

**Preparation of sodium alginate/biosilica/magnetite nanocomposite adsorbent
for cadmium removal from aquatic environments**

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Abstract

Introduction: The application of a novel nanocomposite synthesized through the combination of Fe₃O₄ nanoparticles and biosilica particles for the adsorption of Cadmium in the aquatic medium was investigated.

Materials and methods: As-prepared nanocomposite was immobilized by using sodium alginate polymer. The characterization of the nanocomposite was performed via SEM, XRD and FT-IR together with the determination of zero point charge of the adsorbent surface.

Results: As results, the obtained experimental data were fitted well with pseudo-first order kinetic model ($R^2=0.997$) and Langmuir isotherm model ($R^2=0.990$) with the maximum adsorption capacity of about 42 mg/g. Increasing the dosage of nanocomposite favored the removal of cadmium, while decreasing the initial solute concentration and solution temperature resulted in the enhanced adsorption process.

Conclusion: According to the results of thermodynamic study, the adsorption of cadmium onto the nanocomposite was spontaneous and exothermic in nature.

Keywords: Adsorption; Iron oxide nanostructures; Biosilica; Immobilization, Cadmium

1. Introduction

Water pollution caused by the industrial wastewater has become an environmental and economic critical issue around the world (1). The heavy metals are considered among the most significant pollutants in the industrial wastewater, due to the features such as lack of degradability, persistence, accumulation and toxicity (2). Cadmium, chromium, copper, zinc, and nickel are the most common heavy metals found in high concentrations in the industrial wastewater (3). Cadmium can enter water resources from various sources such as the production of non-ferrous metals, metal plating, battery and paint manufacturing industry, photography, and lead and zinc mines. Moreover, the volcanic eruptions and forest fires are regarded as the major natural resources of cadmium entry into the environment (1, 4). Among the heavy metals, cadmium has been highly regarded by the Environmental Protection Agency (EPA) due to its high toxicity and location in B1 Group of carcinogens, (5, 6). Cadmium can be accumulated similar to the other heavy metals; thus, even low concentrations of it can build up in tissues and can cause cancer (4). The studies have shown that the exposure to various concentrations of cadmium can lead to the acute and chronic disorders of the nervous systems, kidneys, liver and cardiovascular system (1). The World Health Organization (WHO) has determined the maximum concentration of 0.003 mg/l for cadmium in the drinking water (7).

Due to the cadmium health problems in the water, the development of effective methods is essential for removal of the cadmium. Various methods such as chemical precipitation, flotation, ion exchange, membrane processes, electrochemical techniques, biological processes, and adsorption have been reported for removal of the cadmium from water (7). Among these methods, the adsorption process is considered by the researchers for the simplicity, reliability, and safety as an effective economic method for removal of the heavy metals (2, 7, 8). Different

adsorbents such as activated carbon, clay, natural zeolite, furnace ash, bentonite, polymers, resins, biologic adsorbents, and hazelnut shells have been reported for removal of the heavy metals from water and wastewater (9, 10). Siliceous materials are considered as a favorable adsorbent, due to the ability of their surface functional groups in adsorbing the target pollutants (11). Diatomaceous soil, which is also called Bio-Silica, is a siliceous biological sedimentary stone with a porous structure containing 87-91% silicon dioxide. Bio-Silica is considered as a proper adsorbent to absorb the pollutants from wastewater, because of the large surface areas and surface functional groups (12, 13). Among various adsorbents, the nanostructured adsorbents have been noticed by the researchers for the large surface areas and surface active sites compared to the large adsorbents (14, 15). One of the famous nanostructured compounds is the magnetite nanoparticles that have been used due to the large surface area, as well as the ease of synthesis as the adsorbent, or mixed with other adsorbents (1, 4, 10). Moreover, the major advantage of the magnetite nanoparticles is the simple separation ability of the materials from the aqueous solutions by an external magnetic field. However, the adsorption capacity and selectivity were not satisfactory, and also have shown poor stability in the acidic conditions (16).

