



## Optimization of effective parameters in the biosorption of Cr(VI) using acid treated date palm fiber from aqueous solution

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### ABSTRACT

The study tries to determine the optimal condition to achieve the maximum Cr(VI) removal in the biosorption process from aqueous solution using acid-treated date palm fiber as the biosorbent. Three factors including initial pH, initial Cr(VI) concentration, and biosorbent dosage were optimized using response surface methodology. Maximum Cr(VI) removal was 95% at the optimum condition of initial pH 3.3, initial Cr(VI) concentration 180 (mg/L), and biosorbent dosage of 0.8% (w/v). The kinetic study was done to acquire a deeper understanding of the mechanism of biosorption process and its results showed that the pseudo-second-order models controlled the process. Isotherm study showed that Langmuir model described the experimental data thoroughly.

*Keywords:* Date palm; Cr(VI); Response surface methodology; Kinetic; Isotherm

### 1. Introduction

Chromium is one of the most commonly used heavy metals in a variety of industries such as electroplating, fertilizers, pigments, tanning, mining, and metallurgical [1]. In aqueous solutions, there are two forms of the hexavalent chromium (Cr(VI)), as dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) and chromate ( $\text{CrO}_4^{2-}$ ) in acidic and alkaline conditions, respectively [2]. Cr(VI) can cause disorders such as liver, kidney, lung, and gastrointestinal cancer [3]. Although chemical precipitation is good enough for the removal of solution matrixes, it produces high sludge volume containing toxic metal ions

whose disposal not only requires relative high costs, but increases the possibility of ground water contamination [4]. Therefore, the development of a simple, robust, and cost-efficient technology for chromium removal is necessary. Several researchers have investigated chromium adsorption using certain, easily available and low-cost materials such as waste sludge, clays, and sawdust [5–7].

Using biomaterials for heavy metals removal from diluted water, industrial effluents and large volume solutions is of great interest. Compared with traditional methods of wastewater treatment such as adsorption, coagulation and precipitation, biological adsorption (called biosorption) was applied because of its economical and environmental advantages [8–12].

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Recent investigations by various researchers have shown that a number of biomass possesses impressive sorption capacities or removal efficiencies for the biosorption of the Cr(VI) from aqueous solutions [13–17].

There are more than 100 million date palm trees in the world and each tree can grow for more than 100 years [18]. It has been reported in different studies that the date palm as a biomaterial has metal adsorption capacity, still superior than the other biomaterials [18,19]. El Nemr et al. reported that activated carbon developed from date palm seed, that was treated using sulfuric acid, could remove 100% of Cr(VI) [20]. The purpose of biomass treatment is to increase the surface porosity and also adsorption capacity. Moreover, treatment of biomass results in protonation, which displaces the light metal ions from the binding sites like carboxylic and this increases the metal adsorption capacity [21,22].

Optimization processes may involve the study of many biochemical and physical parameters including media formulation and parameters. Conventionally, one studied parameter could be set as variable, while keeping the other parameters at fixed value. So obtaining optimum value for each parameter is to some extent difficult. To solve this problem in term of process scale up, statistical analysis offers several advantages including being more reliable and rapid over conventional method, which helps us to understand the interactions among the adsorbents and adsorbates and reduces the total number of experiments. Response surface methodology (RSM) is an efficient strategic experimental tool based on statistical analysis in which the optimal conditions of a multivariable system are determined. Danish et al. used RSM to optimize the surface area-activated carbon from date treated by phosphoric acid. Using this method, date stone has much improved thermal stability compared with physically activated carbon up to 900 °C [23].

In the literature, there is no information available regarding the optimization of effective parameters on the biosorption of Cr(VI) from aqueous solution using date palm fiber. The aim of present work is described as following: (1) determination of biosorption potential for chromium removal, (2) modeling and optimization of biosorption using RSM, and (3) isotherm and kinetic of chromium biosorption at the optimized condition.

## 2. Materials and methods

### 2.1. Collection of biomass

Date palm fiber that was collected from the Persian Gulf (Bandar Boshehr, Iran) was washed thoroughly

with tap water. In order to get silt, sand, diatoms, and other epiphytic organisms were removed; the biomass was washed three times with deionized water and, finally, by glass distilled water. Having been cleaned, the date palm was dried and stored at room temperature. The acid-treated date palm was prepared by transferring the date palm into 0.1 M HCl and then stirring the mixture at 200 rpm for 8.0 h at room temperature. The date palm was then centrifuged (Eppendorf Centrifuge model HM-150 IV, Korea), washed with the physiological saline solution and dried in an oven at 60 °C. Subsequently, it was ground on an agate stone pestle mortar then sieved to select the particles between 200 and 300 mesh sizes for use.

