Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1106342

57 (2016) 19877–19889
September

Taylor & Francis
Taylor & Francis Group

Biosorption of chromium in aqueous solutions using Bivalve Mollusk Shells through central composite design (CCD) model

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Received 27 December 2014; Accepted 6 October 2015

ABSTRACT

Pollution of water resources caused by heavy metals has been among the greatest concerns of environmentalists in recent years. Industrial wastewater contains chromium. Therefore, removing or reducing chromium from the industrial wastewater seems to be essential. In the present research, bivalve mollusk shells acted as the adsorbent. The statistical model in this research was central composite design, which analyzed the experiments. The optimal pH range for an adsorbent was about 3–5. An increase in the adsorbent dosage led to an increased efficiency. The optimal exposure time for the ion absorption mechanism of the solution was about 35 min. The absorption mechanism followed the Freundlich adsorption isotherm model. The most significant factor was found to be the independent effect of chromium initial concentration ($p = 0.0007$). Compared with other adsorbents such as fruit peels and the like whose availability depends on their consumption, the use of this adsorbent was economically beneficial due to its low cost and high availability.

Keywords: Adsorption; Heavy metals; Isotherm; Langmuir; Freundlich

1. Introduction

Pollution of water resources caused by heavy metals has been among the greatest environmental concerns in recent years [1]. Such concerns are due to high toxicity, huge discharge into the environment, and nondegradability; therefore, controlling the pollution of water sources is prioritized. Chromium is a heavy metal that is found in the wastewater of many industries such as tannery, dyeing, plating, textile, pulp, and paper manufacturing. Generally, chromium exists either at trivalent or at hexavalent oxidation levels in natural water sources. The latter is 500 times as toxic as the former. Transforming the hexavalent chromium into the trivalent, which has high solvability, happens very quickly in natural environments [2,3]. Chromium toxicities for humans are skin irritations and kidney, liver, as well as gastrointestinal problems. World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have recommended the concentration of chromium in drinking water to be less than 50 µg/L [4]. There are a number of methods for removing chromium from aqueous solutions, which include chemical deposition, ion exchange, membrane technology, electrodialysis, and adsorption. Each one of these processes has technological limitations. High chemical cost and sludge

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production are important defects of chemical precipitation processes. Electrical floatation requires high-voltage electricity and continuous monitoring. Reverse osmosis and ion exchange require high initial investments and skilled operators. Chemical deposition is the most prevalent method for industrial wastewater; however, it requires huge amounts of chemicals and space as well as the production of a great amount of sludge [5,6].

Adsorption process is one of the available options that is increasingly used to remove heavy metals such as hexavalent chromium. The use of activated carbon is the most common method for adsorbing chromium; however, it is costly [7]. Therefore, much cheaper adsorbents are being investigated. Some cost-effective materials include biological sludge, chitosan, zeolite, coal, alum sludge, red mud, agricultural waste (e.g. rice husks) [8,9].

Bivalve mollusk shells (BMSs) are skeletal structures that can be readily found after their death on the coastline. In case, their efficiency is proven, BMSs can be widely used as adsorbents.

In the present study, central composite design (CCD) model was used to obtain the highest amount of data with the minimum number of experiments.

Although many studies have been conducted on the adsorption rate of heavy metals by BMSs [10–13], based on our research, no one has been performed on the efficacy of BMSs for removing chromium. Since these shells are easily and abundantly found on the Caspian Sea coastlines, we try to investigate its effectiveness in this research.

2. Material and methods

2.1. Adsorbent characteristics

BMS is made up of two main parts including organic and mineral. The organic part plays a key role in determining the shell structure and is usually composed of 0.1 to 5% of the total weight of the shell. The majority of the organic part contains protein fibers. Chitin and lignin are the most important parts of the organic section and key elements of BMSs. Calcium carbonate comprises about 95% of BMSs structure and is the most important part of the mineral part [12,13].

2.2. Adsorbent preparation

BMSs used in this study were collected from the Caspian Sea. After brushing, the BMSs were washed in distilled water and dried in an oven at 105˚C. Initial grinding was done by a mortar and, finally, they were pulverized using a laboratory mill, after which they were sieved through 70–100 meshes.

2.3. Synthetic sampling and adsorption experiments

In order for chromium solutions to have the desired concentrations (10–100 mg/L), a stock chromium(VI) solution of 1,000 mg/L was prepared by potassium dichromate ($K_2Cr_2O_7$) in deionized water. All the tests were done discontinuously in an Erlenmeyer (250 mL). The sample size in the Erlenmeyer was 100 mL. All the solutions were prepared by deionized water in this study, and the required pH value was reached by adding 0.1 N of NaOH and HCl. The desired adsorbent size (0.1–1 g) was to be examined at different concentrations 10–100 mg/L, retention time of 10–110 min, and different pH of 3–9. After the sorption experiment, the solids were separated using a cellulose nitrate filter. The concentration of the remaining chromium was measured by atomic absorption spectrophotometer (AAS). All the tests were performed in duplicate to ensure the reproducibility of the results and the mean of these two measurements was taken to represent each evaluation. To prevent the deposition of chromium in the solution and to create an acidic condition, 0.5 mL of sulfuric acid was added after filtration to each sample in order to prepare it to be read by AAS.

2.4. Sample detecting

After passing through cellulose nitrate filters, whose pore diameter was 0.45 μm, the samples were kept in polyethylene terephthalate (PET) bottles at the laboratory temperature and, then, read by AAS (Perklin-Elmer AA100 Wellesley, MA). Before AAS reading, the standard curve was needed to be plotted. A standard solution had to be used for this purpose.

Many researchers have reported the concentration of chromium in aqueous solutions based on hexavalent chromium. According to similar works, in cases which Atomic absorption spectrophotometer (AAS) or Inductively Coupled Plasma (ICP) is used for sample reading, the obtained chromium concentration is the total chromium because of the existing possibility of converting chromium(VI) into chromium(III) [4]. In this research, the reported values of chromium were in fact total values.