One of the major problems in the use of adsorbents with nano-dimensions is the separation and recycling of these adsorbents, and one of the most important strategies to achieve this goal is the consolidation of the adsorbent material within another material. Polymer compounds such as chitosan and alginate are among the most widely and aptly used materials for consolidation of nanoparticles. Among the different polymers, the alginate is considered as a major group of organic materials. Alginate contains unique properties such as environmental compatibility, low cost, and lack of reactivity in the adsorbent compound (17). Therefore, this research was aimed to prepare sodium alginate/bio-silica/magnetite nanocomposite adsorbent and evaluate its efficiency

in the uptake of cadmium from the aquatic environments. The nanostructure, in addition to its high adsorption capacity and resistance in the environment, can be easily extracted from the environment by an external magnetic field from the outside and recycled after being used.

2. Materials and methods

2.1. Materials

All materials utilized in this study were laboratory grade and were being used in pure form. Bentonite was purchased from the representative of Sigma-Aldrich Corporation. Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), and other chemicals have been bought from a representative of the Merck Group, Germany.

2.2. Preparation of nanocomposite adsorbent

2.2.1. Preparation of magnetic bio-silica

In this study, the chemical co-precipitation method has been employed using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and bio-silica in an ammonia solution under nitrogen gas to produce the magnetic bio-silica. Then, 2 g of bio-silica was added to 100 ml of distilled water and was exposed to ultrasonic waves for 12 hours, and 0.8457 g of iron chloride (II) and 2.2992 g of iron chloride (III) was dissolved in 50 ml of distilled water. Then, 50 ml of bio-silica mixture was added to 50 ml of iron chlorides solution. The resulting mixture was stirred at a temperature of 80 °C under nitrogen gas for 30 minutes. Afterward, 25 ml of ammonia 25% (W/W) was injected into the obtained mixture in an intense stirring state, and the action of mixing continued under nitrogen gas for another 1 hour. Once the time is over, the magnetic bio-silica was collected using a

magnet and was washed for several times using the ethanol and pure distilled water. Finally, the magnetic bio-silica was dried at the temperature of 70 °C (18).

2.2.2. Preparation of alginate/magnetic bio-silica nanocomposite

First, 100 ml of 1 M acetic acid was prepared, and then, 1 g of sodium alginate was added to it before mixing. Then, 1 g of magnetic bio-silica was added to the mixture of acetic acid and sodium alginate, and mixing was continued until a homogeneous viscous mixture was obtained. Then, a mixture with a volume of 100 ml was obtained from 15% NaOH and 95% ethanol with a ratio of 4 to 1. The viscous mixture of sodium alginate/magnetic bio-silica was added drop by drop to NaOH and ethanol mixture using a syringe. The developed bullet-shaped compounds should be maintained for 24 hours. Then, the obtained compound was washed with distilled water (to reach the neutral pH of solution) and was dried at laboratory temperature. Finally, the dried mixture was meshed using the sieves (19).

2.3. Adsorption process method

The adsorption process was carried out in the 100 ml Erlenmeyer flasks. The preferred cadmium concentrations were prepared in 50 ml of distilled water, and then the required changes were made. Afterward, the Erlenmeyer flasks were placed on a shaker for mixing. After passing the required time, the samples were taken and studied. In this study, effects of variables of pH (2, 5, 7, 9 and 11), adsorbent dose (0.5, 1, 2 and 4 g/L), contact time (15, 30, 60, 120 and 180 min), cadmium concentration (10, 20, 40, 80 and 160 mg/L), and temperature (25, 35 and 45) were studied as one factor at a time.

2.4. Analysis

The residual concentration of cadmium after the adsorption process was determined using atomic adsorption spectrophotometer (Germany). As-prepared immobilized nanocomposite was characterized using a scanning electron microscope (TESCAN, Czech Republic). Scanning electron microscopy (SEM) was performed for morphological characterization. Furthermore, X-ray diffraction (XRD) analysis was conducted on a PANalytical diffractometer (Model: X'Pert PRO MPD, the Netherlands) scanned between 10 and 80° using a Cu anode. Considering the fact that surficial functional groups play important role in the adsorption of target pollutants onto the adsorbent, Fourier transform infrared (FT-IR) spectroscopy was performed via a Bruker spectrometer (Model: Tensor 27, Germany) in the wavenumber range of 400-4000 cm⁻¹.