### 2.2. Preparation of chromium solutions

Using analytical grade  $K_2Cr_2O_7$  provided by Merck Company, a stock solution of 500 ppm concentration of Cr(VI) was prepared and stored at room temperature. This stock solution was used to prepare dilute solutions of chromium ion by dilution with double-distilled water.

### 2.3. Batch adsorption experiments

The magnetic mixer rate was 300 rpm throughout the study. At the end of predetermined time intervals, the sample was filtered and the concentration of Cr(VI) ion was determined. All experiments were carried out twice and the given adsorbed Cr(VI) ion concentrations were the means of duplicate experimental results. Atomic absorption spectrometer (Model 929, Unicam) was used to analyze the concentration of heavy metal ions. Removal efficiency Cr(VI) was calculated according to the following equation:

$$\text{Removal efficiency \%} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial Cr(VI) concentration (mg/L) and  $C_f$  is the final Cr(VI) concentration (mg/L).

The value for  $q$  is the amount of metal adsorbed per specific amount of adsorbent (mg/g). The sorption capacity at time  $t$ ,  $q_t$  (mg/g) was obtained using Eq. (2):

$$q_t = (C_i - C_t) \times V/m \quad (2)$$

where  $C_i$  and  $C_t$  (mg/L) are the liquid-phase concentrations of solutes at initial and a given time  $t$ , and  $V$  is the solution volume with  $m$  being the mass of acid treated date palm (g).

The amount of adsorption at equilibrium,  $q_e$  was acquired by Eq. (3):

$$q_e = (C_i - C_e) \times V/m \quad (3)$$

where  $C_e$  (mg/L) is the ion concentration at equilibrium.

#### 2.4. Experimental design and optimization

Experimental design was performed to investigate the effect of three main parameters including pH, initial Cr(VI) concentration, and biosorbent dosage on the process efficiency and also obtaining optimum condition. Each factor in experimental designs based on the RSM varied at five different levels, while the other parameters were kept fixed. Once the desired ranges of the variables had been defined, they were coded to lie at  $\pm 1$  for the factorial points, 0 for the center points, and  $\pm\alpha$  for the axial points. The range and the levels of the variables investigated in this study are shown in Table 1. RSM is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses [24]. CCD was widely used for fitting a polynomial model. Using this method, modeling is possible while requiring only a minimum number of experiments. It is not necessary during the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. Using the CCD method and  $2k + n_a + n_0$  equation, a total of 20 runs with different combination of main variables were performed, where  $k$  is the number of independent variables,  $n_a$  is axial points and  $n_0$  center points [24,25]. In this study using design-expert 7.0, a 8 ( $2^3$ ) factorial design, 6 ( $2 \times 3$ ) axial points with 6 central points were selected. The behavior of the system is explained by the following quadratic polynomial empirical model:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i<j}^3 \sum_{j=1}^3 \beta_{ij} X_i X_j + \varepsilon \quad (4)$$

Table 1  
Experimental variables at different levels used for biosorption experiment

	$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Initial Cr Conc. (mg/l)	100	200	300	400	500
Initial pH	2	4.5	6	7.5	8
Biosorbent dosage (%w/v)	0.1	0.33	0.55	0.78	1

where  $y$  is the expected value of the response variable,  $\beta_0$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are the model parameters, and  $X_i$  and  $X_j$  are the coded factors evaluated. In this study,  $y$  represents the Cr(VI) removal percentage in different empirical models [24,25].

#### 2.5. Verification of optimum condition

In order to verify the optimum condition obtained from RSM, an experiment at optimal factor levels was performed and the experimental biosorption of Cr(VI) was compared to the predicted result by the model.

### 3. Results and discussion

#### 3.1. Characterization of the biosorbent

To indicate the functional group on the surface of the date palm, the FTIR spectra in natural and acid-treated form are shown in Fig. 1. According to Fig. 1(a), there is a strong peak at  $3,340 \text{ cm}^{-1}$  representing the N–H stretching of amino group, while the peak at  $2,918 \text{ cm}^{-1}$  indicates the presence of C–H stretching. The appearance of peaks at  $1,636$  and  $1,437 \text{ cm}^{-1}$  indicate the presence of C=O stretching and C–O stretching in carbonyl and carboxyl groups. Cell protein is typically indicated by a number of amide bands, which dominate at  $1,055 \text{ cm}^{-1}$  (C–N stretching) [26,27]. During the acid treatment of biosorbent, the main functional groups remain unchanged which is shown in Fig. 1(b). Additional peaks found at  $1,374$ ,  $1,514$ , and  $1,720 \text{ cm}^{-1}$  in acid-treated form confirm the production of additional functional groups.