2.5. Adsorbent characterization

In the experiment, pH_{zpc} was determined to evaluate how the surface of the adsorbent depending on pH. For the determination of $pH_{zpc,}$ 0.01 M NaCl solution (100 mL in a 250-mL Erylenmeyer flask) was prepared and its initial pH was adjusted between 2 and 12 using NaOH/HCl. Then, 0.55 g of the adsorbent was added to the solution and agitated for 36 h. The final pH of the solution was measured by a pH meter after the filtration. A graph was plotted by $\mathrm{pH_{final}}$ vs. $\mathrm{pH_{initial}}$ and the intersection point of the curves of $\mathrm{pH_{final}}$ vs. $\mathrm{pH_{initial}}$ was recorded as $\mathrm{pH_{zpc}}$. To determine the functional groups of the adsorbent, an amount of the adsorbent was dried at 70℃ and was then examined using FTIR (German Perklin-Elmer. 1600 series FTIR Spectrometer) at the wavelengths of 400–4,000 $\mathrm{cm^{-1}}$. Moreover, SEM (HITACHI S4160, Japanese FESEM) was used in order to determine the morphological changes of the adsorbent before and after the test.

2.6. Sorption isotherms

The sorption isotherm equations of an adsorbent indicate its sorption characteristics and are important for the sorption processes. The tests estimating the sorption isotherm of chromium on shells were done through adding 0.55 g of the adsorbent to a series of 100-mL flasks containing 10–100 mg/L of the chromium solution. The pH solution was set at about 4 (the optimal value obtained from the test) in order to determine its isotherm. Subsequently, the samples (exposed to the adsorbent) were kept on a lab shaker (180 rpm) for 4 h at the constant temperature of 25℃. After the passage of this time, the concentration of the remaining metal was measured and reported. The amount of the absorbed metal on the adsorbent particles was estimated based on the mass balance equation shown below:

$$q_\mathrm{e} = \frac{V(C_0 - C_\mathrm{e})}{m} \tag{1}$$

in which q_e is absorption capacity (mg of the absorbed metal per unit of adsorbent, mg/g), V is the volume of solution (mL per Liter), and m is the mass of the added adsorbent (g). What is considered the sorption isotherm is in fact the balance equation of the amount of the absorbed material to the adsorbent unit (q_e) and the final concentration of the solution (C_e) at constant temperature. A diversity of isothermal models has been proposed to measure the sorption equation of the compounds of a solution, among which Langmuir and Freundlich are the most commonly used ones. The results of the present study were analyzed based on these two models. In linear Langmuir model, it is hypothesized that the single-layer sorption occurs at the continuous level of the adsorbent as in:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{k_\mathrm{L} q_\mathrm{max}} + \frac{C_\mathrm{e}}{q_\mathrm{max}} \tag{2}$$

in which q_max (mg/g) is the surface concentration in the single-layered coverage and indicates the maximal values of q_e which is obtained through increasing C_e. K_L is the coefficient of energy absorption which is increased through a rise in the power of the sorption layers. q_max and K_L values are obtained through a linear regression ($C_\mathrm{e}/q_\mathrm{e}$) vs. C_e. Also, Freundlich's equation is shown in the following linear form:

$$\log q_\mathrm{e} = \log K_\mathrm{F} + \frac{1}{n}\log C_\mathrm{e} \tag{3}$$

in which K_F and n are constants. K_F indicates the adsorbent capacity and $1/n$ sis the reversed reaction degree which represents the sorption power. Plotting linear regression of $\ln q_\mathrm{e}$ vs. $\ln C_\mathrm{e}$ yields K_F and n [1,14].

2.7. Experimental design and statistical analysis

Response surface method (RSM) is a collection of statistical techniques used in optimizing the processes in which the target response is affected by a number of variables. CCD was employed in the present research so that a maximum data could be obtained through the least number of experiments. As indicated in Table 1, four factors identified for the present research were X_1, X_2, X_3, and X_4. Each of these factors included three levels coded as −1, 0, and +1 for low, average, and high values, respectively. Codes +2 and −2 were considered "helping codes" for the fitness of the model. The four variables were coded according to the following equation:

$$1/2X_i = \frac{l - \dfrac{\max + \min}{2}}{\dfrac{\max - \min}{2}} \tag{4}$$

in which X_i = target codes of the formula, l = target location of each factor, max = maximum, min = minimum.

The predicted responses were analyzed for different factors using RSM by Expert-Design software (version 7). The obtained data were analyzed through analysis of variance (ANOVA) method. Each response variable to the secondary concentration of chromium (Y) was presented in multiple regression as a function of the independent variables:

$$Y = \beta_0 + \sum_{i=0}^{4} \beta_i X_i + \sum_{j=0}^{4} \beta_{ii} X_i^2 + \sum_{i=0}^{4}\sum_{j=0}^{4} \beta_{ij} X_i X_j \tag{5}$$

Table 1
Variables and their experimental levels for each factor

Independent vs. code		Levels				
		−2	−1	0	+1	+2
pH	X_1	3	4.5	6	7.5	9
Adsorbent dosage (g)	X_2	0.1	0.325	0.55	0.775	1
Contact time (min)	X_3	10	35	60	85	110
Initial concentration (mg)	X_4	10	32.5	55	77.5	100

where Y is the response variable of each factor level (secondary concentration of chromium), β_0 is the intercept, β_1 is the analyzed regression coefficient from the obtained values of Y, and X_1 is the coded levels. X_iX_j and X_i^2 are, respectively, the interaction criteria and the second degree [15].

Fitness of the multinominal equation was evaluated using the obtained R^2 coefficients along with the adjusted R^2. The level of significance was set at $p < 0.05$.