3. Results and discussion

3.1. Characterization

SEM analysis was performed to show surface morphology of the adsorbent. The images taken via SEM are provided in Fig. 1. As shown in Fig. 1 (a), as-synthesized pure Fe₃O₄ nanoparticles are in nano-size with diameter size of lower than 50 nm. However, as can be seen in Fig. 1 (a), some aggregated particles can be found among as-prepared nanoparticles. Fig. 1 (b) shows the surface morphology of immobilized form of Fe₃O₄/biosilica/alginate nanocomposite. As depicted, surface of the immobilized nanocomposite is rough. This rough surface would be appropriate for molecular diffusion of the target pollutant, providing a larger reaction surface for adsorbing the contaminant. Furthermore, the combination of Fe₃O₄ nanoparticles with biosilica resulted in the growth and formation of nanoparticles with lower particle size, which may be due

to the deterrent role of biosilica against the aggregation of Fe_3O_4 nanoparticles during the synthesis (Fig. 1 (b)).

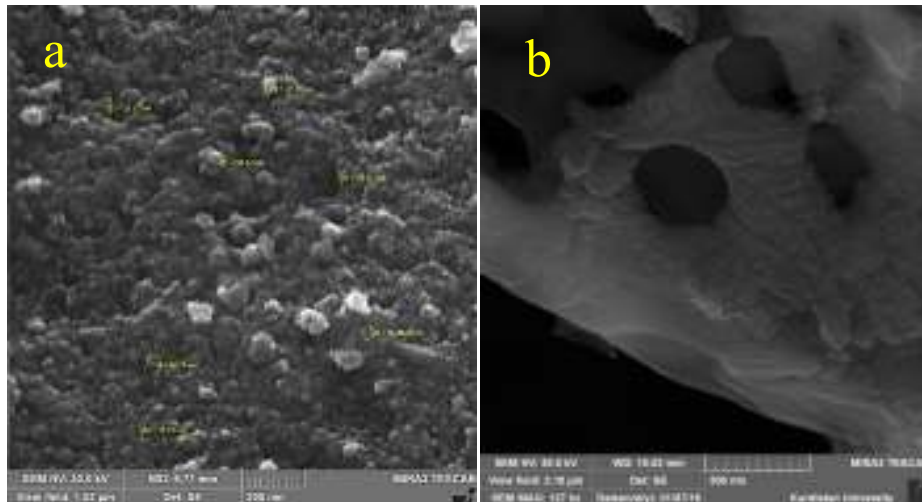


Fig. 1. SEM images of pure Fe_3O_4 nanoparticles (a) and Fe_3O_4 /biosilica/alginate (b)

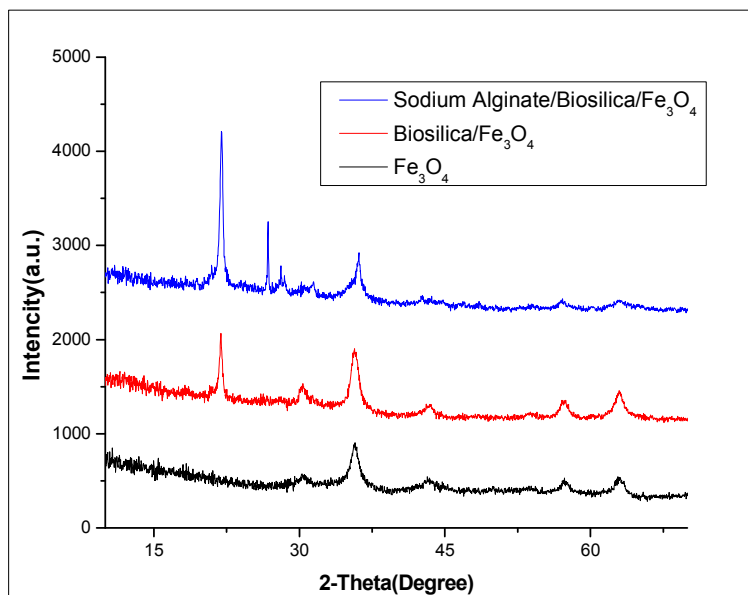


Fig. 2. XRD patterns for pristine Fe_3O_4 nanoparticles, Fe_3O_4 /biosilica and Fe_3O_4 /biosilica/alginate nanocomposite

The patterns of XRD analysis for pure Fe₃O₄ nanoparticles and Fe₃O₄/biosilica nanocomposite are illustrated in Fig. 2. The peaks placed at 35, 43, 57 and 62° are associated with Fe₃O₄ nanoparticles with JCPDS Card No. 19-0629 (20). The appearance of biosilica peaks alongside the characteristic peaks of Fe₃O₄ nanoparticles confirmed the perfect combination of nano-sized Fe₃O₄ with biosilica particles.

