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Use of experimental design to evaluate the adsorption of chromium (VI) by alginate/polyaniline beads

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Abstract: Low-cost decorated sodium alginate beads with polyaniline (Alg@PANI beads) were easily prepared using a cross-linking method, and employed for the adsorption of Cr(VI) from aqueous solutions. The effect of several influencing parameters, including temperature, contact time, Cr(VI) concentration, and adsorbent dosage, was investigated and optimized using central composite design (CCD) under response surface methodology (RSM). The analysis of variance (ANOVA) of the quadratic model and the analyzed model revealed that the models were statistically significant, with a low *P*-value (<0.0001) and a high correlation coefficient value (R^2 = 0.93). The optimum parameters for total adsorption were as follows: adsorbent dose 0.027 g, pH 2, contact time 45 min, temperature 38 °C, and Cr(VI) concentration 29.24 ppm. The findings of this study indicate that the prepared Alg@PANI beads could be effectively used to remove Cr(VI) ions from aqueous solutions.

Keywords: bioadsorbent; central composite design; response surface; ANOVA.

INTRODUCTION

The discharge of different hazardous materials into the environment, such as heavy metals, causes a large pollution issue that can affect the quality of air, water and soil. Chromium is one of the most common heavy metal contaminants. Generally, chromium exists in several stable oxidation states, *i.e.*, Cr(0), trivalent Cr(III) and hexavalent Cr(VI) species. The hexavalent form Cr(VI) causes serious health effects, such as liver damage, pulmonary congestion, shortness of breath, coughing, and wheezing.[1] Traditional sewage methods for the removal of Cr(VI) from aqueous solutions, such as chemical precipitation,[2] membrane separ-

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ation,[3] adsorption,[4,5] ion exchange,[6] electrolysis[7] and coagulation[8] have been shown to be efficient. However, due to its high performance, low cost, ease of use, and lack of polluting by-products, the adsorption process has been extensively studied and widely applied on a large scale.[9–11]

Many adsorbents have been studied for the removal of Cr(VI) from aqueous solutions, including activated carbon, graphene and magnetic nanoparticles.[12,13] In recent years, low-cost adsorbents, such as biopolymers, have received much interest due to their ability to adsorb harmful heavy metal ions while still being environmentally friendly. The current example is alginate (Alg), a salt of alginic acid, which is a natural polysaccharide extracted from brown macroalgae, which consists of the anionic bloc of (1→4) linked α-L-gluronic acid (G) and β-D-mannuroric acid.[14] Thus, numerous physiochemical modifications of alginate, such as grafting and composite formation, have been developed to improve its weak mechanical stability, rigidity and adsorption properties.[15,16]

Furthermore, polyaniline, a common conductive polymer, has attracted the attention of researchers in recent years due to its low cost, ease of synthesis and environmental stability.[17,18] Then, most studies about adsorption focused on the use of polyaniline and its composites because they contain large amounts of aniline and imine nitrogen.[19]

A traditional study can be conducted to determine the best conditions of the effect treatment, but it requires more time and reactive products, which raises the cost invested in the study and the design of the treatment. Hence, predictive analytics studies were used by scientists for resolving environmental problems.[18,20,21] Thus, response surface methodology (RSM) can be used to study the effect of different variables influencing the removal of Cr(VI) from water in order to determine the best possible operating conditions.

Hence, in this study, alginate beads were decorated with polyaniline to prepare non-toxic Alg@PANI beads, and their activity and properties for adsorbing Cr(VI) in an aqueous solution were studied. The influence of different variables, namely temperature, contact time, Cr(VI) concentration, and adsorbent dosage, were investigated and optimized by central composite design combined with response surface methodology. Furthermore, the optimum parameters of the adsorption of chromium *via* Alg@PANI beads were optimized.

EXPERIMENTAL

Materials and methods

Aniline was purchased from Sigma–Aldrich and was distilled before use. All other chemicals, including sodium alginate, were purchased from Sigma–Aldrich and BIOCHEM, and used without further purification. Double distilled water was used in all experiments.