#### 3.2. Effect of contact time

To identify the equilibrium time, the effect of time on sorption of Cr(VI) was investigated with the result being shown in Fig. 2. For these cases, initial Cr(VI) concentration was of 200 mg/L, pH was 3, and biosorbent dosage was 0.8 (%w/v). With the contact time being 50 min, sorption rate reaches up to nearly 95% and then little change of sorption rate is observed. It revealed that the adsorption of Cr(VI) is fast and the equilibrium was achieved during 50 min of contact time. Contact time of 50 min was chosen for further experiments.

#### 3.3. Statistical analysis

The CCD which presents the experimental conditions and their response is shown in Table 2. To identify the significant and insignificant effects, the

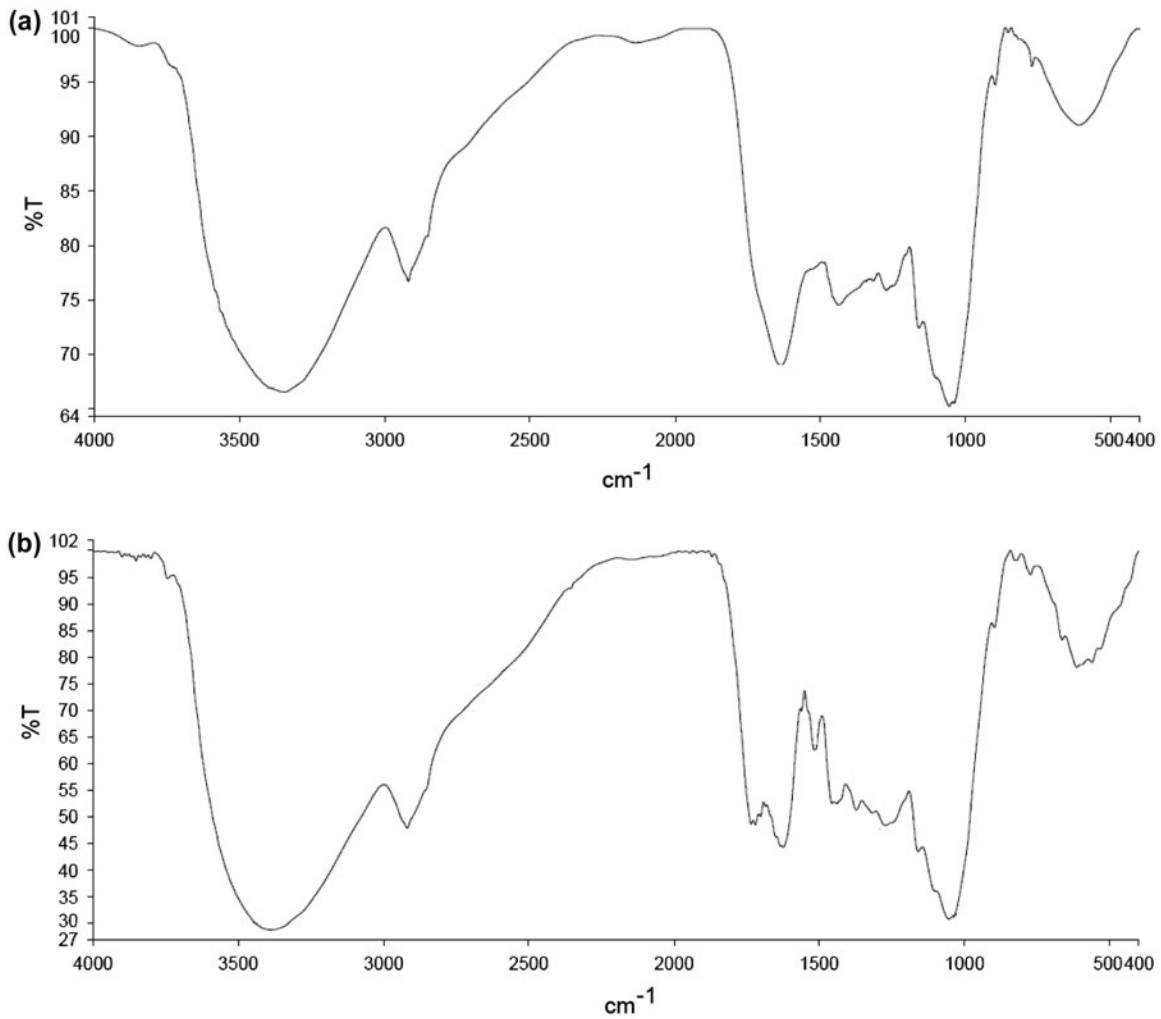


Fig. 1. FTIR spectra of the biosorbent. (a) Before acid treatment and (b) after acid treatment.