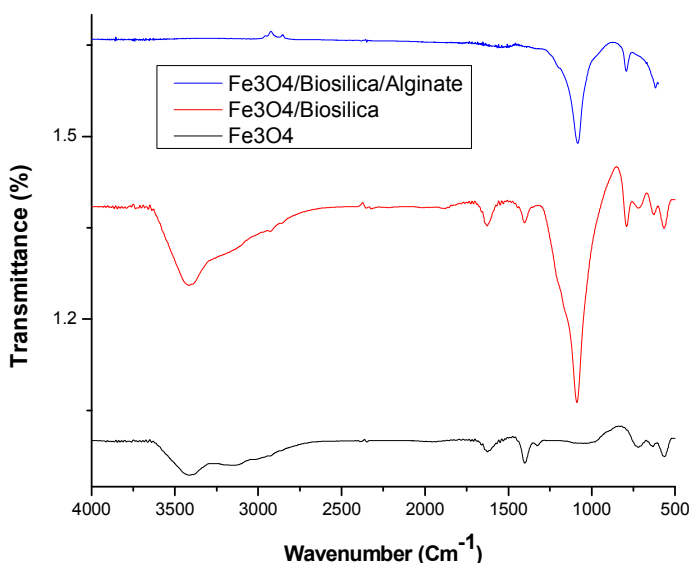


Fig. 3. FT-IR spectroscopy peaks for each material incorporated into the nanocomposite

Infrared spectroscopy was performed to reveal the presence and also involvement of surficial functional groups during the adsorption of cadmium. The peaks associated with each material are shown in Fig. 3. The peak around 3570 cm⁻¹ is related to OH of hydrogen bond stretch (17). The intensity of this peak was changed after the combination of biosilica with Fe₃O₄ nanoparticle, indicating the main role of hydroxyl functional group in the formation of Fe₃O₄/biosilica composite. The peaks centered at 1452 cm⁻¹ and 1589 cm⁻¹ are associated with C=C vibration and C-H bending of alginate matrix, respectively (20).

3.2. Effects of operational parameters

3.3. Effect of initial pH

As one of the most important parameters during the adsorption of metal ions, the effect of initial pH on the adsorption efficiency was evaluated. The results, which are represented in Fig. 4, showed that increasing the initial pH from acidic values to neutral conditions resulted in improvement in the removal efficiency from 38 to 66%, while its shift from neutral conditions to basic conditions caused a sharp decrease in the efficiency. At initial pH of 11, a negligible removal efficiency of 9% was obtained. Therefore, solutions with neutral conditions were subjected to conduct the rest of experimental runs. In fact, surface charge of the adsorbent is largely dependent on the initial pH of solution containing cadmium. The pH dependence of the adsorption of cadmium is elucidated regarding the ionization of both adsorbent surface and adsorbent species. To assess the surface charge of the adsorbent, the pH_{zpc} value of immobilized $\text{Fe}_3\text{O}_4/\text{biosilica}/\text{alginate}$ nanocomposite was measured. The electrostatic attraction between protonated surface of the nanocomposite (at pH values lower than pH_{zpc}), resulting in the increased removal efficiency of cadmium at pH values lower than 9.7. In fact, the adsorption of cadmium onto the heterogeneous nanocomposite takes place by way of different mechanisms. Less removal efficiency (%) of cadmium at basic conditions may be also ascribed to the increase in the concentration of competing OH^- ions for active adsorption sites (21).