The method of preparation of 1000 ppm stock solution of Cr(VI) consisted of the dissolution of 2.829 g of $K_2Cr_2O_7$ in 1 L of double-distilled water, and standard solutions were

prepared by successive dilution. The pH of the standard solution was 6.5, which corresponds to the predominant species of CrO_4^{2-}.[22]

Preparation of Alg@PANI beads

A low-cost adsorbent was prepared by the polymerization of aniline on the surface of Alg beads. A solution of 2 % of sodium alginate was prepared by mixing the fine sodium alginate powder with double distilled water and stirring for 3 h. Separately, 0.05 M $CaCl_2$ was prepared, and both of the solutions were left standing overnight in a refrigerators. The alginate solution was then added dropwise into 500 mL of $CaCl_2$ solution under gentle stirring at room temperature. Upon contact with the cross-linker solution, calcium-alginate beads, denoted Alg beads, were formed and left to stabilize overnight. The excess of the cross-linker solution was removed by filtration.[15]

In order to activate the surface of the Alg beads, they were soaked by gentle stirring in a solution of HCl (1 M) for 1 h at room temperature. Then, a known amount of aniline was added and after 2 h, ammonium persulfate solution was added dropwise, and the reaction was allowed to proceed for 6 h at room temperature. The final synthesized product was filtered and washed several times with double distilled water and then left to air dry for 48 h.

Batch adsorption experiments

The adsorption studies of Cr(VI) on Alg@PANI beads were performed on the batch scale in the laboratory. Adsorbate solution (25 mL) was treated with a known amount of adsorbent at 150 rpm for a defined contact time under determined concentration and temperature conditions. The pH of the adsorption medium was adjusted with 0.1 M NaOH and HCl solutions in the range from 1 to 8. After the desired contact time, the adsorbate and adsorbent were separated by filtration and the residual adsorbate concentration was determined using a UV-spectrophotometer (Optizen 1412V model) at 540 nm by measuring the optical density of the resultant purple complex of Cr(VI) with 1,5-diphenylcarbazide.[23] The removal percentage (R) of the adsorbate was computed using Eq. (1):

$$R = 100\frac{C_0 - C_t}{C_0} \tag{1}$$

where C_t and C_0 are the final and initial concentrations of the adsorbate in ppm.

Experimental design

In this study, a central composite design (CCD) was chosen to assess the relationship between the variables and to evaluate the optimal conditions for the experiments.[24] Design Expert 8.0.7.1 Trial software was used for generating the statistical experimental design and analyzing the observed data. The factor levels were coded as −1 (low), 0 (central point) and 1 (high), and star points +2 (+α) and −2 (−α). According to some preliminary experiments, Table I shows the studied parameters consisting of temperature (X_1), contact time (X_2), Cr(VI) concentration (X_3) and adsorbent dosage (X_4). A quadratic equation was developed by using the second-degree polynomial equation to express the correlation between response and the selected variables, which was defined as:

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i X_i + \sum_{i=1}^{4}\sum_{j=1}^{4}\beta_{ij} X_i X_j + \sum_{i=1}^{4}\beta_{ii} X_i^2 \tag{2}$$

where Y is the predicted response; β_0, β_i, β_{ii} and β_{ij} are the unknown regression coefficients; and X_i, X_j, X_i^2 are the coded values and interaction terms of the variables.

TABLE I. Central composite design experimental factors and levels

Factor		Level			Star points, $\alpha = 2$	
		Low (−1)	Middle (0)	High (+1)	$-\alpha$	$+\alpha$
X_1	Temperature, °C	25	35	45	15	55
X_2	Contact time, min	30	45	60	15	75
X_3	Cr (VI) concentration, ppm	25	45	65	5	85
X_4	Adsorbent dose, g	0.015	0.025	0.035	0.005	0.045

RESULTS AND DISCUSSION

Characterization of adsorbent

Point of zero charges (pH$_{PZC}$). pH$_{PZC}$ is the pH value at which the total surface charge of an adsorbent is zero.[25] A pH-drift approach was used to determine the pH$_{PZC}$ of the Alg@PANI beads.[26] The sample was measured in NaCl electrolyte solutions of varying ionic strength (0.1, 0.01 and 0.001 mol/L). As can be seen in Fig. 1, the pH$_{PZC}$ value of Alg@PANI was found at 6.5±0.2. The composite reacts as a negative surface when the pH of the solution is >pH$_{PZC}$ and as a positive surface when the pH of the solution <pH$_{PZC}$.

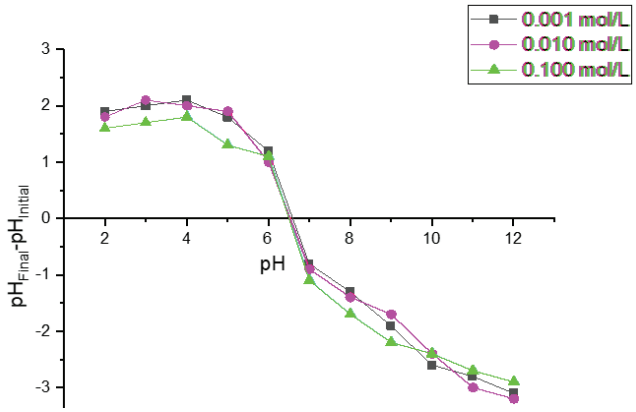

Fig. 1. Point of zero charge of Alg@PANI beads.