3. Results and discussion

3.1. Model fitting and statistical analysis

RSM is much more effective than older one-parameter optimizing methods, since it prevents the loss of time, space, and materials [14]. Table 2 indicates the experimental conditions and the obtained results based on a factorial design. In this research, removal efficiency (Y) was based on the secondary concentration of Cr. Using multiple regression, the response variable was found to be a quadratic polynomial. For the secondary concentration of Cr (Y), it was as follows:

$$\begin{aligned} Y = 29.7 &+ 1.57\,X_1 + 1.48\,X_2 - 3.01\,X_3 + 6.28\,X_4 \\ &- 0.469\,X_1X_2 + 1.38\,X_1X_3 + 0.0206\,X_1X_4 \\ &- 3.52\,X_2X_3 + 4.77\,X_2X_4 - 3.86\,X_3X_4 + 0.997\,X_1^2 \\ &+ 0.473\,X_2^2 - 4.18\,X_3^2 - 3.74\,X_4^2 \end{aligned} \tag{6}$$

In order to determine whether the 2-degree model was significant for the metal or not, the data were analyzed using Expert-Design software and ANOVA and the results are indicated in Table 3.

The regression values along with the p-value of each variable are indicated in Table 4. Based on the p-values of each model, it is obvious that the independent variable X_4 significantly affected the removal efficiency. In the removal efficiency, the independent variable of the initial concentration was the most significant parameter. This significance level was minimum for the interactive variables of pH-initial concentration.

3.2. Effect of pH

pH is the most effective environmental factor in the optimal sorption process in aqueous solutions. Its impact is not only due to the surface charge of the adsorbent, but also is related to the ionization degree as well as characteristics and forms of the existing ions in the metal. Chromium sorption is, therefore, strongly dependent on pH values. The interactive effect of this parameter in the removal efficiency of chromium with the other variables is presented in Fig. 1 (in contour and surface). Such figures show the bi-factorial effects of variables on efficiency. In all figures related to this model, two factors are taken into account at a neutral (zero) level and the interactive effects of the other two variables are measured on the removal efficiency. Fig. 1(a) shows the interaction of pH (X_1) and the adsorbent dosage (X_2) at the secondary concentration of chromium (Y). As illustrated, the gradual increase of pH from 3 to 6 (level −1 to 0) was accompanied by an increase at the secondary concentration of chromium. This, in turn, could indicate a decrease in the removal efficiency of the metal. At acidic pH, the functional groups got saturated with positive ions and protons on the BMS surfaces and limited the access of cations to the adsorbent. However, when the pH was increased, the functional groups were charged negatively ($pH > pK_a$). Chromium(VI) of an aqueous solution existed in several forms including H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, $Cr_2O_7^{2-}$, etc. Its distribution depended on the pH and the total concentration of chromium. $Cr_3O_{10}^{2-}$ and $HCr_2O_7^-$ existed only at $pH < 1$ or chromium concentration of higher than 1 M [16]. At pH 1–2, the dominant form was $H_2Cr_2O_7$. At $3 < pH < 6$, the ions of chromium(VI) were usually in the form of $HCrO_4^-$ and $HCr_2O_7^-$. At pH > 6–7, only the chromate ion (CrO_4^{2-}) was the dominant form of chromium in the solution. Since the concentration of

Table 2
CCD model with 4 variables and the secondary concentrations of chromium

Set no.	X_1 (pH)	X_2 (adsorbent dosage) (g)	X_3 (retention time) (min)	X_4 (initial concentration) (mg/L)	Y (secondary concentration) (mg/L)
1	6	0.55	110	55	14.01
2	6	0.55	60	55	35.04
3	6	0.55	60	55	21.99
4	6	0.55	60	55	25.23
5	3	0.55	60	55	30.80
6	6	0.55	10	55	17.95
7	7.5	0.325	85	32.5	21.58
8	7.5	0.325	85	77.5	24.53
9	4.5	0.325	35	77.5	21.41
10	4.5	0.325	85	77.5	17.51
11	6	0.55	60	10	8.54
12	6	1	60	55	34.07
13	4.5	0.325	35	32.5	21.27
14	6	0.1	60	55	35.1
15	4.5	0.775	85	32.5	11.05
16	7.5	0.325	35	77.5	23.38
17	4.5	0.775	35	77.5	51.44
18	7.5	0.775	85	32.5	13.3
19	7.5	0.775	35	32.5	13.6
20	6	0.55	60	55	35.78
21	6	0.55	60	100	26.95
22	7.5	0.325	35	32.5	13.38
23	4.5	0.325	85	32.5	11.79
24	7.5	0.775	85	77.5	20.44
25	6	0.55	60	55	32.37
26	6	0.55	60	55	16.25
27	4.5	0.775	35	32.5	10.71
28	6	0.55	60	55	30.95
29	4.5	0.775	85	77.5	21.27
30	9	0.55	60	55	42.56
31	7.5	0.775	35	77.5	50.58

Table 3
ANOVA results for the efficiency removal of chromium

Source	Degree of freedom	Mean square	*F*-value	*p*-value
Model	14	218	3.96	0.00507
Lack of fit	10	53.4	0.929	0.564
Pure error	6	57.5		
Correlation total	30			

$HCr_2O_7^-$ in the acidic condition and the low concentration of chromium (<75 mg/L) were negligible, $HCrO_4^-$ was considered the dominate form of the chromium existing at pH 3–6 [9]. These anion types could be absorbed on the positively charged parts of the adsorbent. The sorption equation could be written as follows for the hexavalent anions of the solution chromium on the adsorbent:

$$H_2CrO_4 \longleftrightarrow HCrO_4^- + H^+ \quad k = 1.21 \tag{7}$$

$$Cr_2O_7^{2-} + H_2O \longleftrightarrow 2HCrO_4^- \quad k_2 = 35.5 \tag{8}$$

$$HCrO_4^- \longleftrightarrow CrO_4^{2-} + H^+ \quad k_3 = 3 \times 10^{-7} \tag{9}$$