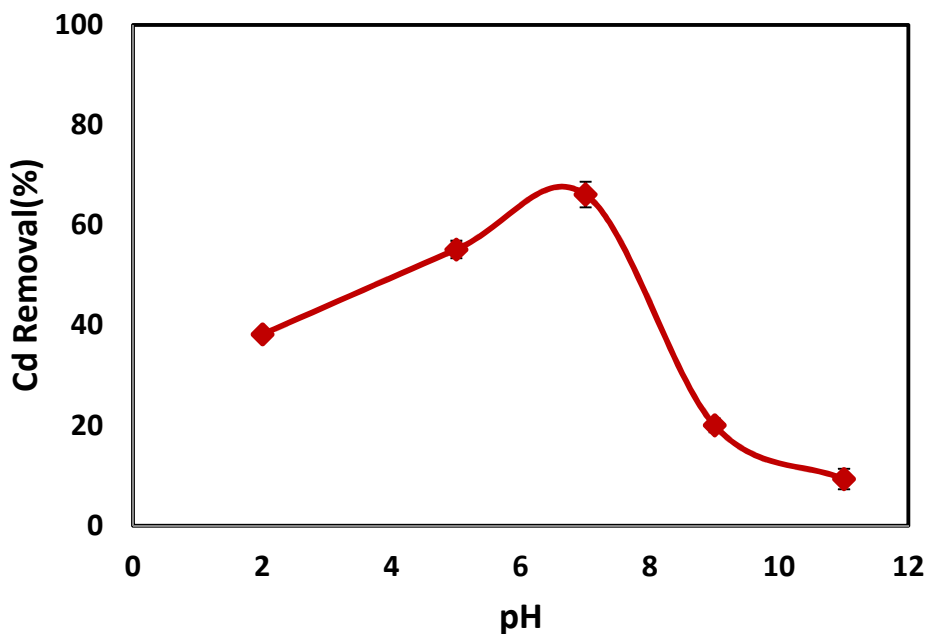


Fig. 4.Influence of the initial pH on the adsorption of Cadmium by immobilized Fe_3O_4 /biosilica/alginate nanocomposite

3.4. Effect of reaction time

The effect of reaction time on the adsorption of cadmium was assessed within an elapsed time of 180 min (Fig. 5). Fig. 5 shows that increasing the reaction time to 60 min caused a rapid increase in the removal efficiency (69%). However, increasing the time from 60 to 180 min resulted in no significant increase in the removal efficiency. Within this period of time, the removal efficiency (%) of Cd via the adsorption onto the nanocomposite is at the same level (almost constant), which is controlled by the intra-particle diffusion(22). Only 10% removal efficiency was obtained by increasing the reaction time from 60 to 180 min. So, a reaction time of 60 min was chosen for subsequent experiments considering economical point of view for full scale application of the nanocomposite. Kinetic study was performed using both pseudo-first and pseudo-second order

kinetic models as the most extensively used models. The pseudo-first order and pseudo-second order models are represented via Eqs. (1-2) (23):

$$\text{Pseudo-first order: } \log(q_e - q) = \log q_e - \left(\frac{k_{1,ad}}{2.303}\right) t \quad (1)$$

$$\text{Pseudo-second order: } \frac{t}{q} = \left(\frac{1}{k_{2,ad}q_e^2}\right) + \left(\frac{1}{q_e}\right) t \quad (2)$$

where q_e ($\mu\text{g/g}$) and q ($\mu\text{g/g}$) are the amounts of Cd sequestered by the nanocomposite at equilibrium time and specified time, respectively. Moreover, $k_{1,ad}$ ($1/\text{min}$) and $k_{2,ad}$ ($\text{g}/\mu\text{g min}$) are the rate constant of pseudo-first order and pseudo-second order reactions, respectively. According to the obtained correlation coefficients, the fitness of experimental data to the pseudo-second order kinetic model ($R^2=0.997$) was higher compared with the pseudo-first order model ($R^2=0.892$). The results of kinetic study are provided in Table 1.