FTIR analysis. the functional groups of the formed beads were analyzed by Fourier transform infrared spectroscopy (FTIR, Agilent Technologies Cary 600 Series) in the 500-4000 cm^{-1} region (Fig. 2). With such a minor change, the spectrum of Alg@PANI is very similar to the Alg spectrum. The peaks at about 3241, 1592, 1419 and 1024 cm^{-1} in the alginate spectrum (Fig. 2, a) are assigned to the –OH, –COO– (asymmetric), –COO– (symmetric) groups, and oxygen stretching in cyclic ether bridge, respectively.[27] The spectrum of Alg@PANI beads (Fig. 2, b) shows an absorption peak at 3286 and 1731 cm^{-1}, which are related, respectively, to OH and the carboxyl groups in the alginate blocks after combination with the imine groups of PANI.[28] In addition, other PANI specific

peaks appeared in the spectrum of the Alg@PANI beads, *i.e.*, C=C stretching vibration of quinoid and benzenoid rings at 1577 and 1309 cm^{-1}, C–N stretching vibrations of secondary amine at 1230 cm^{-1} and C–H stretching of aromatic rings. These peaks are indicate the presence of PANI and are according with literature data.[29,30]

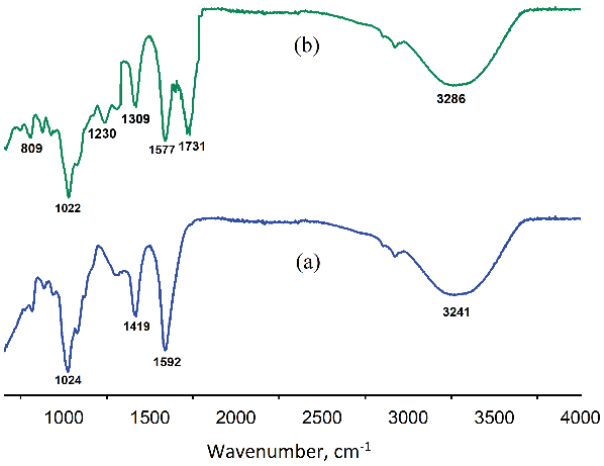

Fig. 2. FTIR spectra of Alg (a) and Alg@PANI (b).

Effect of pH

It is well known that chromium species can exist in different forms,[3] *i.e.*, H_2CrO_4, $HCrO_4^-$, $HCr_2O_7^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}. Whereby, H_2CrO_4 is the main form at pH < 2, while in the pH range 2 to 6, the predominant species are $HCrO_4^-$ and $Cr_2O_7^{2-}$ and CrO_4^{2-} is the main precipitated form of Cr(VI) at pH > 6.

The effect of solution pH for removal of Cr(VI) on Alg@PANI beads was separately investigated in the pH ranges between 1 and 8 (Fig. 3), and results revealed that the adsorption capacity reached the maximum value at pH 2.

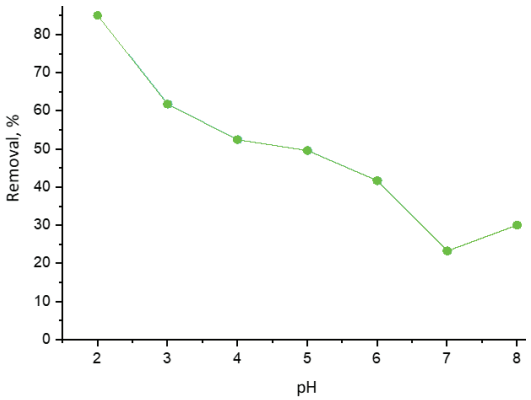

Fig. 3. Effect of the pH on Cr(VI) adsorption onto Alg@PANI beads.

This behavior could be attributed to the attraction between these anionic species of chromium and the positively charged surface of Alg@PANI beads (carboxylate, hydroxyl, and amine groups) at lower solution pH values, *i.e.* at pH values lower than pH_{PZC}.

