



Investigation of biosorption on *Ceratophyllum demersum* L. biomass: removal of cadmium(II) from aqueous solution

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ABSTRACT

This study aimed to investigate the effect of modified *Ceratophyllum demersum* on the removal of heavy metal cadmium. The effect of pH (3–8), contact time (5–240 min), biomass concentration (0.02–4 g/L) and initial concentration of metal (10–200 mg/L) on the removal of cadmium, as well as kinetic and isotherm adsorption models were studied using the batch adsorption experiments. The results showed that with an increase in pH from 3 to 8, the removal efficiency increased from 93% to 97%, then decreased to 85%. By increasing the contact time from 5 to 180 min, the removal efficiency ranged from 67% to 98% and then slightly decreased until to 240 min. Also, increased adsorbent dosage from 0.02 to 4 g/L, the removal efficiency increased from 37% to 99%. The removal efficiency decreased from 96% to 31% with an increase in the initial concentration of cadmium from 10 to 200 mg/L. Optimum condition was found to be at pH, contact time, biomass concentration and cadmium concentration of 7, 60 min, 1 g/L and 10 mg/L, respectively. Pseudo-second-order kinetic and Langmuir model ($R^2 > 0.99$) were well fitted to the data. The results of study confirmed the high ability of biosorption process through *Ceratophyllum demersum* for wastewater treatment polluted with cadmium.

Keywords: Biosorption; Heavy metal; Wastewater treatment; Adsorption process

1. Introduction

Environmental pollution of heavy metals and their health effects are one of the most important environmental issues due to their sustainability and accumulation in the organs and tissues of living organisms [1]. Unfortunately, due to the uncontrolled entry of various types of industrial wastewater, the rate of their entry into air, water and soil is increasing sharply [2]. Heavy metals of cadmium, copper, lead, mercury, nickel and zinc are among the most hazardous pollutants and are listed in the U.S. Environmental Protection Agency (EPA)'s priority list of pollutants [3]. Cadmium is known to be a carcinogen and the cause of itai-itai disease [4]. Industrial wastewaters from mines, metal processing, plating, electronics, atmosphere, runoff and lithosphere are

the sources of these metals. Therefore, the treatment of contaminated water from these metals is very important before they are discharged [1].

Recently, biological methods such as biosorption and bio-accumulation have been used to help researchers to deal with the problem of removing heavy metals from the sewage streams. Bio-accumulation is done by living biota. However, dead or inactive biota is used in the biosorption. Among biosorption and bio-accumulation, biosorption is a more efficient method in term of economics and more simple elimination. In addition, the dead biomass does not require nutrients and is not sensitive to environmental parameters, also it can be retrieved and reused [5].

A research was conducted to study the biosorption of modified *Ceratophyllum demersum* from aqueous solution polluted with chromium. The best conditions for adsorption

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of chromium(VI) in this study were at pH = 2, adsorbent dosage 10 g/L and contact time of 60 min. Under these conditions, the maximum adsorption capacity of modified *Ceratophyllum demersum* was 10.20 mg/g [6]. Montazer Rahmati et al. [7] tested biosorption of cadmium, lead and nickel by modified *Sargassum glaucescens*, *Padina australis*, *Nizimuddiniana zanardini* and *Cystoseria indica*. Among the two-parameter isotherm models, the Freundlich model, and among the three-parameter adsorption models, the Toth, Khan and Radke–Präusnitz models were suitable models for removal of cadmium, nickel and lead, respectively [7].

Kililç et al. [8] conducted a study on the removal and recycling of copper(II) from an aqueous solution by modified *Marrubium globosum* leaf. They showed that at optimum pH of 5.5, the adsorption capacity was 16.23 mg/g. The increased metal concentration and temperature improved the adsorption capacity and the process was equilibrated in 60 min [8].

Sari and Tuzen [9] investigated biosorption of total chromium in the aqueous solutions using red algae of *Ceramium virgatum*. The Langmuir model was well fitted on the experimental data. The adsorption capacity for total chromium was 26.5 mg/g at pH value 1.5, biomass dosage 10 g/L, contact time 90 min and temperature 20°C [9].

Keskinkan et al. [10] used *Myriophyllum spicatum* and *Ceratophyllum demersum* adsorption for biosorption of lead, zinc and copper. The results indicated that maximum adsorption capacity of *Myriophyllum spicatum* for each tested metal was better than that observed for *Ceratophyllum demersum* which gave the results of 10.37 mg/g for lead, 15.59 mg/g for copper and 46.49 mg/g for zinc [10].

A large quantity of *Ceratophyllum demersum* is found in irrigation canals in Iran that it can be used as economic bioadsorbent. The main objective of this study was to determine the capability of modified *Ceratophyllum demersum* for removal of cadmium.

2. Materials and methods

2.1. Chemicals

In this study, all materials included Cd (NO₃)₂·4H₂O, H₂SO₄ (1 N) and NaOH (0.5 and 1 N) were purchased from Merck brand in Ahvaz.

2.2. Adsorbent synthesis

According to the purpose of present study, that was mentioned, one of the requirement materials was *Ceratophyllum demersum*, which is an underwater herb and usually found in aqueous media with a slow flow containing medium or high levels of nutrients [10]. In this regard, a search was conducted on irrigation channels inside Shahid Chamran University of Ahvaz and large quantities of this plant were observed in many parts of these channels. After collecting the plant and washing it with tap and distilled water, it was sun dried. Plant was dried in an oven at 70°C then it was completely crushed by mill and passed from standard sieve No. 50. Biomass was modified by NaOH 0.5 N. This method had a good effect in similar studies and has greatly increased the adsorption capability [6].