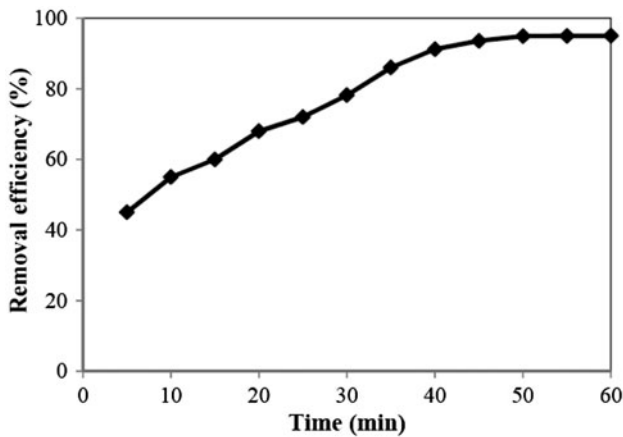


Fig. 2. Effect of contact time on chromium removal efficiency (the initial concentration was 200 mg/l, pH was 3, and the amount of biosorbent was 0.8% (w/v)).

interaction effects as well as obtaining the best possible regression model, the data obtained from the shake flask experiments were statistically analyzed using analysis of variance (ANOVA) as shown in Table 3.

This statistical procedure is required to have the significance and adequacy of the model tested. The mean squares (MS) are obtained as:  $MS = SS/DF$ , where SS = sum squares (SS) of each variation source and DF = the respective degrees of freedom (DF). According to Table 3, the model provided for Cr removal is significant at *p*-value less than 0.05 at 95% confidence interval.

### 3.4. Determination of Cr(VI) removal model

The experimental results of the CCD were fitted with a 2FI model polynomial equation that was

Table 2  
Experimental plan based on CCD and the results of metals recoveries

Run	Initial Cr Conc. (mg/l)	Initial pH	Biosorbent dosage (%w/v)	Cr removal (%)
1	181	3.2	0.3	73
2	300	5.0	0.6	35
3	300	5.0	0.6	50
4	419	6.8	0.8	27
5	300	8.0	0.6	8
6	300	5.0	0.1	37
7	419	3.2	0.3	60
8	419	6.8	0.3	27
9	300	2.0	0.6	90
10	181	6.8	0.3	27
11	300	5.0	0.6	51
12	300	5.0	0.6	52
13	100	5.0	0.6	65
14	181	6.8	0.8	30
15	300	5.0	0.6	50
16	181	3.2	0.8	90
17	500	5.0	0.6	41
18	300	5.0	1.0	64
19	419	3.2	0.8	63
20	300	5.0	0.6	50

Table 3  
ANOVA for response surface models applied

Response	Model	Source	S.S.	Df	ANOVA		
					M.S.	F-value	Prob > F
Cr removal (%)	2FI model	Model	8,264.25	6	1,377.37	47.03	<0.0001
		A—Initial Cr(VI) conc.	508.86	1	508.86	17.37	0.0011
		B—Initial pH	7,169.35	1	7,169.35	244.78	<0.0001
		C—Biosorbent dosage	342.66	1	342.66	11.70	0.0046
		AB	171.13	1	171.13	5.84	0.0311
		AC	36.13	1	36.13	1.23	0.2869
		BC	36.13	1	36.13	1.23	0.2869
		Residual	380.75	13	29.29		
		( $R^2 = 0.95$ )	( $R^2_{adj} = 0.93$ )				

obtained from the 20-batch runs using the design-expert 7.0 software. The empirical relationship between removal and the three test variables in coded units obtained by the application of RSM is acquired by:

$$\begin{aligned} \text{Cr removal (\%)} = & 49.50 - 6.10 A - 22.91 B \\ & + 5.01 C + 4.63 AB - 2.12 AC \\ & - 2.12 BC \end{aligned} \quad (5)$$

where  $A$  is the initial Cr(VI) concentration,  $B$  is the pH and  $C$  is the biosorbent dosage (%w/v). It should be

noted that polynomial models are reasonable approximations of the true functional relationship over relatively small regions of the entire space of independent variables. Fig. 3 shows the predicted data (data that were gathered from model for percentage of metals recovery) vs. actual data (data that were gathered from experimental condition for percentage of metals recovery).  $R^2$  and adjusted  $R^2$  ( $R^2_{adj}$ ) were found to be 0.95 and 0.93, respectively, indicating that the actual and predicted Cr(VI) removal efficiencies were in agreement. Also, the relatively high  $R^2$  (0.95) value indicates that the 2FI model equation for the Cr removal is capable of representing the system under the given experimental conditions.