Table 4
Regression coefficients, significance of each independent variable and the second-degree fit of RSM for the efficiency of removing chromium

Model term	Coefficient estimate	Degree of freedom	Standard error	Probability (P) > F
Intercept	29.7	1	2.8	
X_1	1.57	1	1.51	0.314
X_2	1.48	1	1.51	0.344
X_3	−3.01	1	1.51	0.064
X_4	6.28	1	1.51	0.00075[a]
X_1X_2	−0.469	1	1.85	0.803
X_1X_3	1.38	1	1.85	0.468
X_1X_4	0.0206	1	1.85	0.991
X_2X_3	−3.52	1	1.85	0.0758
X_2X_4	4.77	1	1.85	0.0204[a]
X_3X_4	−3.86	1	1.85	0.0537
X_1^2	0.997	1	1.39	0.0482[a]
X_2^2	0.473	1	1.39	0.737
X_3^2	−4.18	1	1.39	0.0082[a]
X_4^2	−3.74	1	1.39	0.0159[a]

[a] Significant at p-value < 0.05.

The amount of chromium(VI) was not found to be significant at pH > 6–7, which could be due to the competition of $HCrO_4^-$ and $Cr_2O_7^{2-}$ with the existing OH^- in the solution [4].

At the neutral or basic pH, the activity of the existing Cr ion in the solution was in the form of oxygen radicals on the adsorbent surface. It could then lead to the reduction of the sorption of chromate and other forms of chromium [17].

A large number of studies have considered the removal of chromium from aqueous solutions to be dependent on a sorption mechanism of the sites with positive loads and anion types of Cr^{6+} [18–21]. Moreover, the surface of the BMS particles gets positively charged at pH < 5.4 (pHzpc). Probably, at pH < pHzpc, the chromium of the solution gets absorbed into the hydrogen ions on the shell through an electrostatic sorption mechanism with $HCrO_4^-$ and $Cr_2O_7^{2-}$ bonds with acidic functional groups. Through a reaction, the final form of chromium is transformed into $H_2CrO_4^-$ which leads to the sorption onto the adsorbent. Once the solution pH gets lower than 5.4, the number of accessible protons on the surface of the adsorbent is increased, which would lead to an increase in the sorption of $H_2CrO_4^-$ and, finally, result in decreased chromium concentration of the solution. On the other hand, with an increase in the solution's pH to higher than pHzpc, the adsorbent's surface becomes negatively charged, which would lead to the creation of repulsion among the ions of the solution chromium and adsorbent and, eventually, cause a reduction of sorption [22]. Fig. 2 indicates the interactive effects of the initial concentration-pH. As can be observed, with an increase in these two factors, the secondary concentration of chromium (Y) was increased as well; but, with decreasing themes, the concentration was reduced. This issue could demonstrate the effect of pH parameter on the acidic condition (levels −1 to 1). The interactive effect of these parameters was not statistically significant; however, as in Figs. 1 and 2, the best sorption range of pH for metal sorption was about 3–5, which was close to the findings of the similar previous works [4,23,24]. The optimal pH in these studies was reported as 1.5–2.5. In the present research, it was reported to be a bit higher, which could be due to the interference of other variables such as adsorbent dosage, initial concentration, etc., because in CCD, the secondary concentration was measured based on the simultaneous effect of two variables. The other probable factor could be the constructing compound of the adsorbent's surface. As previously mentioned, 95% of BMSs is made up of calcium carbonate (as a basic factor). Once exposed to water, it could increase pH. In the present research, it was found that chromium sorption in an acidic condition had higher efficiency. The wastewaters of the industries containing chromium (e.g. electronic industries, plating, etc.) are usually acidic. Therefore, removing this pollutant using BMSs without the readjustment of pH could cut down on extra costs.

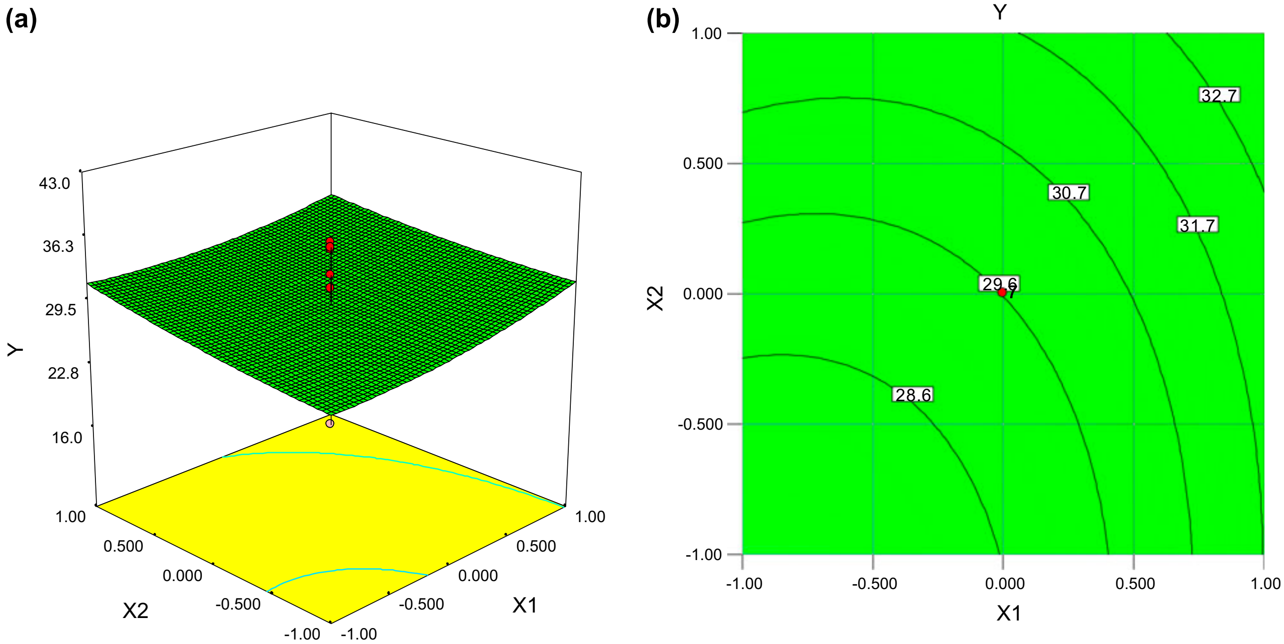

Fig. 1. The interactive effect of pH (X_1) and adsorbent dosage (X_2) on the secondary concentration of chromium (Y): (a) contour plot and (b) surface plot.