2.3. Characterization of adsorbent

Adsorbent was characterized as raw, modified and after adsorption process. The morphological structure of *Ceratophyllum demersum* and its elemental content were analyzed with an energy-dispersive spectroscopy (EDX) along with scanning electron microscopy (SEM) (PHENOM Pro X SEM, WEGA/TESCAN; Czech Republic). The mean pore diameter, specific surface area and pore volume were investigated through the Brunauer–Emmett–Teller (BET) (nitrogen sorption isotherm) method, using a micromeritics particle size analyzer (BELsorp-miniII, Japan). The Fourier transform infrared spectroscopy (FTIR) study was done by the HP 6890. Adsorbent was analyzed by X-ray diffraction (XRD; Philips, Model XPERT PW 3040/60) and the thermo gravimetric analysis (TGA) (i1000, Instrument Specialists Incorporated, USA) from 20°C to 120°C in nitrogen.

2.4. Batch adsorption studies

The effect of pH (3–8), contact time (5–240 min), biomass concentration (0.02–4 g/L) and initial concentration of metal (10–200 mg/L) on the removal efficiency was determined through batch adsorption studies. Stock solution of cadmium was prepared based on Standard Methods for Examination of Water and Wastewater [11]. For preparation of stock solution, 2.744 g of Cd(NO₃)₂ was added to 1 L of distilled water. Different concentrations of cadmium(II) solution were obtained by diluting the stock solution. All adsorption experiments were done at 25°C. Cadmium concentration was analyzed in samples by an atomic adsorption spectrometer (vario 6). The amount of adsorbed cadmium at equilibrium (q_e) and its removal efficiency (Y) were calculated from the mass balance equation presented in Eqs. (1) and (2), respectively [12]:

$$q_e = \frac{V}{M} \times (C_0 - C_e) \quad (1)$$

$$Y(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_e and C_0 are cadmium concentrations in inlet and outlet solution (mg/L), respectively. V and M are the volume of solution (L) and the mass of adsorbents (g), respectively.

First-order and pseudo-second-order kinetic models and Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were investigated in the current study. The isotherm adsorption equation is in fact a mathematical explanation for determining the degree of adsorption in a constant temperature to reach the equilibrium condition [13]. Based on this definition, various empirical and theoretical equations for describing the adsorption process have been presented [14].

3. Results and discussion

3.1. *Ceratophyllum demersum* characteristics

SEM and EDX images of raw, modified and spent adsorbent at a magnification of 1,000× are illustrated in Fig. 1. Raw plant of *Ceratophyllum demersum* (Fig. 1a) had a smooth and

uniform surface structure and regular porous. The arrangement of porous and pores on the surface was as vertical and horizontal regular rows and had a brick layout. After modification (Fig. 1b), the surface morphology of the *Ceratophyllum demersum* had completely changed. The particle arrangement on the surface was completely irregular and entangled, and the new structure created consists of a large difference in height at the surface and new fractures. This new formation caused holes and more pores on the surface. These holes and pores increased specific particle area. The new holes provided more space for adsorption of cadmium to keep it in a less competitive and easy way. According to the explanation, it can be said that modification of *Ceratophyllum demersum* with NaOH solution significantly altered its surface morphology. Fig. 1c shows the *Ceratophyllum demersum* particles after the cadmium adsorption, as it is found that the surface structure of the adsorbent does not change in comparison with Fig. 1b. The only significant difference is the discoloration of the adsorbent surface, which has become dark in

white and light. These changes indicated that the coverage of the absorbent surface was with cadmium particles and optimum adsorption had taken place.

According to the EDX analysis results in Figs. 1a–c, O, C, N and S were major elements with a weight percentage of 46.31%, 38.05%, 15.44% and 0.20% in the raw adsorbent. Dominant elements were detected as O (42.13%), C (36.22%), N (14.34%), Na (7.27%) and S (0.04%) and for modified adsorbent and O (43.35%), C (32.47%), N (13.04%), Na (8.11%), Cd (3.00%) and S (0.03%), for spent adsorbent. Changes in the weight percentage of elements between raw, modified and spent adsorbents approved the modification of *Ceratophyllum demersum* by NaOH solution and adsorption of cadmium on the surface of adsorbent. These results were in accordance with the study of Teymouri et al. [6].

Specific surface area (m^2/g) and mean pore diameter (nm) were found to be 3.93 and 9.05, 4.26 and 12.99 for raw and modified and, respectively. BET results described that modification of adsorbent was resulted in the increased specific