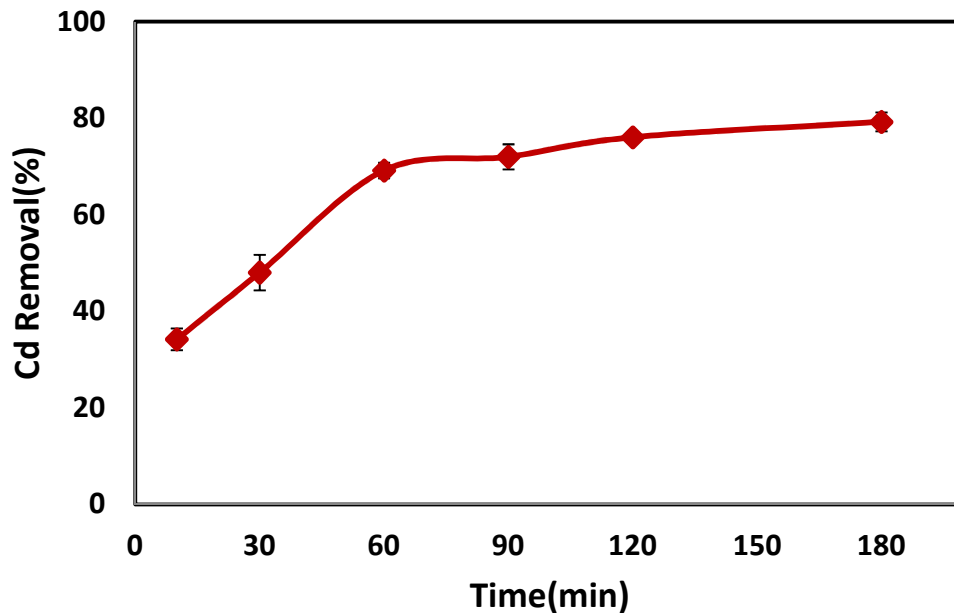


Fig. 5. Variations of the removal efficiency (%) of Cd as the function of elapsed time

Table1. Kinetic and isotherm parameters for the adsorption of Cd onto immobilized Fe₃O₄/Biosilica/alginate nanocomposite.

	Model type	Parameters	Value
Kinetic models	Pseudo-first order model	k _{1,ad} (1/min)	0.024
		q _e (mg/g)	40.71
		R ²	0.892
	Pseudo-second order model	k _{2,ad} (1/min)	0.0006
		q _e (mg/g)	87.72
		R ²	0.997
Isotherm models	Langmuir model	q _{max} (mg/g)	42.36
		K (L/mg)	0.036
		R ²	0.990
		R _L	0.034-0.526
	Freundlich model	K _F	25.17
		1/n	0.413
R ²		0.974	

3.5. Solute concentration and isotherm study

The concentration of Cd as solute substance was varied between 10 and 160 mg/L in order to evaluate its effect on the efficiency of adsorption process (Fig. 6). As can be observed in Fig. 6, increasing the initial Cd concentration from 10 to 160 mg/L led to decreasing the removal efficiency from 96 to 23%, respectively. As a matter of fact, increasing the concentration up to 40 mg/L caused a fast drop in the adsorption performance (40%). The results of this section were used to carry out isotherm study. For this, experimental data were fitted to the most widely used isotherm models (Freundlich and Langmuir models). The Langmuir and Freundlich isotherm models are shown in Eqs. (3-4) (24, 25):

Langmuir model:
$$\frac{C_e}{q_e} = \frac{1}{Kq_m} + \frac{C_e}{q_m} \quad (3)$$

Freundlich model: $\log q_e = \log K_f + \frac{1}{n} \log C_e$ (4)

where q_m (mg/g), C_e (mg/L) and K (L/mg) are the maximum adsorption capacity of the nanocomposite, the remaining Cd concentration and the affinity of adsorptive binding sites for the adsorption of Cd, respectively. In the case of Freundlich equation, K_F and n values can be used to show adsorption capacity and adsorption intensity, respectively. The data tabulated in Table 1 displayed that Langmuir model ($R^2=0.990$) is more suitable than Freundlich model ($R^2=0.974$) for describing the adsorption of Cd onto immobilized Fe_3O_4 /biosilica/alginate nanocomposite. Thus, the monolayer adsorption of Cd onto the nanocomposite is expected.

$$R_L = \frac{1}{(1+C_0K)}(5)$$

If the value of R_L is between 0 and 1, then the process is favorable. The values greater than 1 represent the unfavorable adsorption process. Therefore, the range of R_L values (0.034-0.526), which are represented in Table 1, shows the effectiveness of immobilized Fe_3O_4 /biosilica/alginate nanocomposite for removing Cd via adsorption process. Moreover, the value of $1/n$ associated with Freundlich model was found to be 0.413, indicating strong and effective attraction between Cd and adsorptive sites of the nanocomposite. On the other hand, the value of $1/n$, which is lower than one, confirmed the chemical nature of the adsorption process (26, 27).

