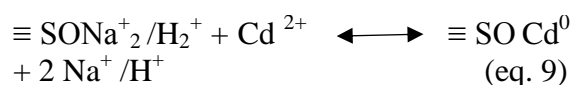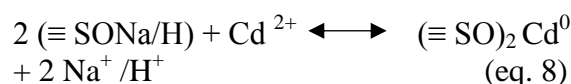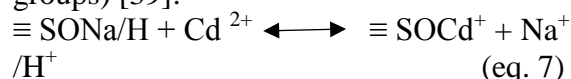### 3.4.4 Effect of stirring rate on the adsorption efficiency

To optimize the stirring rate for adsorption of cadmium ions 50 ml of the pollutant was prepared including 3 mg/L of Cd^{2+} concentration. Then 0.15 g of the prepared beads were added and the solution pH adjusted at 7 and the adsorption time was 8 h. Different stirring rate of 50, 100, 150 and 200 rpm, were performed and the residual concentration of Cd^{2+} was analyzed by atomic adsorption. Fig. 4d shows the results of the adsorption efficiency using different stirring rate of the pollutant solution. The results showed that at 50, 100, 150 and 200 rpm, the contamination of water was decreased from 3 mg/L to 2.43, 0.69, 0.56 and 0.50 mg/L respectively, which was 19%, 80%, 81% and 83% respectively. So, the rate of 200 rpm choose as the best quantity. By increasing the stirring rate more than 200 rpm, several magnetic Alginate/Bentonite beads were hitting each other tightly and the beads were broken and the adsorption efficiency was decreased by increasing the turbidity of the solution and cracking of the beads. At the lower stirring rate, the surface contact between the pollutant and the adsorbent was not effective, so the adsorption efficiency was decreased.

3.4.5 Effect of pH on the adsorption efficiency

As pH can affect the composition of the sorbent and the solution properties, it considered as an important factor in adsorption process [37]. For this purpose, 0.15 g of the prepared beads were put in 50 ml of cadmium contaminated water containing 3 mg/L of Cd^{2+}, stirring rate of 200 rpm and duration of 8 h. Different pH
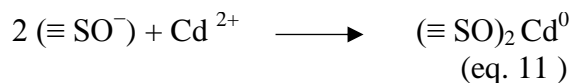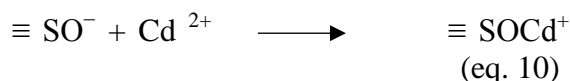
of 2, 4, 7, 10 and 12 of the solution were applied and the results showed in Fig. 4e The results revealed that the concentration of cadmium at pH of 10, decreased from 3 mg/L to 0.6 mg/L that is about 80% adsorption efficiency.

Two mechanisms affect the adsorption process using bentonite: one is ion exchanging and the other is formation of chalate complexes [38]. The adsorption of Cd^{2+} ions by ion exchange process that happens between surface hydroxyl groups and cadmium ions can be described as follows ($\equiv$ S represents negative surface groups) [39]:

$$\equiv SONa/H + Cd^{2+} \longleftrightarrow \equiv SOCd^+ + Na^+/H^+ \qquad (eq. 7)$$

$$2 (\equiv SONa/H) + Cd^{2+} \longleftrightarrow (\equiv SO)_2 Cd^0 + 2 Na^+/H^+ \qquad (eq. 8)$$

$$\equiv SONa^+_2/H_2^+ + Cd^{2+} \longleftrightarrow \equiv SO Cd^0 + 2 Na^+/H^+ \qquad (eq. 9)$$

Lead (II) ions have a large ionic radius (1.20Å) with low density of charge, so protonation of the surface groups affect the adsorption process [40].

As the pk_a of the carboxylic groups of the alginate have been reported to be in the range of 3.4 to 3.9, by decreasing the pH under 3.4, positive charge on the sorbent causes electric repulsion between metal ions and functional groups on the surface of the beads, as a result Cd^{2+} absorption is reduced [37, 41]. Furthermore as hydrogen ions (H^+) are strong adsorbate, in highly acidic conditions competition between hydronium ions and metal binding site occurs, so the attraction between the adsorbent and adsorbate is reduced [37]. Protonation and deprotonation of silanol on the bentonite, which interacted with carboxylate groups on the alginate, make the surface charges of the sorbent [42], the process is as follows [39]:

$$\equiv SO^- + Cd^{\,2+} \longrightarrow \equiv SOCd^+ \qquad (eq.\ 10)$$

$$2\,(\equiv SO^-) + Cd^{\,2+} \longrightarrow (\equiv SO)_2\,Cd^0 \qquad (eq.\ 11\ )$$

By increasing the pH of the solution in the range of concentrations, the number of -COO$^-$ ions on the surface of adsorbent increase, so electrostatic attraction of Cd^{2+} ions and the functional groups on the surface of the adsorbent will increase as well. As the point of zero charge (pH$_{pzc}$) of bentonite is about 6-8, alkali medium increases the adsorption capacity, because beside the electrostatic attraction of Cd^{2+} ions, at pH higher than pH$_{pzc}$ cation exchange will happens and the adsorption capacity increases. Of course, the hydrolyzed species with a larger ion that facilitates contact between the functional groups and the metal will be created.