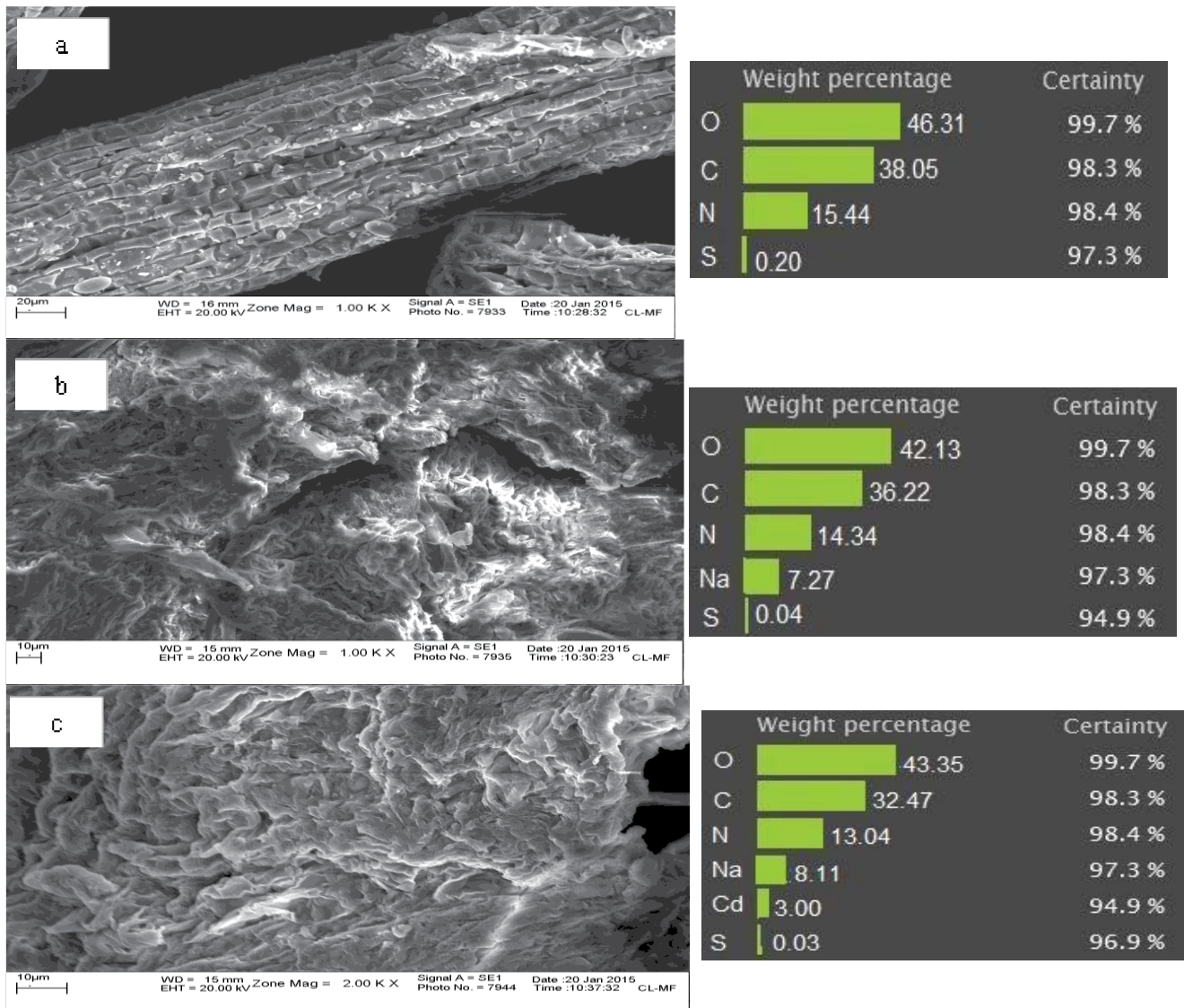


Fig. 1. SEM–EDX image of *Ceratophyllum demersum*, raw (a), modified (b), spent adsorbent (c).

surface area and mean pore diameter. Results of the current study were in agreement with other studies [15]. Therefore, it could be concluded that the NaOH solution changed well the structure of the surface morphology of *Ceratophyllum demersum* and, by creating new pores and increasing the specific surface area, increased the adsorption capacity of *Ceratophyllum demersum*.

XRD pattern of raw, modified and spent of adsorbent is illustrated in Figs. 2a–c. The major peaks at 2θ between 20° and 40° can be assigned to the adsorbent modification with NaOH. Difference of pattern for spent adsorbent with other patterns may be associated to the coverage of cadmium on the spent adsorbent.

FTIR spectrum of raw, modified and spent adsorbent is displayed in Fig. 3. Compared with the raw biomass, the shifts in the wavenumbers of the NaOH-modified biomass occurred between 521 and $2,920\text{ cm}^{-1}$ bands that it shows the possible interaction of the Na^+ and Cl^- ions. Cadmium adsorption on the biosorbent caused variations at the bands between 500 and $1,000\text{ cm}^{-1}$. However, these changes were not significant that this result was similar to the previous studies [6].

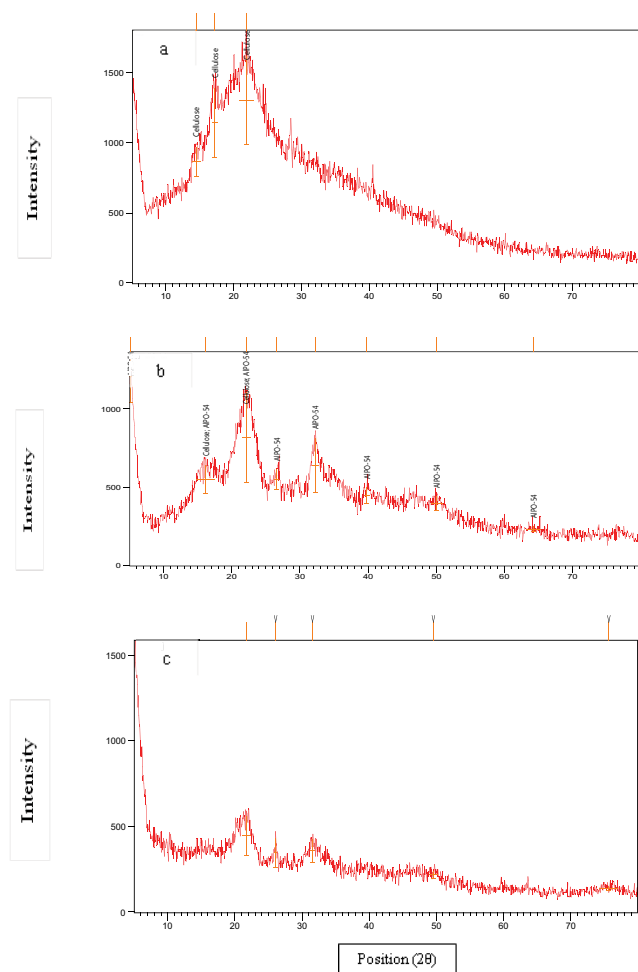


Fig. 2. XRD pattern of *Ceratophyllum demersum*, raw (a), modified (b), spent adsorbent (c).

The thermo gravimetric (TG) curve of raw, NaOH-modified and spent biosorbent is depicted in Fig. 4. It can be seen that all adsorbents lost the weight from 30°C to 105°C . It may be related to the escape of gas molecules from the cavities or the decomposition of adsorbent [16].