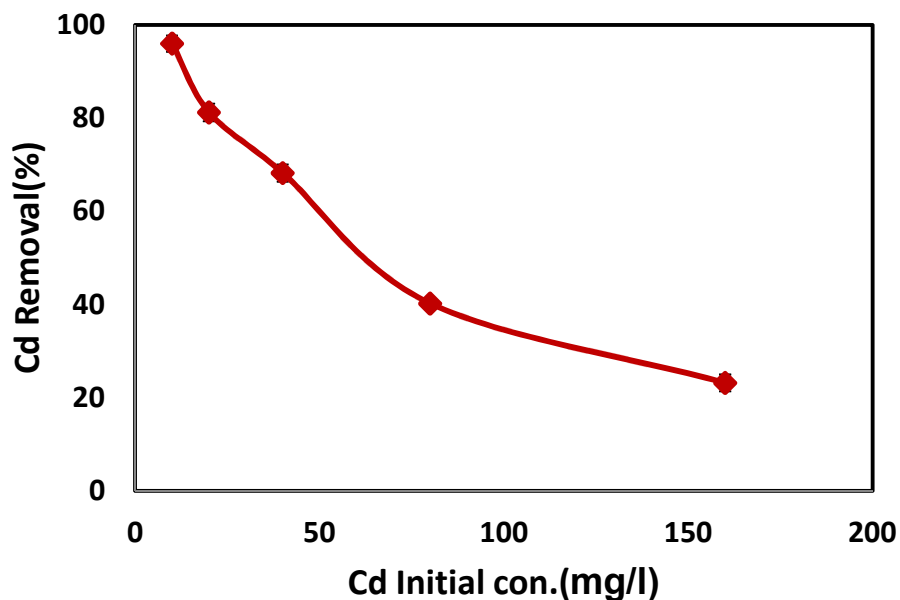


Fig. 6. Influence of the initial Cd concentration on its removal efficiency

3.6. Effect of adsorbent dosage

The dosage of immobilized Fe_3O_4 /biosilica nanocomposite was varied between 0.25 and 2 g/L to specify the role of this important parameter in the adsorption of Cd. The determination of the optimized amount of adsorbent is very important regarding economical considerations. As depicted in Fig. 7, at adsorbent dosages of 0.25, 0.5, 1.0, 1.5 and 2.0 g/L, the removal efficiencies were obtained to be 29, 44, 69, 84 and 96%, respectively. The increase in the removal of Cd with increasing the nanocomposite dosage may be associated with the increased available active adsorptive sites for Cd to be adsorbed by the as-synthesized adsorbent (19, 28).

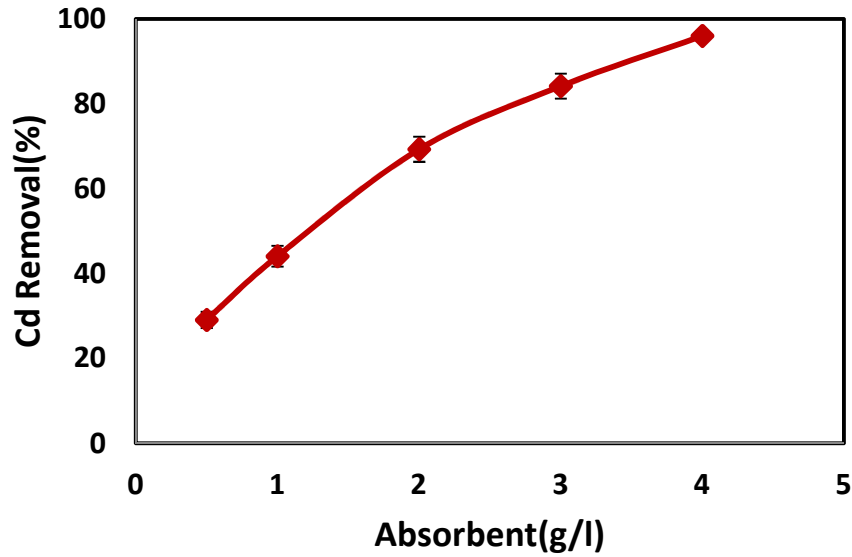


Fig. 7. Influence of the adsorbent dosage on the removal efficiency (%) of Cd

3.7. Thermodynamic study

The effect of solution temperature on the amount of adsorbed Cd was studied in order to obtain thermodynamic parameters. The smaller plot depicted on Fig. 8 shows that increasing solution temperature from 298 to 328 K results in decreasing the removal efficiency from 68 to 50%, respectively. Accordingly, thermodynamic parameters such as Gibbs free energy (ΔG°) (kJ/mol), enthalpy change (ΔH°) (kJ/mol) and entropy change (ΔS°) (kJ/mol K) were obtained using the following equations(29, 30, 31):