Higher pH may be give partial formation of CdOH$^+$ [10, 43]. CdOH$^+$ ions have lower energetic barriers (because of being monovalent) and come closer to the surface of the adsorbent comparing with Cd^{2+} ions and results in decreasing the adsorption efficiency [44, 45]. On the other hand, at higher pH, Cd^{2+} ions can form insoluble Cd(OH)$_2$ compound so, the carboxyl groups on the alginate can't bind with insoluble precipitates [46]. As Cd(OH)$_2$ had amphoteric characterization, at alkali pH, dissolution of Cd(OH)$_2$ resulted in the formation of Cd(OH)$_3^-$ ions and decreasing the adsorption capacity [46, 47].

3.4.6 Effect of Cd^{2+} concentration on the adsorption efficiency

Based on the optimal conditions, the experiment was performed for different concentrations of contaminants and the concentrations of Cd^{2+} in solution changed to 100, 200, 400 and 500 mg/L. The atomic adsorption results showed that the amount of Cd^{2+} in the solution decreases from 100 mg/L to 1.806 mg/L, which shows 98 % adsorption efficiency (Fig. 4f).

Increasing the adsorbent efficiency by increasing the pollutant concentration is due to the gradient between the solution Cd^{2+} concentration and the surface Cd^{2+} concentration [48]. The surface area and total pore volume of the Fe$_3$O$_4$ / bentonite were all larger than the nature bentonite and pure Fe$_3$O$_4$. Moreover, the magsorbent was easily collected from aqueous media by using an external magnetic field. These results permitted to conclude that magnetic alginate beads could be efficiently used to remove heavy metals in a water treatment process.

As a result, the optimal conditions adsorption of Cd^{2+} from the solution achieved using 0.15 g of magnetic beads which was prepared by using 0.4 g bentonite in the nano composite structure, solution pH of 10, adsorption time of 8 h and stirring rate of 200 rpm which van reduces the concentration of Cd^{2+} concentration from 100 mg/L to 1.806 mg/L, which is 98 % adsorption efficiency. Table 3 shows the adsorption efficiency of some adsorbents prepared by other researchers.

3.5 Langmuir and Freundlich adsorption isotherms

Fig. 5 (a, b) shows Langmuir and Freundlich isotherm for adsorption of Cd^{2+} ions. The Langmuir model explains the monolayer adsorption process that occurs on the homogeneous adsorbent surface, the Freundlich isotherm model is an empirical equation used to describe the multilayer adsorption on heterogeneous surface [49].