3.2. Effect of solution pH on the cadmium biosorption

The pH of solution has a great influence on the adsorption process. A part of this effect is related to the adsorption of hydrogen ions, which is a competitor in the adsorption of cations. The pH variations were investigated from 3 to 8 according to data in the literatures [17,18]. Variations of removal efficiency of cadmium and adsorption capacity in the pH range studied at the contact time of 60 min, adsorbent concentration 1 g/L and cadmium concentrations 10 mg/L are shown in Fig. 5. According to Fig. 5, with increasing pH, the cadmium removal efficiency increased very slightly (about 3%) and reached the maximum at pH value 7. The removal efficiency dropped at pH 8 by 12%. Therefore, pH 7 was considered as optimal pH. The removal efficiency and adsorption capacity at pH value 7 were 97.28% and 7.35 mg/g, respectively (Fig. 5). These changes in the removal efficiency can be related to capacity of cadmium. Cadmium for adsorption process requires replacing with one two-capacity ion or two mononuclear ions, which are adjacent to two sites, and if these two sites have distance together, there is no possibility of this substitution. In other words, at lower pH values, some of the linking sites are not available in metal ions. On the other hand, at low pH values, H_3O^+ ions present in the environment are competing with cations in the solution to occupy chemical bound sites.

Therefore, with increasing pH, the adsorption also increases, which can be said that in this range, most of the metals are soluble and free-cation is available for adsorption. Pagnanelli et al. [19] had shown increase in the rate of metal adsorption with increasing pH. The study found that this incremental trend is not only due to the competitive adsorption of H^+ ions at low pH values but also due to the poor acidity of active sites on the adsorbent surface, which, by increasing the pH, performs a deprotonation process that improves the adsorption of metals [19]. On the other hand, most literature showed that the removal efficiency is reduced from pH 6 to 2.5 [20]. In other words, in the present study, increasing the removal efficiency by increasing the pH from 3 to 7 can be attributed to two factors: (1) at low pHs, there are enough H^+ ions in the solution that compete with cadmium for adsorption. (2) For each hydrolyzed metal ion, there is a critical pH range where the efficiency of the metal adsorption from a small amount reaches a maximum value. This is called the threshold of adsorption. Also, the decrease in the adsorption of cadmium ions at pH values higher than 7 is probably due to the formation of hydroxyl groups. Also, in low pH values, the biosorbent surface has positive charge, and because of the electrostatic disposals of biosorption, cadmium cations are low on the adsorbent surface. In addition, in such an acidic pH, there is a high competition between H^+ and $\text{Cd}(\text{II})$ cations for adsorption sites. By increasing the pH, the charges of biosorbent tend to negative charge affected. On the other hand, reducing the removal efficiency in high amounts of 7 can be due to anionic compounds $\text{Cd}(\text{II})$ that

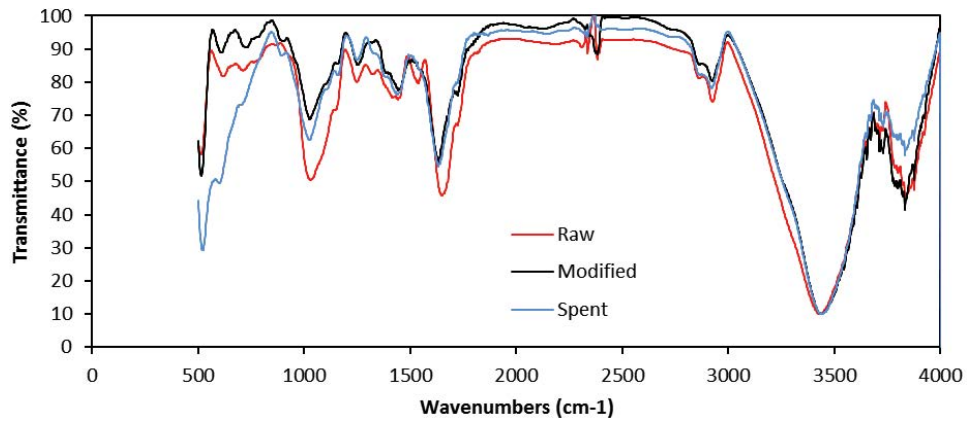


Fig. 3. FTIR spectra of *Ceratophyllum demersum*.

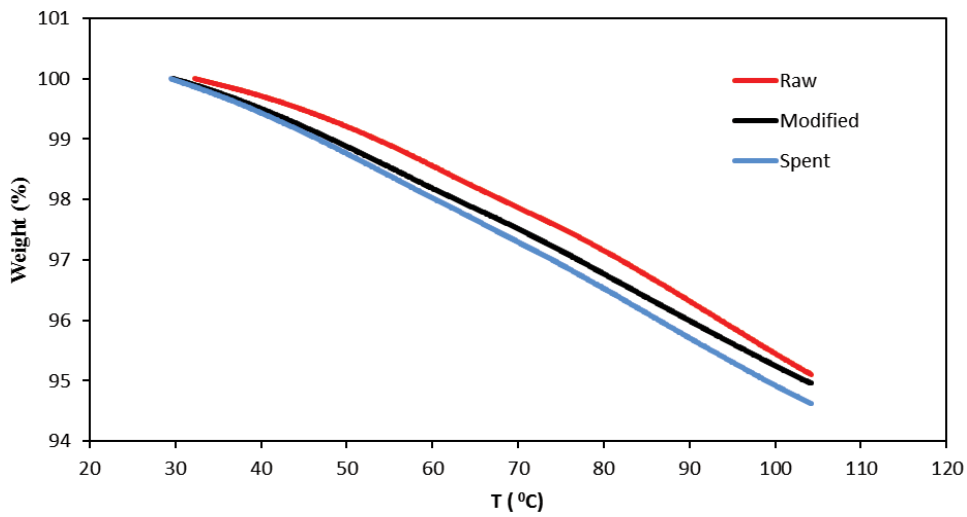


Fig. 4. Thermo gravimetric analysis (TGA) curve of *Ceratophyllum demersum*.