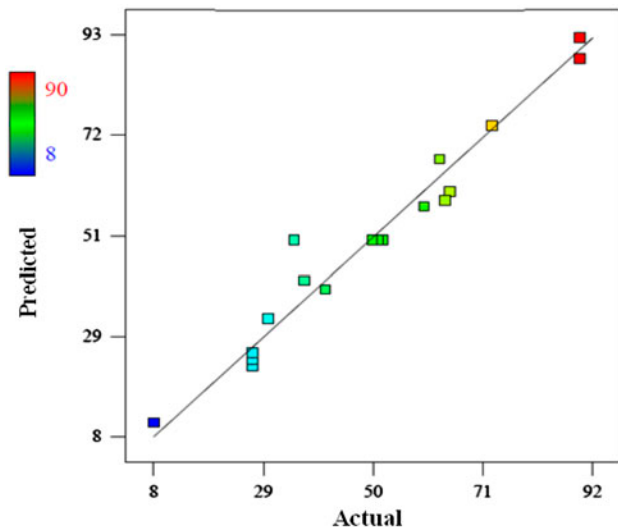


Fig. 3. Actual vs. predicted values for chromium biosorption.

3.5. Two-dimensional plots to Cr(VI) removal

Fig. 4 represented the two-dimensional response surfaces of Cr removal (%) of the relationship among different parameters. Fig. 4(a) clearly shows a combined effect of initial Cr(VI) concentration on the amount of pH at the constant biosorption dosage (0.8%w/v). Figure shows that decreasing pH and initial Cr(VI) concentration have positive effect on Cr removal. The maximum Cr removal (89%) was observed for chromium concentration of 240 (mg/L) and the amount of pH at of 3.5.

The relationship between biosorption dosage and amount of pH for Cr removal (%) is shown in Fig. 4(b). According to this figure, a maximum removal of Cr of >83% was observed in amount of pH 3 and biosorption dosage 0.8 (%w/v) at the constant initial Cr(VI) concentration of 200 (mg/L). According to this figure, the amount of Cr(VI) removal would be increased with biosorption dosage increasing from 0.3 to 0.8 (%w/v) at a constant pH.

3.6. Determination of optimum conditions

It should be noted that the goal of optimization is to find a proper set of experimental conditions. The optimum conditions proposed by the model were pH 3.3, chromium concentration 180 (mg/L), and biosorption dosage 0.8 (%w/v), where maximum removal of 90% was achieved. These values match the results obtained from the contour plots. It is necessary to note that qualitative and statistical analysis of biosorption dosage indicates that the removal of Cr(VI) is favored