$$\Delta G^\circ = -RT \ln K_D (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ (7)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} (8)$$

where T (K), K_D and R are the absolute temperature and distribution coefficient of temperature, respectively. In addition, R is defined as universal gas constant. The values of Gibbs free energy (ΔG°) (kJ/mol), enthalpy change (ΔH°) (kJ/mol) and entropy change (ΔS°) (kJ/mol K) were obtained by plotting $\ln K_D$ versus $1/T$. The value for each parameter is written on Fig. 8. Negative values for ΔG° parameters (ranged between 0 and -1.87 kJ/mol), indicated spontaneous nature of the adsorption of Cd onto immobilized Fe_3O_4 /biosilica/alginate nanocomposite (32, 33). The negative value of enthalpy change (ΔH°) confirmed the possible attraction between Cd and active adsorptive sites of the nanocomposite. Besides, it can be concluded that the adsorption of Cd is exothermic in nature because of the obtained negative value for ΔH° (19).

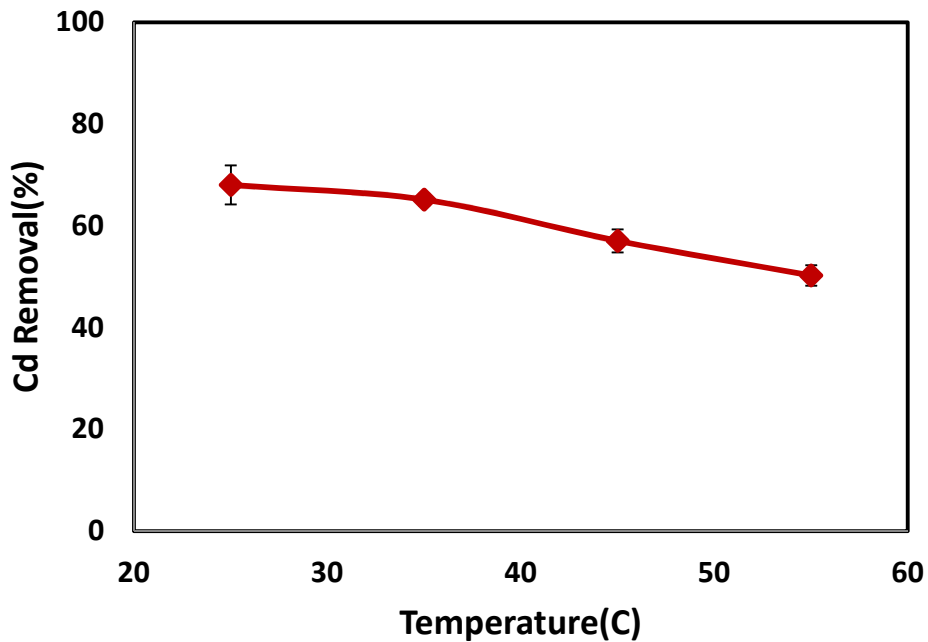


Fig. 8. Results of thermodynamic study on the basis of solution temperature

4. Conclusions

The combination of Fe₃O₄ nanoparticles with biosilica particles in immobilized form was applied for the removal of Cd from the liquid phase. The results of XRD analysis confirmed the desirable combination of Fe₃O₄ nanoparticles with biosilica particles. Moreover, SEM images showed that the immobilization of the compound within alginate has been implemented well. The process of Cd adsorption was pH dependent. The simulation of real conditions exhibited a significant decrease in the adsorption performance in the presence of organic compounds such as humic acid and some ionic species like phosphate, sulfate and nitrate. The presence of metal ions resulted in no considerable effect on the adsorption of Cd. It can be concluded that Fe₃O₄/biosilica/alginate nanocomposite in immobilized form can be efficiently used for sequestering Cd from aqueous solutions.

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