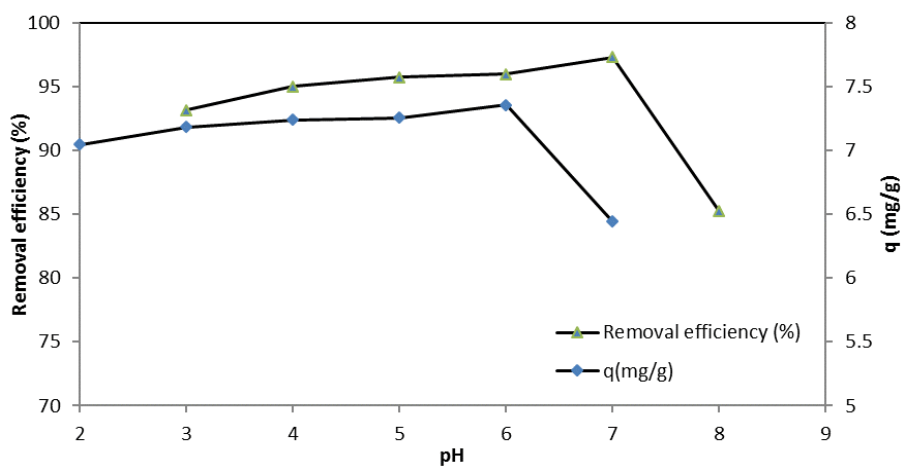


Fig. 5. Effect of pH solution on the cadmium adsorption.

reduce their biosorption. In another study, was reported that cadmium at pH higher than 8 was as $Cd(OH)_2$ and at pH less than 8, it was as $Cd(OH)^+$ in solution, and the highest adsorption rate was within the pH range of 5 to 8 [21]. According

to the results obtained in the experiment, it can be assumed that pH changes in the range of 3 to 6 resulted in a very modest increase in the removal efficiency, so, it can be concluded that pH changes in the acid range shows a slight increase in

the removal efficiency and as the pH approaches to 7, the removal efficiency reaches its maximum. This increase was also true for adsorption capacity and the maximum cadmium adsorption capacity was observed at pH 7. However, after the alkalization of the solution, it was observed that the removal efficiency decreased by 12%.

3.3. Effect of contact time on the cadmium biosorption

Fig. 6 shows the changes in residual concentration, adsorption capacity and removal efficiency of cadmium at different contact times at pH equal to 7, amount of adsorbent 1 g/L for the input concentration of 10 mg/L. According to Fig. 6, with the increase in contact time, the efficiency of removal of cadmium has increased rapidly. In 5 min, the removal efficiency was 67.63%. This rapid increase was continued until 40 min. At this time, the removal efficiency reached 94.95%. After 40 min, the removal rate was reduced and the process continued at a lower rate for 180 min. At this time, the highest removal efficiency was occurred and it was equal to 98.71%, and then, at 240 min, the removal efficiency was reduced slightly, which test was stopped at this time. In order to obtain the time of equilibrium, between the three times of 40, 60 and 90 min, which reduced the rate of change in the efficiency of removal, according to the results of the contact time, 60 min was considered as equilibrium time. The main reason for selection of 60 min compared with 90 min is since the contact time is longer, it means the energy consumed is higher and it imposes more cost to the purification system, so, it seems that 60 min is more economical than 90 min. The removal efficiency and adsorption capacity at this time were 96.16% and 8.89 mg/g, respectively. Most researchers who have studied biosorption indicated high adsorption rates in the first 10 min of the process due to the rapid occupancy of adsorbent surface areas. The high percentage of removal of heavy metals at the start of the process due to the large surface of the adsorbent is to absorb metal ions. Also, this two-stage adsorption mechanism, the fast and noticeable phase and then a slow and insignificant amount of adsorption have been presented in numerous papers and studies [22].

3.4. Effect of adsorbent dosage on the cadmium biosorption

Fig. 7 shows the variations in residual concentration, adsorption capacity and removal efficiency of cadmium in different amounts of adsorbent at optimal pH 7 and the contact time 60 min for the input concentration of 10 mg/L. As it is seen, the amount of adsorbent in each step has almost doubled compared with the previous one. According to Fig. 7, with the increase in the amount of adsorbent, the efficiency of removal of cadmium in the initial stage changed slightly and increased by 3%, but in the next step and for the adsorbent content of 0.1 g/L, the removal efficiency increased by 37% at the same time. From this stage, the increasing of the quantities and the rate of change in the efficiency of the removal is reduced and for the next values of the adsorbent, the removal efficiency increased by 1.6% and 4.8%, respectively. In the next step, and for the adsorbent dosage of 1 g/L, the removal efficiency was again increased by 12.38% to 96.67%. Since then, the amount of changes was negligible for 2 and 4 g/L, and the highest percentage of adsorption in the amount of 4 g/L and was calculated 99.34%. Based on the data in the literature, this behavior can be due to the availability of more adsorption sites for low adsorbent concentrations and the accumulation of adsorption sites together for greater amounts of adsorbent. Also, the high adsorption capacity in initial and low amounts of adsorbent can be attributed to an increase in the area on the adsorbent surface and the availability of more adsorption sites [23].

3.5. Effect of metal initial concentration on the cadmium biosorption

Fig. 8 presents the changes in residual concentration, adsorption capacity and removal efficiency of cadmium in various initial metal concentrations at pH 7, contact time of 60 min and adsorbent dosage of 1 g/L. At this stage, for each concentration of cadmium, a control sample was prepared and for further accuracy of the study, subsequent calculations using the results of the control samples were performed. By increasing the initial concentration of cadmium, the removal efficiency was reduced by a moderate trend, as the removal

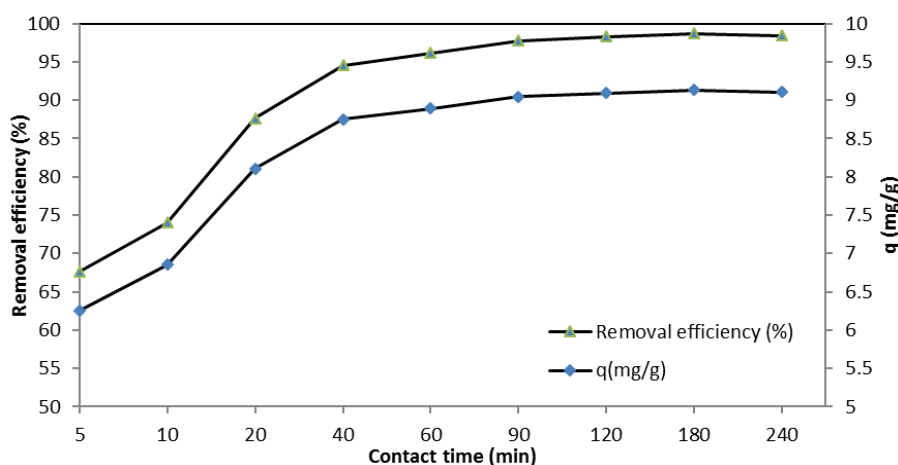


Fig. 6. Effect of contact time on the cadmium adsorption.