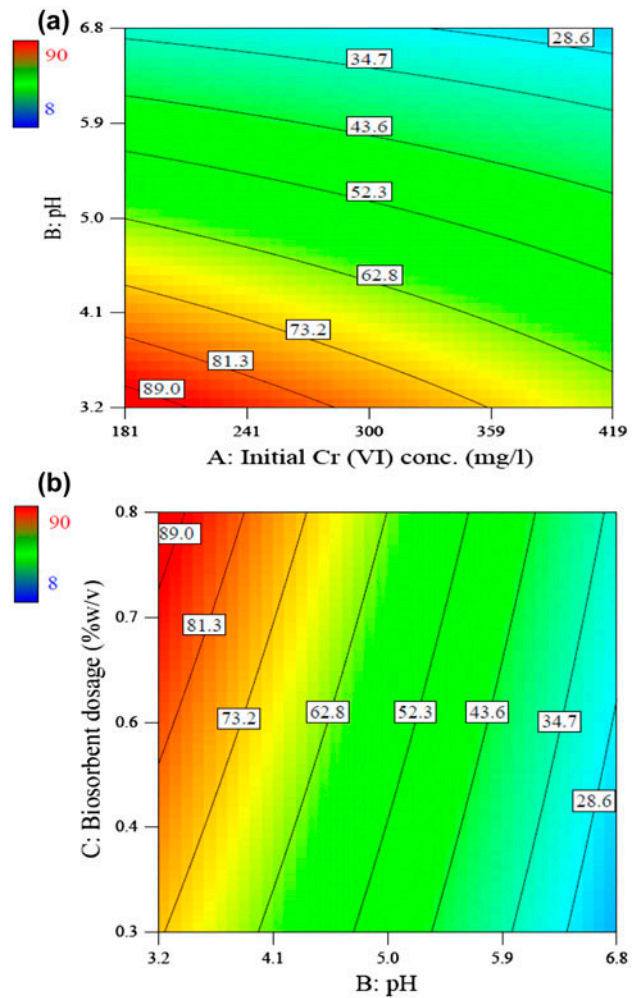


Fig. 4. Contour plots of the interactive effect for chromium biosorption. (a) Effect of pH and initial chromium concentration at the constant amount of biosorbent dosage 0.8% (w/v) and (b) effect of pH and amount of biosorbent dosage at the constant initial chromium concentration 200 (mg/l).

with the increase in it, but it is restricted from an economical point of view.

3.7. Validation of optimal condition

To test the validity of the optimized conditions given by the model, an experiment was carried out with the parameters suggested by the model. Table 4 presents the results of the experiment conducted at the optimal conditions showing the verification experiment and the predicted values from fitted correlations mostly matched at a 95% confidence interval. These results confirmed the validity of the model, and the experimental values were determined to be quite close to the predicted values. Under these conditions, the

Table 4  
Verification of optimum condition

Response (%)	Target	Correlation predicted (%)	Confirmation experiment (%)	95% CI Low	95% CI High
Cr removal	Maximize	90	95	81	98

experimental and predicted values for the Cr removal were 90 and 95%, respectively. The 95% confidence interval (C.I.) is the range in which the process average was expected to fall 95% of the time.

### 3.8. Kinetic study

The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to determine the mechanism and dynamic interactions of Cr(VI) onto date palm fiber, several kinetic models such as Morris–Weber, pseudo-first-order, and pseudo second-order have been applied to discuss the controlling mechanism [28]. It was assumed to offer no mass transfer (both external and internal external) resistance to the overall adsorption process. Therefore, kinetic can be studied through the residual Cr(VI) ion concentration in the solution. The study of adsorption kinetics describes the solute uptake rate, evidently controlling the residence time of adsorbate uptake at the solid–solution interface including the diffusion process [21].

According to Eq. (6), Morris–Weber was applied to investigate the change in the concentration of Cr(VI) onto sorbent with shaking time [21,22]:

$$q_t = K_{id}(t)^{0.5} + C \quad (6)$$

where  $q_t$  is the amount of chromium adsorbed on the adsorbent at time “ $t$ ,”  $K_{id}$  is the diffusion rate constant, and  $C$  is the intercept. The value of  $C$  depends on the thickness of the boundary layer. According to Eq. (4), the plot of  $q_t$  against  $t^{1/2}$  must show a linear relationship that was given in Fig. 5(a). The rate constant  $K_{id} = 2.49 \text{ min}^{-1}$  and  $C = 5.8$  were calculated from the slope and intercept of the straight line with a correlation factor of 0.97 was obtained.

To determine the rate constant of sorption [21,22], the pseudo-first-order of the sorption of Cr(VI) onto biosorbent was evaluated by feeding the data into the following form of Lagergren rate expression (Eq. (7)):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \quad (7)$$