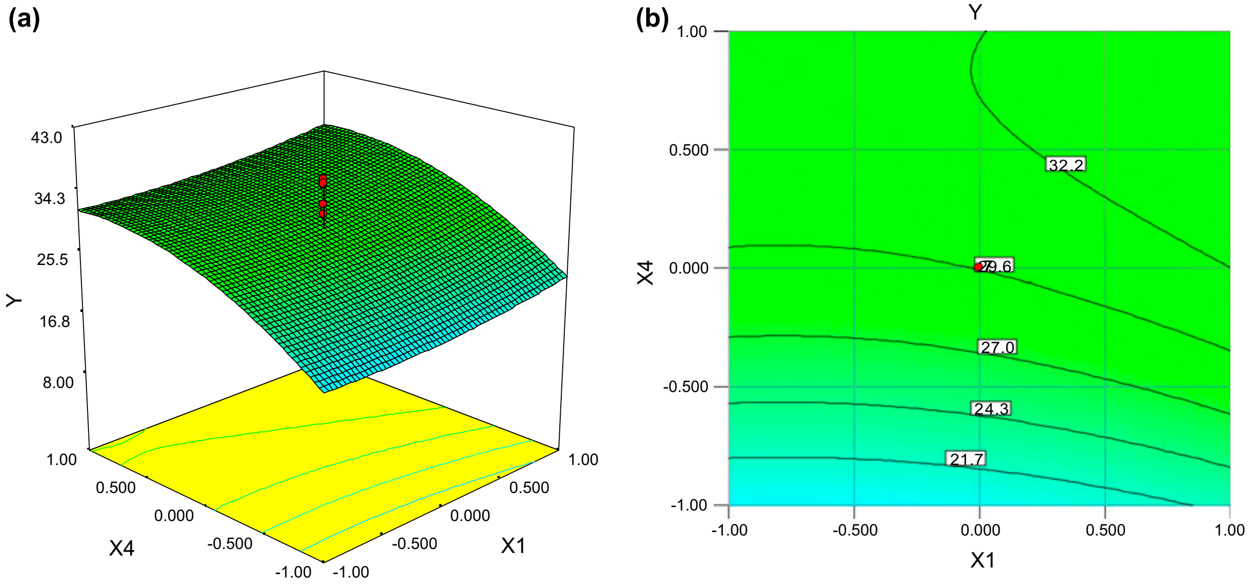

Fig. 2. The interactive effect of pH (X_1) and initial concentration of Chromium (X_4) on the secondary concentration of Cr (Y): (a) contour plot and (b) surface plot.

3.3. *Effect of adsorbent dosage and initial concentration*

Determining the adsorbent dosage and estimating the sorption capacity are important parameters in sorption experiments, which could help reduce the operational costs of refinement and reduce pollution and produced sludge. As indicated in Fig. 3, a gradual increase in the adsorbent dosage was followed by a reduction in the secondary concentration of chromium, because along with an increase in adsorbent dosage, the area of the BMSs was expanded, which

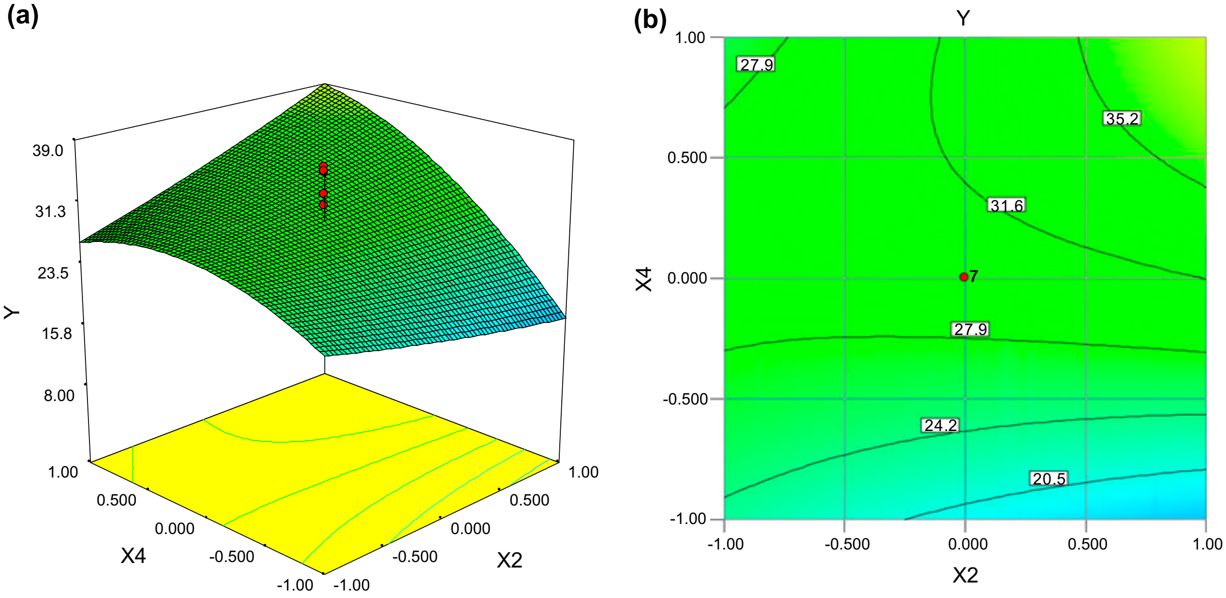

Fig. 3. The interactive effect of adsorbent dosage (X_2) and initial concentration (X_4) on the secondary concentration of chromium (Y): (a) contour plot and (b) surface plot.