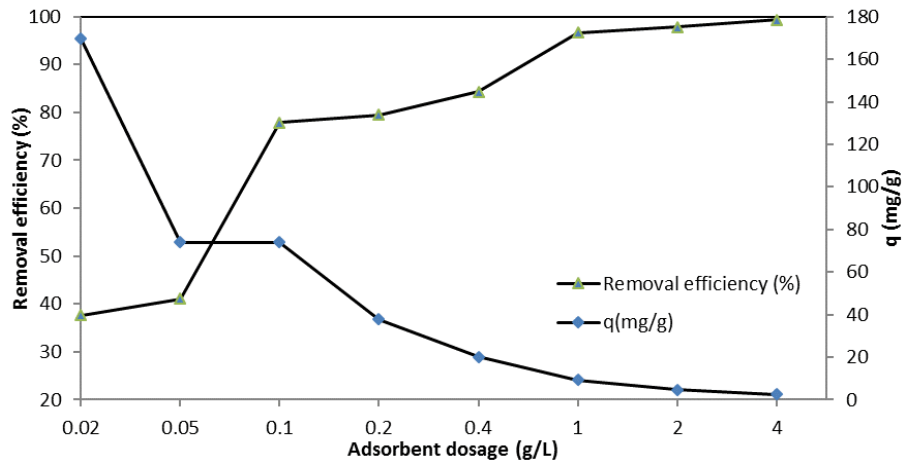


Fig. 7. Effect of adsorbent dosage on the cadmium adsorption.

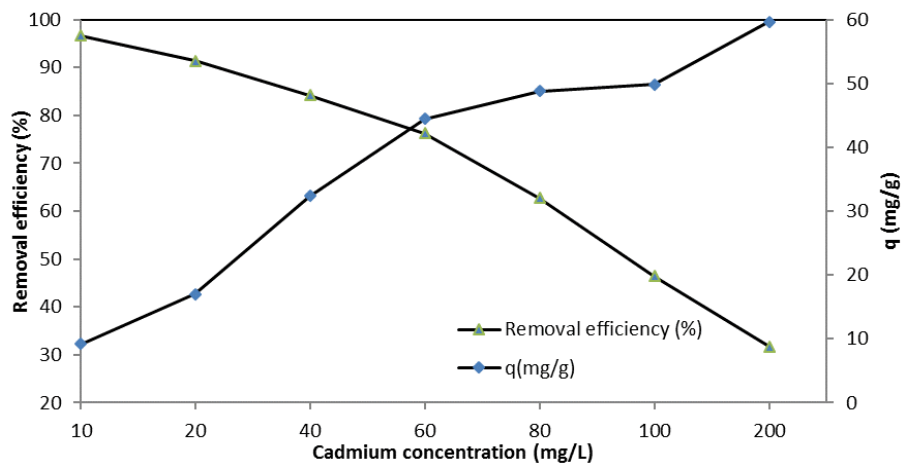


Fig. 8. Effect of cadmium concentration on the cadmium adsorption.

efficiency from 96.67% at a concentration of 10 mg/L reached to 31.75% at a concentration of 200 mg/L. In contrast to this, by increasing the initial concentration of cadmium, the amount of adsorption capacity increased.

This trend is due to the numbers of cadmium metal moles are many in the high concentration of cadmium metal in aqueous solution. Therefore, it can be concluded that the adsorption is strongly dependent on the initial concentration of metal, as well as the adsorption characteristics it also shows that saturation of the adsorbent surface depends on the initial concentration of the metal in the solution. In fact, the initial concentration of the solution is an important driving force to overcome all resistant forces on the exchange of metal ions between the soluble phase (aqueous media) and solid (adsorbent) [22]. It was observed from the studies by Argun et al. [23] and Miretzky and Cirelli [24] that the process of increasing the percentage removal and reduction in the adsorption capacity depends on the initial concentration of the solution. According to the results, concentration of 10 mg/L was considered as the suitable concentration for cadmium, because in this concentration, the adsorption efficiency

was 96.67% and the adsorption capacity of cadmium was 9.18 mg/g, which is acceptable. Table 1 shows the optimal values obtained from the variables examined during the experiment.

3.6. Isotherm study

The data of isothermal biosorption present the better understanding of the characteristics and surface properties

Table 1
Optimum condition for removal of cadmium by modified *Ceratophyllum demersum*