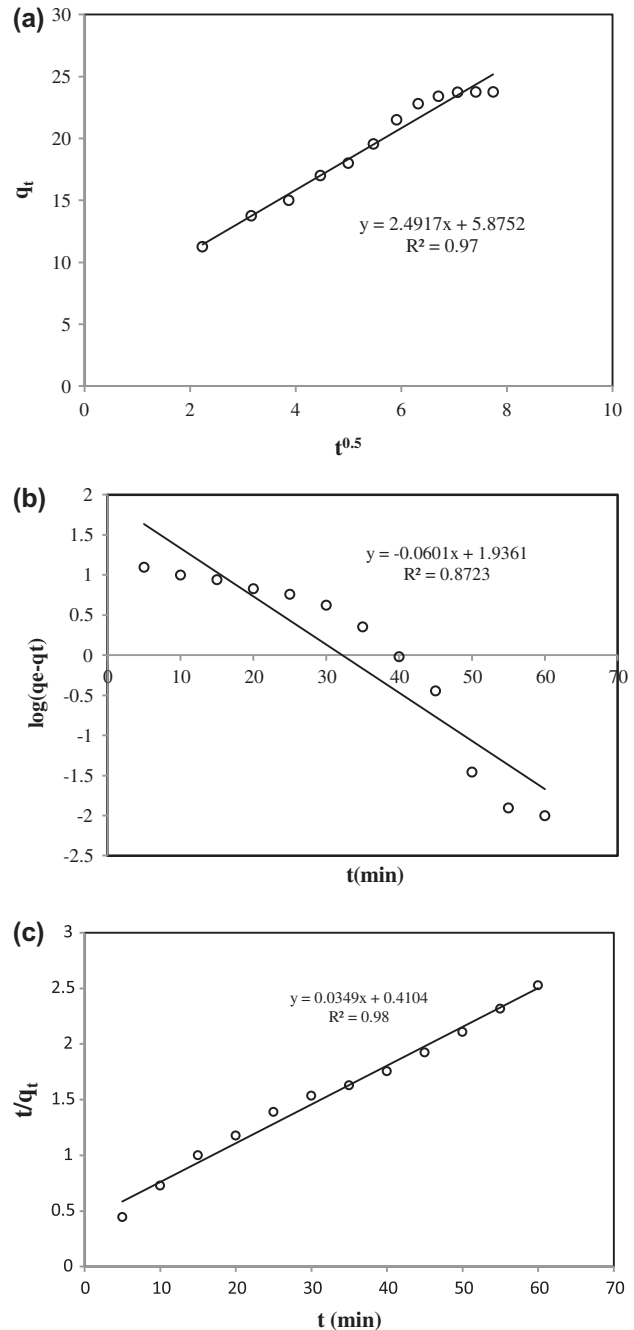


Fig. 5. Kinetics model to chromium biosorption onto date palm at the optimum conditions. (a) Morris–Weber, (b) Pseudo-first-order, and (c) Pseudo-second-order.

where  $q_e$  is the sorbed concentration at equilibrium and  $K_1$  is the first-order rate constant. Fig. 5(b) shows the linear plot of  $\log (q_e - q_t)$  against time “ $t$ ”. The rate constant ( $K_1$ ) and correlation factor ( $R^2$ ) were 0.13 and 0.87, respectively. Since both low value of correlation coefficient and the  $q_e$  value obtained by this method are in contrast with the experimental value, the reaction cannot be classified as first order.

Pseudo-second-order (Eq. (8)) was another kinetic model that was applied to study the sorption of Cr (VI) onto date palm fiber:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \tag{8}$$

where  $K_2$  is the second-order adsorption rate constant, and  $q_e$  is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg/g). The rate constant  $K_2 = 0.06 \text{ min}^{-1}$  and  $q_e = 28.65 \text{ (mg/g)}$  were calculated from the straight line with a correlation factor of 0.98 that are shown in the Fig. 5(c).

According the results of correlation factor, the adsorption process was controlled by pseudo-second-order equation and the intra-particle diffusion model. The correlation coefficient of the intra-particle diffusion equation is lower than the pseudo-second-order equation. The two reasons demonstrate that the correlation coefficient of the intra-particle diffusion equation is not suitable: (1) the removal of Cr(VI) from aqueous solution cannot be neglected relative to the amount of Cr(VI) in the solution; (2) the intra-particle diffusivity relies on the solid phase concentration in a large degree [22].

The pseudo-second-order model for the Cr(VI) uptake process is due to chemisorptions. The pseudo-second-order kinetic model was based on the assumption that the rate-limiting step might be chemisorptions engaging valence forces through sharing or exchanging electrons between adsorbent and adsorbate. The shape and coefficients of the adsorption kinetics depends considerably on the concentration of metal, pH of the solution, and the physical and chemical properties of both the adsorbent and adsorbate [22,29].

### 3.9. The isotherm model

The adsorption equilibrium information is the most important piece of information needed in understanding the adsorption process. The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether adjacent sites are occupied or not [21,22]. Isotherms show the

relationship between metal concentration in solution and the amount of Cr(VI) adsorbed on a specific sorbent at a constant temperature. In the following, two isotherm models including Langmuir and Freundlich equations are studied.

#### 3.9.1. The Langmuir isotherm model

Eq. (9) presented the Langmuir isotherm model that is valid for monolayer adsorption onto surface containing finite number of identical sorption sites:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

where  $q_e$  is the amount of Cr(VI) adsorbed per specific amount of adsorbent (mg/g),  $C_e$  is equilibrium concentration of the solution (mg/L), and  $q_m$  is the