led to more access points to the sorption site and creation of bonds with the existing chromium ions. This issue was, however, possible through keeping the other parameter (the initial concentration of the metal-X_4) constant. In case both parameters were increased, the secondary concentration was also increased, while the removal efficiency was reduced. It became the optimal amount due to the increase in metal concentration and inadequacy of the amount of adsorbent. Overall, with an increase in the adsorbent dosage and a constant amount of the adsorbent, the amount of the absorbed chromium ions into per unit of adsorbent weight (q_e) was decreased as well [25]. When the chromium sorption approached 100%, no adsorbent would be left to be absorbed into the surface. This was not, however, the case in Fig. 3, since while the adsorbent dosage was increased, there was an increase in chromium concentration which would remain rather constant to the final sorption capacity. As can be observed in the figure, at the concentrations of lower than the initial concentration of chromium (at levels between −1 and −0.5), with an increase in the dosage, the secondary concentration decreased significantly ($p = 0.0204$).

3.4. Effect of retention time

Fig. 4 indicates the interactive effects of exposure time (X_3) and initial concentration (X_4) on the final concentration of chromium. As can be observed, in case the initial concentration was kept constant, no significant change would occur in the optimal retention time within the first 35 min of the reaction (level −0.5) and the final concentration. The amount of removal would be rather the same at the outset and end of the retention time, which would imply that ion absorption actually happened at the outset of exposure. It is evident in the figures that the initial concentration, at the beginning of retention time, was on average less than 18 mg/L. As mentioned previously, this occurred when the initial concentration parameter (X_4) was kept constant. Through the effect of the initial concentration of chromium and the simultaneous increase in these two parameters, the secondary concentration of chromium (Y) was increased, which proved the effect of the initial concentration and the result of its interaction with the other parameters that finally led to the reduction of sorption. No transformation of the secondary concentration of Cr through the passage of time could explain that the ion sorption mechanism was highly dependent on the number of sorption sites and the number of ions existing in the solution at the optimal pH, because the sorption amount had no significant change through the passage of time and the sorption process occurred very fast.

3.5. Characteristics of BMSs

Dependence of the sorption process on pH is mainly due to the adsorbent functional groups and

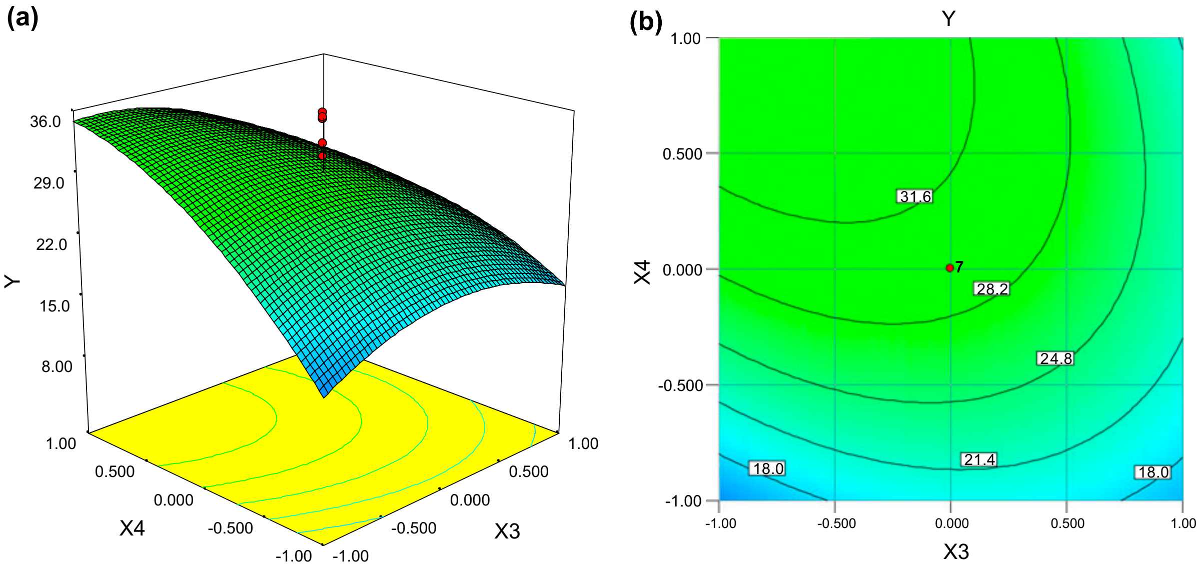

Fig. 4. The interactive effect of retention time (X_3) and initial concentration (X_4) on secondary concentration of chromium (Y): (a) contour plot and (b) surface plot.

the chemistry of the metals in the solution [17]. To identify the characteristics of the adsorbent's functional groups, the use of FTIR is necessary. To this aim, the FTIR of BMSs was recorded to register the data related to the vertical and flexural oscillations and vibrations of the functional groups existing on the surface of the adsorbent. Findings of the present research revealed that the BMSs contained many functional groups capable of adsorbing metal ions. The analysis of the visible peaks on the shells is indicated in Fig. 5. The existing peaks at the wavelength of 3,400–3,700 cm^{-1} indicated the existence of the –OH