Parameter	Optimum condition
pH	7
Contact time (min)	60
Dose of biosorbent (g/L)	1
Cadmium concentration (mg/L)	10

of the adsorbent, its capacity to absorb heavy metals and also the biosorption mechanism [6]. In this study, isotherm adsorption models were used at the pH equal to 7, contact time = 60 min, amount of adsorbent 1 g/L and initial concentrations of 10, 20, 40, 60, 80, 100 and 200 mg/L. Table 2 and Fig. 9 shows the results and data obtained from four isothermal models of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich. The Langmuir model is rarely seen in nonporous materials, and is suitable for compounds with high-density of pores (less than 2 nm). The Langmuir equation actually expresses adsorption at very homogeneous surface with insignificant interactions between the adsorbed molecules [25]. In fact, the Langmuir model shows adsorption of a single adsorbent layer in which the adsorbed molecules have no reactive interaction [6]. As can be seen in Table 2, R^2 or the coefficient of determination is equal to 0.99, which indicates that cadmium adsorption by modified *Ceratophyllum demersum* has best fitted by Langmuir’s model. Also, the parameters were: $q_{max} = 61.34$ mg/g, $K_L = 0.19$ L/mg and $R_L = 0.027$ – 0.358 , respectively. Since R_L between 0 and 1 indicates the efficiency of the Langmuir model for describing the adsorption [26]. The maximum adsorption capacity was calculated to be 61.34 mg/g, and the difference was 2% compared with the maximum experimental adsorption capacity (obtained from tests), which is 59.7 mg/g, indicating the accuracy of the model. The Freundlich equation shows the homogeneity of the adsorbent surface and the magnitude of the K_f coefficient, indicating the easier bioadsorption of metal ions from the aqueous media. Also, the parameter n , which indicates the optimal adsorption of metal ions based on this model, should have a value between 1 and 10 [6]. As shown in Table 2, an acceptable determination coefficient for this model is obtained. The parameters obtained from this model are: $K_f = 15.31$ mg/g, $n = 3.08$ and $R^2 = 0.95$ which all parameters represented the ideal adsorption based on this model. Temkin model is considered the effects of indirect adsorption interactions. It is assumed that the trend of heat decreasing is linear and adsorption is determined by a uniform distribution of energy. According to the results of this model, the coefficient of determination is 0.98, which is an acceptable amount and it can be said that the results of the experiment follow Temkin model after Langmuir model. The parameters obtained from this model are $q_m = 8.93$ mg/g and $K_T = 6.93$ L/mg. The Dubinin–Radushkevich equation is usually used to show the adsorption mechanism by distributing Gaussian energy on a homogeneous surface [27]. The Dubinin–Radushkevich model has less accuracy than other model. Parameters derived from this model are $q_m = 41$ mg/g, $D = 10^{-7}$ (mol²kJ⁻²) and $R^2 = 0.73$. In this study, Langmuir model compared with other models had a higher coefficient of determination and therefore was more consistent with the experimental data and the maximum adsorption rate of cadmium obtained by this model was 61.34 mg/g which was closer to the measurement data. Fitness of the Langmuir model on experimental data indicated that biosorption is monolayer and cadmium was adsorbed on a homogeneous surface. Based on this result, it could be stated that cadmium molecules did not have any interactions with each other on the surface of modified adsorbent [6]. Studies on the biosorption [4,25] confirm the result of the current research.

Table 2
Parameters and isotherm equations of cadmium adsorption

Parameter	Langmuir		Freundlich		Temkin		Dubinin–Radushkevich					
	q_{max} (mg/g)	K_L (L/mg)	n	K_f (mg/g)	R^2	q_m (mg/g)	k_t (L/mg)	R^2	q_m (mg/g)	D (mol ² kJ ⁻²)	E (kJ/mol)	R^2
Amount	61.34	0.19	3.08	15.31	0.95	8.93	6.93	0.98	41	10^{-7}	2.23	0.73
Equation	$\frac{C_e}{q_e} = 0.0163(C_e) + 0.0866$		$\text{Ln}q_e = 0.3249(\text{Ln}C_e) + 2.7285$		$q_e = 8.9268(\text{Ln}C_e) + 17.287$		$\text{Ln}q_e = -1E - 07(\epsilon^2) + 3.7138$					