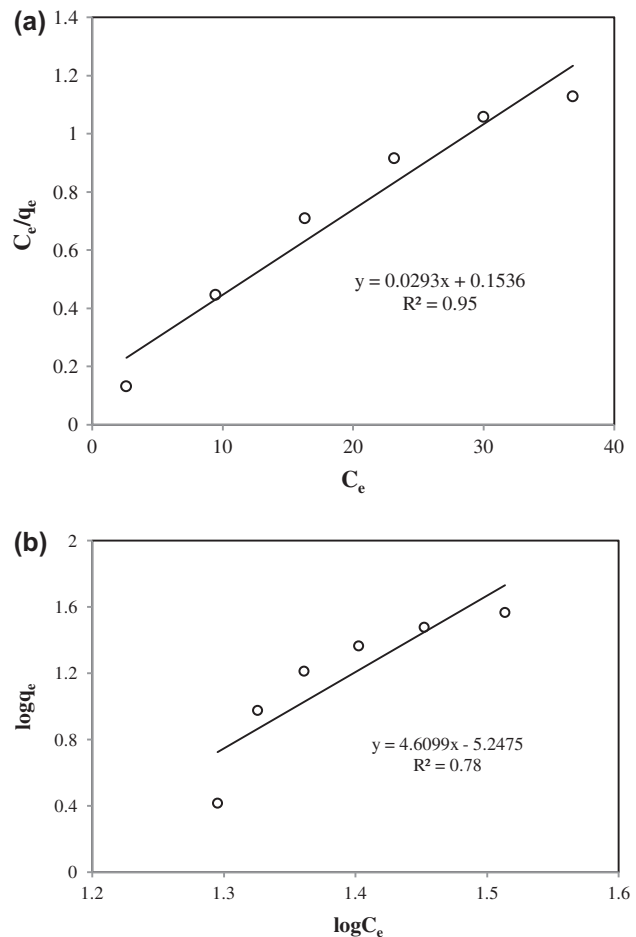


Fig. 6. Isotherm equilibrium of chromium biosorption onto date palm at the optimum conditions. (a) Langmuir isotherm and (b) Freundlich isotherm.



maximum amount of Cr(VI) required to form a monolayer (mg/g). For the convenience of plotting and determining the Langmuir constants ( $K_L$ ), the Langmuir equation can be rearranged in linear form as below. The values of  $q_m$  and  $K_L$  can be determined from the linear plot of  $C_e/q_e$  vs.  $C_e$  [26,27]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (10)$$

According to Eq. (10), the equilibrium data were analyzed using the linearized form of the Langmuir adsorption isotherm. The Langmuir constants, namely  $K_L$ , monolayer sorption capacity and  $q_m$  were calculated from the slope and intercept of the plot between  $C_e/q_e$  and  $C_e$  (Fig. 6(a)). The results indicated that the values of  $q_m$  and  $K_L$  are 34.12 and 0.195, respectively, and  $R^2$  is 0.95.

### 3.9.2. The Freundlich isotherm model

The empirical Freundlich equation can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites, while Langmuir isotherm assumes that the enthalpy of adsorption is independent of the amount adsorbed (Fig. 6(b)). The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is acquired via the following equation [26,27]:

$$q_e = K_F (C_e)^{\frac{1}{n}} \quad (11)$$

where  $K_F$  and  $(1/n)$  are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. According to the intercept and the slope of the linear plot of  $\log q_e$  vs.  $\log C_e$ , equilibrium constants could be evaluated. The Freundlich equation can be linearized in logarithmic form for the determination of the Freundlich constants as shown below:

$$\log (q_e) = \log (K_F) + \frac{1}{n} \log (C_e) \quad (12)$$

The slope and the intercept correspond to  $(1/n)$  and  $K_F$ , respectively. It was revealed that the plot of  $\log q_e$  and  $\log C_e$  yields a straight line (Fig. 6(a)). The results indicated that the values of  $n$  and  $K_F$  are 0.21 and  $5.6 \times 10^{-6}$ , respectively, and  $R^2$  is 0.78.

## 4. Conclusions

The acid-treated date palm fiber was used for the biosorption of Cr(VI) from aqueous solution. Hydro-

chloric acid was used for the modification of the date palm fiber and, therefore, to enhance the adsorption capacity. To optimize the effective factors including initial pH, initial Cr(VI) concentration, and amount of biosorbent, RSM was used. ANOVA showed that the 2FI model equation has relatively higher  $R^2$  (0.95) at 95% confidence level. Optimum values were found to be initial pH of 3.3, initial Cr(VI) concentration of 180 (mg/L), and amount of biosorbent 0.8% (w/v). The maximum Cr(VI) removal at the optimum condition was found 95%. In order to understand the dynamic interactions of Cr(VI) with date palm, kinetic study was conducted. Results show that the sorption kinetics is fast and is well represented by pseudo-second-order models with high  $R^2$  values of 0.92. The adsorption of chromium preferably fitted the Langmuir adsorption isotherm ( $R^2 = 0.87$ ) that is valid for monolayer adsorption

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