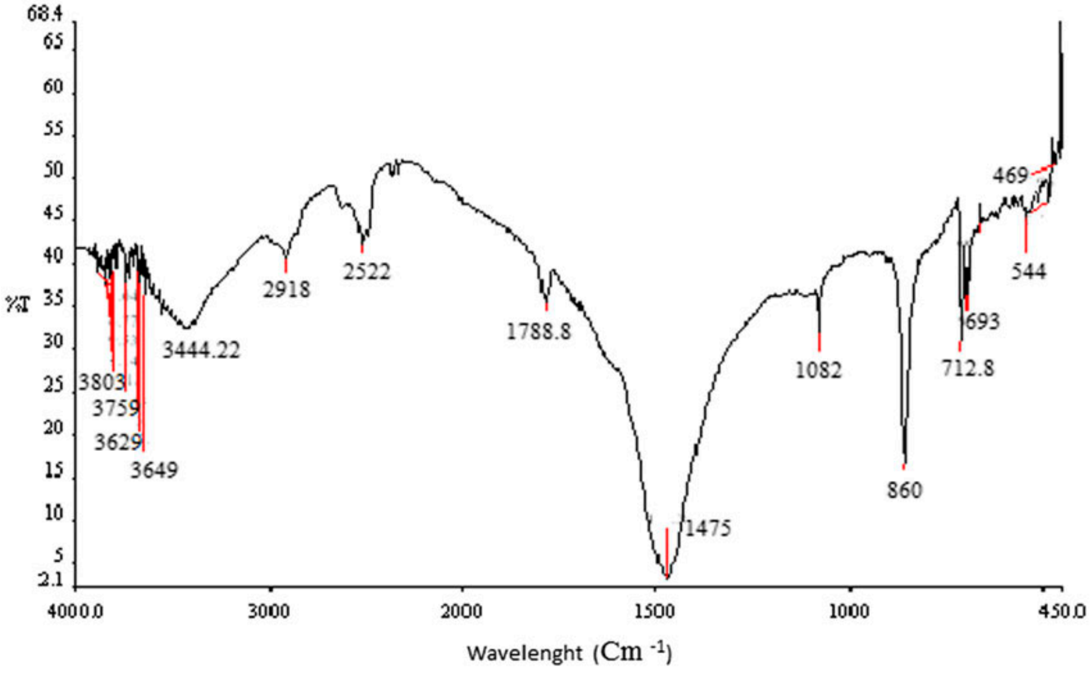

Fig. 5. The FTIR of BMS.

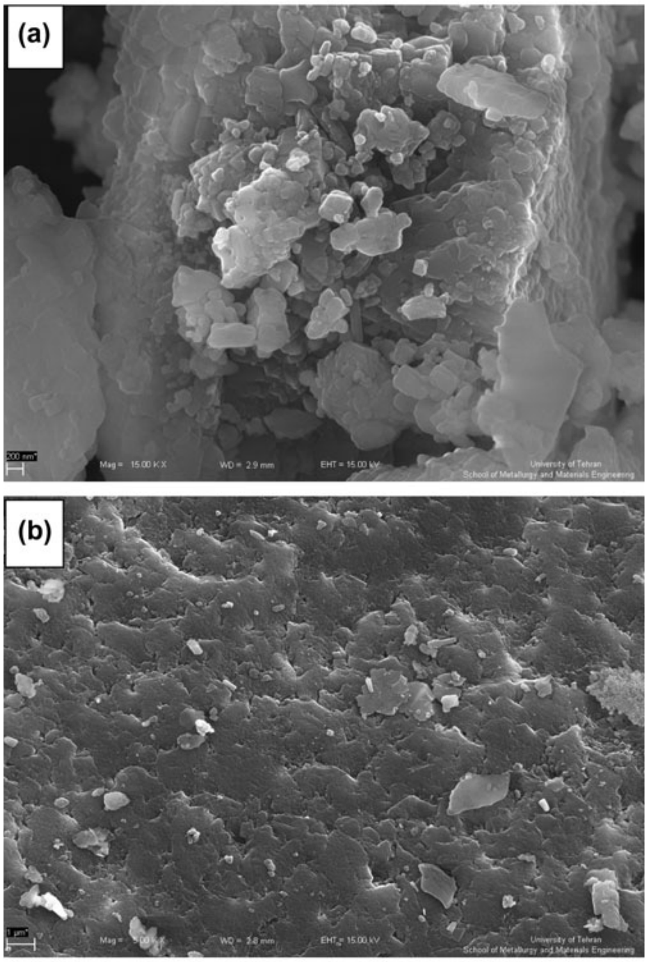

Fig. 6. The SEM of BMSs: (a) Before sorption and (b) After sorption.

functional group [26,27]. This functional group could lead to the bond formation with the chromium of the solution. At the acidic pH, the existing H^+ ions on the surface of the adsorbent which led to its protonation came into reaction with –OH functional group and neutralized it. Then, this functional group was transformed into $–OH_2^+$. These transformations led to an increase in adsorbing negative ions of $Cr_2O_7^{2-}$ and, finally, $HCrO_4^-$. The reaction was as follows [28]:

$$OH_2^+ + HCrO_4^- \longleftrightarrow OH_2^+(HCrO_4^-) \tag{10}$$

The wavelength of 2,918 cm^{-1} indicated the functional group $-CH_2$, the extensive peak of 1,475 cm^{-1} among the carboxylic groups, and aromatic rings (–C=O and COO–) at 1,082 cm^{-1} of the carboxylic (–C–O), which existed due to the lignin in BMSs, at the obvious peak of 860 cm^{-1} in the group of C=N, at 1,788 cm^{-1} of groups $–CO_3^-$ and –COO, and at 550–750 cm^{-1} of groups –O–P–O and $–PO_4$. Considering the present research and other similar studies on the adsorption of metallic ions on BMSs or other basic sea materials in aqueous solutions, it could be concluded that chromium ion adsorption on the adsorbent is highly dependent on the functional groups of hydroxyl (–OH), carboxyl ($–CCO^-$), and carbonate ($–CO_3^-$) [10,29].