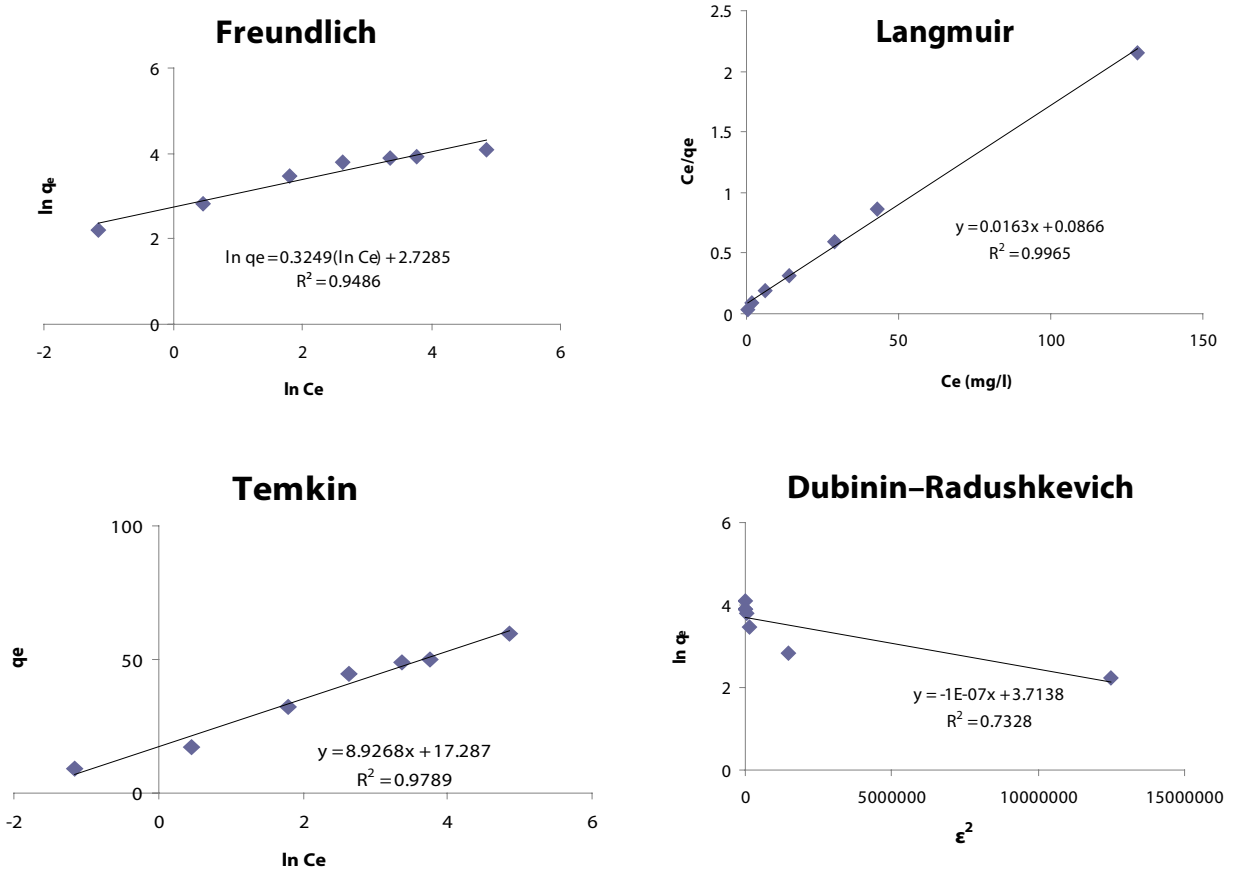


Fig. 9. Fitting the experimental data with isotherm models.

Table 3
Comparison of different adsorbents for cadmium removal

Biosorption	q_{max} (mg/g)	Reference
<i>Cystoseira indica</i>	19.42	[28]
<i>Hylocomium splendens</i>	32.5	[29]
<i>Ceratophyllum demersum</i>	61.34	Present study

The maximum adsorption capacity of different adsorbents is shown in Table 3. Based on obtained capacities in the several studies, it can be stated that NaCl-modified *Ceratophyllum demersum* had a capacity more than other studied adsorbents.

3.7. Kinetic studies

To understand the dynamics of adsorption reactions, the information obtained from the kinetics of adsorption have

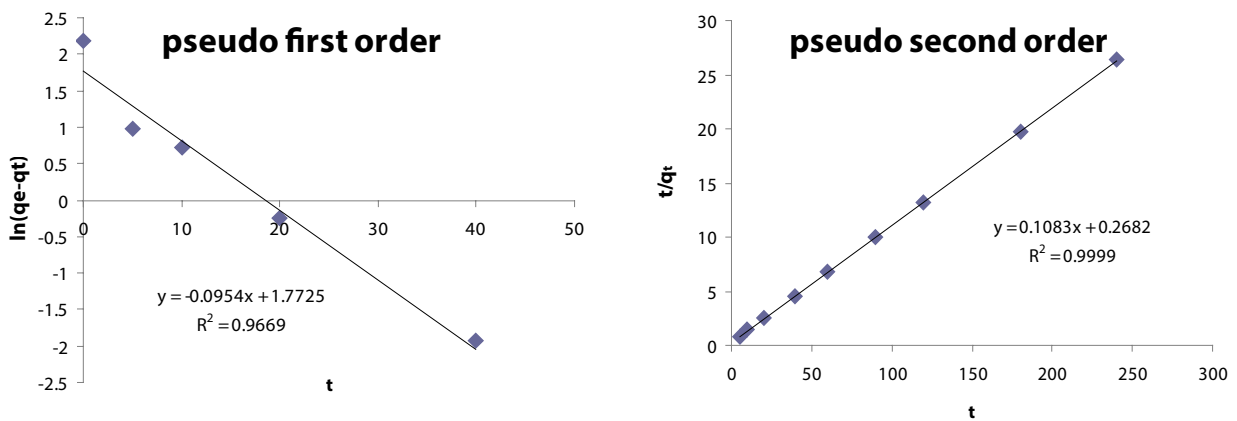


Fig. 10. Fitting the experimental data with kinetic models.

Table 4
Parameters and kinetic equations of cadmium adsorption

Parameter	Experimental	Pseudo-first-order			Pseudo-second-order		
	q_e (mg/g)	K_{1p} (1/min)	q_e (mg/g)	R^2	K_{2p} (mg/g.min)	q_e (mg/g)	R^2
Amount	8.8955	0.0954	5.88	0.97	0.043	9.23	0.99
Equation	–	$\ln(q_e - q_t) = -0.0954t + 1.7725$			$\frac{t}{q_t} = 0.1083t + 0.2682$		

been evaluated. In fact, the kinetics of adsorption is controlled the rate of removal of soluble matter. First-order kinetic is one of the most well-known kinetic models for describing adsorption rate based on adsorption capacity. In fact, this equation is based on the assumption that the metal adsorption process has a first-order nature, since it depends only on the number of metal ions present at the particular time in the solution. If the initial concentration of the adsorbed substance is low, the kinetics of the equation is in most cases of a quadratic type (pseudo-second-order). In this equation, the metal adsorption process is assumed to depend on the number of metal ions present in the solution and also on adsorption sites on the adsorbent surface [6]. Table 4 and Fig. 10 show the traditional models derived from the present study. According to Table 4, the pseudo-second-order model has a very good fit ($R^2 = 0.99$) and it can be said that the cadmium adsorption kinetics follows this model more than the first-order model, which means that the metal adsorption process depends on the number of metal ions and adsorption sites on the adsorbent surface. On the other hand, the amount of q_e which was calculated by this model was close to measurement q_e .

4. Conclusion

Considering the importance of removing pollutants from water and wastewater, this research was conducted to evaluate the removal efficiency of *Ceratophyllum demersum* for Cd(II). The results of this study indicate that modification of adsorbent with NaOH solution altered the surface structure of *Ceratophyllum demersum* and increased the adsorption capacity of the plant to absorb cadmium ions. The pH changes from 3 to 7 caused slight increase in the efficiency and the highest efficiency was obtained at pH equal to 7. With increasing contact time, the efficiency of removal was increased and considering the economic considerations and optimal energy consumption, the time of 60 min was determined as the time of equilibrium. Kinetic modeling showed that pseudo-second-order model has the best match with experimental data due to the highest coefficient of determination, also the proximity of the calculated and obtained q_e . Also, results indicated that the removal of cadmium follows the Langmuir equation.

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