As the results show the adsorption of Cd^{2+} by using alginate magnetic beads following both of the isotherms, but the Freundlich model (Table 4, R^2 = 0.9943) more than the Langmuir one. In the equation, k$_f$ and n are the Freundlich
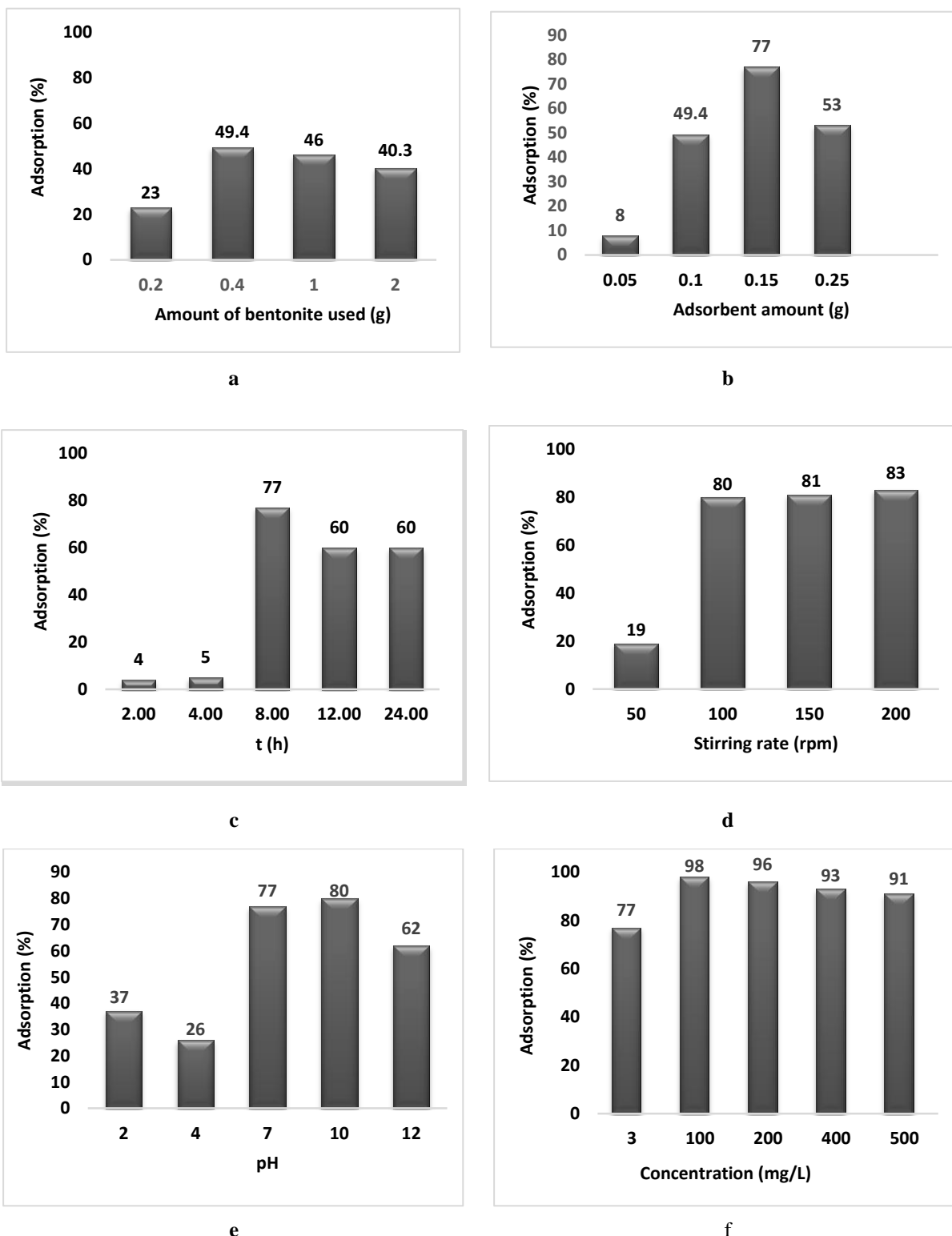
Fig. 4 a) Adsorption efficiency using different amounts of bentonite in the beads, b) Amount of adsorbent on the adsorption efficiency, c) Effect of contact time on the adsorption efficiency, d) Effect of stirring rate on the adsorption efficiency, e) Effect of pH on the adsorption efficiency, f) Adsorption efficiency in different concentration of Cd^{2+} solution

Table 3: Comparison of cadmium uptake parameters with other studies

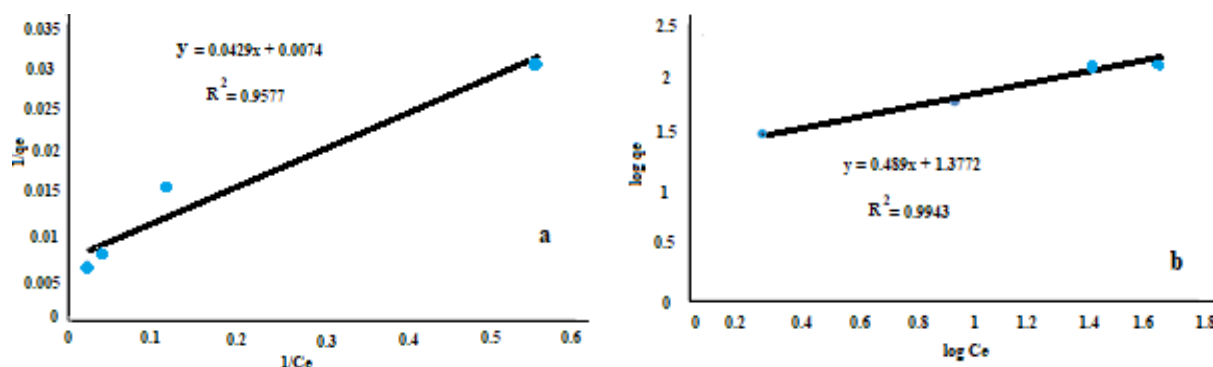| Absorbent	Concentration (mg/L)	Adsorption (%)	Refs.
Bentonite-Fe_3O_4-MnO_2	100	95.2	[11]
Natural Egyptian Bentonitic Clay	0.8	93.4	[52]
Sodic Bentonite	0.394	97.62	[53]
Bentonite/$CoFe_2O_4$@MnO_2 magnetic	10	>97	[54]