In order to describe the basic characteristics of BMSs before and after the metal sorption, we used SEM. It can be seen in Fig. 6(a) that the BMS surface was crystalline and honey-combed shape and depended on natural structure of BMSs. The surface image of BMSs after the reaction of adsorbent had

Table 5
Isotherm results of adsorbing chromium on BMS

Isotherm	Unit	Information
Langmuir model		$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}}$
Plot	-	C_e vs. (C_e/q_e)
Fitted model	-	$\frac{C_e}{q_e} = 0.229 + 0.004\,C_e$
q_{max}	mg/g	214
K_L	L/mg	0.017
R^2	-	0.955
Freundlich model		$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$
Plot	-	$\ln C_e$ vs. $\ln q_e$
Fitted model	-	$\ln q_e = 1.654 + \ln 0.806\, C_e$
K_F	$(mg/g\ (L/mg)^{1/n})$	5.3
n		1.25
R^2	-	0.977

Table 6
Comparison of adsorption capacity for chromium with various adsorbents

Adsorbent	Condition of experiments	Optimum pH	Fitted isotherm model	Adsorption capacity (mg/g)	Refs.
Present study	Initial concentration: 10–110 mg/L pH 2–9 Contact time: 10–110 min	4	Freundlich	214	–
Rose waste biomass	Initial concentration = 10–100 mg/L pH 2–5 Adsorbent concentration: 0.5–2 g/L Contact time: 10–320 min	5	Langmuir	55.79	[26]
Titanium oxide–Ag composite	Initial concentration = 5–50 mg/L pH 2–10	2	Langmuir	25.7	[5]
Growing cells of a bacterial consortium	Initial concentration: 1–100 mg/L pH 3–8 Contact time: 100–800 min at 25˚C	7	Freundlich	90.91	[6]
Nongrowing cells of a bacterial consortium	Initial concentration: 1–100 mg/L pH 3–8	4	Freundlich	75.76	[6]
Pistachio hull	Initial concentration: 50–200 mg/L pH 2–8 Adsorbent concentration: 0.5–8 g/L Contact time: 1–60 min	2	Langmuir	116.3	[7]
Chitosan-coated fly ash	Initial concentration: 40–100 mg/L pH 2–8 Contact time: 10–50 min	5	Langmuir	33.27	[17]
Eichhornia crassipes root biomass-derived activated carbon	Initial concentration: 10–100 mg/L pH 1.5–8.5 Contact time: 2–80 min Adsorbent concentration: 1–7 g/L	4.5	Langmuir	36.34	[18]
Newspapers	Initial concentration:100 mg/L pH 1–7 Contact time: 1–800 min Adsorbent concentration: 1–6 g/L	1	Freundlich and Redlich–Peterson	55.06	[19]
Low-cost adsorbent Alligator weed	Initial concentration: 40–120 mg/L pH 1–6 Contact time: 1–500 min Adsorbent concentration: 1–8 g/L	1	Langmuir	88.11	[20]

other properties with an almost flat shape (Fig. 6(b)). These changes might be related to the interaction of adsorbent to Cr at acidic pH.

3.6. Estimating sorption isotherms

In order to describe the reactive behavior of the adsorbent and the adsorbed material in an aqueous solution, sorption isothermal equations are necessary. Therefore, we analyzed the experiment results of chromium adsorption on BMSs using Langmuir and Freundlich models. The data obtained from these isothermal models are summarized in Table 5. The obtained R^2 from Langmuir and Freundlich equations were 0.955 and 0.977, respectively, indicating that the sorption of chromium ions on BMSs better fitted Freundlich model than the other one. According to Freundlich's theory (the main theoretical basis of the present research), the heterogeneous surface of bivalve shells might be an appropriate site for absorbing chromium ions in the solution. These results were in accordance with the observations obtained from Wang et al. [30] and Yavuz et al. [31]. According to this model, the adsorption of chromium was not exclusive to a certain point on the surface of an adsorbent, which could be the result of the reaction of different sites of the adsorbent. Moreover, appropriateness of the reaction was also crucial for the sorption process. In Freundlich model, this appropriateness is measured using constant n with the desirable range of 1–10. In the present research, n was 1.25, which pointed to the desirability of the BMSs surface as an adsorbent in removing chromium from the aqueous solutions [9,32].

As seen in Table 5, the Langmuir model estimated the maximum chromium adsorption capacity on BMSs as about 214 mg/g, representing that the BMSS might have relatively high potential to the adsorption of Cr in aqueous solution compared with another adsorbent. Moreover, in contrast to some bio-adsorbent such as banana peels [22] and agricultural waste [24], BMSs could be a superior adsorbent for the adsorption of Cr due to their availability in high quantities as well as accessibility in no cost. Furthermore, BMSs are not the by-product of human activity, nor are they consumer-dependent; they are accessible in large amounts without any cost at the seashore. Table 6 shows the summarized comparison of adsorption capacity of chromium by various adsorbents.

4. Conclusion

In the present study, BMSs, as noncost and efficient biosorbents, were investigated for the removal of chromium from aqueous solution by CCD model in various experiment conditions. Basic adsorption experiments represented that the adsorption of chromium on BMSs depended on solution's pH level and favorable under-acidic conditions. The experimental data fitted the Freundlich model. The maximum adsorption capacity calculated from the Langmuir isotherm was found to be 214 mg chromium per g BMSs. The feasible availability and no-cost properties of BMSs could make it a favorable and promising alternative adsorbent for chromium removal in aqueous solutions.

Acknowledgment

The present study was carried out with the financial support of Mazandaran University of Medical Sciences to whom the gratitude is expressed. Our appreciation is extended to the Chemistry department of Mazandaran University for detecting of samples by AAS.

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