Fig. 5 a) Langmuir, b) Freundlich plot of adsorption data for Cd^{2+}

Table 4: Langmuir and Freundlich equation parameters

Langmuir				Freundlich		
q_{max}	k_L	R^2	RL	k_f	n	R^2
135.13	0.17	0.9577	0.05	28.83	2.04	0.9943

Table 5: Comparison of adsorption parameters for Cd^{2+} removal using other adsorbents

Adsorbent	Langmuir parameter		Freundlich parameter		Refs.
	q_{max}	k_L	kf	n	
Bentonite-Fe_3O_4-MnO_2	35.35	3.53	23.43	11.36	[11]
Fe_3O_4/Bentonite/Heavy Metal (Cd^{2+})	21.7	1.31	9.95	4.975	[18]
Alginate/Bentonite	4.2	14.2	-	-	[28]
Hydroxyapatite-bentonite clay-nano cellulose composite	10.34	64.15	28.38	2.17	[36]
Sodic Bentonite (293 ^{0}C)	0.13	7.68	0.12	0.4	[53]
Natural Egyptian Bentonitic Clay	8.2	1.83	5.09	2.631	[55]
Alginate/ImmobilizedBentonite	130.58	2.3	2.84	2.64	[56]

constants denoting relative adsorption capacity and intensity of adsorption, respectively. Favorability of adsorption indicated by the value of n. When values of n is more than 1, then favorable nature of adsorption happens [50]. As $1/n$ in Freundlich isotherm model indicates the type of adsorption process, if $1/n = 0$, it shows irreversible adsorption, if $0 <1/n <1$ the adsorption status is optimal and $1/n >1$ shows undesirable adsorption status [51]. In the present work, value of 2.04 shows favorable adsorption. Furthermore, the value of RL= 0.05 which is less than 1 and more than zero shows favorable adsorption in Langmuir isotherm, but higher

correlation coefficient belongs to Freundlich isotherm model. Table 5 shows the comparison of the Langmuir and Freundlich equation parameters which were published in the other papers.

CONCLUSIONS

In this research, Fe_3O_4/bentonite nanoparticles were prepared and characterized by VSM and FE-SEM analyses, then the magnetic nano particles were immobilized on calcium alginate beads. The structural properties of the beads were studies by FT_IR and FE-SEM analyses. After that, the removal efficiency of Cd^{2+} ions were studied in different conditions. The adsorption results show that the optimum condition for removal of Cd^{2+} was using 0.15 g of magnetic beads in solution pH of 10, duration of 8 hours for adsorption time and stirring rate of 200 rpm. Furthermore, adsorption efficiency of the beads for adsorption of 100 ppm of Cd^{2+} solution was achieved about 98% and the adsorption of Cd^{2+} by using magnetic alginate beads following Freundlich model.

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جذب یون کادمیم (II) بر روی نانو ذرات مغناطیسی بنتونیت/Fe₃O₄ بارگذاری شده بر روی مهره‌های آلژینات در پساب مصنوعی شبیه‌سازی شده برای حفاظت از محیط زیست

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چکیده

نانوذرات بنتونیت / Fe₃O₄ و آلژینات سدیم راندمان بالایی برای جذب یون‌های فلزات سنگین دارند. بدین منظور چهار گروه از نانوذرات مغناطیسی بنتونیت در نسبت‌های مختلف وزن سنتز شدند و نانوذرات مغناطیسی تهیه شده بر روی آلژینات سدیم بار گذاری شدند تا دانه های آلژینات کلسیم برای حذف یون‌های کادمیم در محلول آلاینده مصنوعی در شرایط مختلف دوز جاذب، pH، دور همزن، میزان نانو ذره، غلظت آلاینده ها و زمان جذب.بررسی شد. نتایج نشان می‌دهد که شرایط مطلوب برای حذف ⁺²Cd استفاده از ۰/۱۵ گرم دانه‌های آلژینات مغناطیسی/بنتونیت تهیه شده حاوی ۰/٤ گرم نانو بنتونیت مغناطیسی، مدت زمان جذب ۸ ساعت و سرعت هم زدن ۲۰۰ دور در دقسیقه بود. علاوه بر این، بازده جذب مهره‌ها برای جذب ۱۰۰ میلی‌گرم بر لیتر محلول ⁺²Cd حدود ۹۸٪ و جذب داشت و از مدل ایزوترم فروندلیچ پیروی می‌کند.

کلید واژه‌ها: دانه‌های آلژینات؛ بنتونیت؛ یون‌های ⁺²Cd؛ مدل‌های ایزوترم؛ جذب

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