Central composite design

Relationship between temperature, contact time, initial concentration of Cr(VI) in the solution and adsorbent dosage is indicated in Table II and shows the results of the removal of chromium from the aqueous solution by Alg@PANI beads.

TABLE II. Experimental design factors coded, real values, and predicted removal values by RSM-CCD

Run	Coded value				Real value				Removal, %		
	X_1	X_2	X_3	X_4	T / °C	t / min	C / ppm	Dose, g	Experimental	Predicted by RSM-CCD	Difference
1	–1	–1	–1	–1	25	30	25	0.015	76.2	74.1	2.1
2	+1	–1	–1	–1	45	30	25	0.015	80.3	82.8	–2.5
3	–1	+1	–1	–1	25	60	25	0.015	81.6	82.6	–1.0
4	+1	+1	–1	–1	45	60	25	0.015	85.3	84.1	1.2
5	–1	–1	+1	–1	25	30	65	0.015	71.9	71.5	0.4
6	+1	–1	+1	–1	45	30	65	0.015	75.5	75.4	0.1
7	–1	+1	+1	–1	25	60	65	0.015	81.7	80.1	1.6
8	+1	+1	+1	–1	45	60	65	0.015	74.8	76.9	–2.1
9	–1	–1	–1	+1	25	30	25	0.035	85.3	85.3	0.0
10	+1	–1	–1	+1	45	30	25	0.035	94.4	95.8	–1.4
11	–1	+1	–1	+1	25	60	25	0.035	94.7	94.5	0.2
12	+1	+1	–1	+1	45	60	25	0.035	95.4	97.8	–2.4
13	–1	–1	+1	+1	25	30	65	0.035	76.0	76.9	–0.9
14	+1	–1	+1	+1	45	30	65	0.035	81.6	82.6	–1.0
15	–1	+1	+1	+1	25	60	65	0.035	86.7	86.3	0.3
16	+1	+1	+1	+1	45	60	65	0.035	83.1	84.9	–1.8
17	–2	0	0	0	15	45	45	0.025	68.2	70.4	–2.2
18	+2	0	0	0	55	45	45	0.025	77.8	77.7	0.1
19	0	–2	0	0	35	15	45	0.025	80.2	79.4	0.8
20	0	+2	0	0	35	75	45	0.025	99.1	90.0	9.1
21	0	0	–2	0	35	45	5	0.025	98.6	97.6	1.0
22	0	0	+2	0	35	45	85	0.025	82.8	82.0	0.8
23	0	0	0	–2	35	45	45	0.005	74.1	74.8	–0.7
24	0	0	0	+2	35	45	45	0.045	96.6	94.0	2.6
25	0	0	0	0	35	45	45	0.025	98.9	98.6	0.3
26	0	0	0	0	35	45	45	0.025	98.4	98.6	–0.2
27	0	0	0	0	35	45	45	0.025	98.5	98.6	–0.1

The ANOVA analysis for response surface reduced quadratic model, using *P*-value and *F*-value to evaluate the regression coefficients of the model equation is reported in Table III. The model *F*-value of 25.80 indicates the model is sig-

nificant. Furthermore, the value of 111.50 implies the lack of fit of the *F*-value is significant. It has been reported that values of *P* less than 0.05 indicate the model terms are significant. On the other hand, values greater than 0.1 indicate the model terms are not significant.[31] In the present case, the linear coefficients X_1, X_2, X_3 and X_4, their interactions X_1X_2 and X_3X_4 and the quadratic effects X_1^2, X_2^2, X_3^2 and X_4^2 are significant model terms. shown The quadratic model equation for Cr(VI) removal and their corresponding coded values are shown in Eq. (3):

$$\begin{aligned}\text{Removal} = 98.60 + 1.48X_1 + 3.33X_2 - 3.90X_3 + 4.79X_4 - 1.78X_1X_2 - \\ - 1.18X_1X_3 + 0.46X_1X_4 + 0.031X_2X_3 + 0.19X_2X_4 - 1.43X_3X_4 - \\ - 6.72X_1^2 - 2.55X_2^2 - 2.69X_3^2 - 3.63X_4^2\end{aligned} \quad (3)$$

TABLE III. Analysis of variance (ANOVA) for the CCD model

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*P*-value Prob > *F*	Significance
Model	2353.39	14	168.10	25.80	< 0.0001	Significant
X_1	52.51	1	52.51	8.06	0.0149	
X_2	266.00	1	266.00	40.82	< 0.0001	
X_3	364.26	1	364.26	55.90	< 0.0001	
X_4	550.08	1	550.08	84.42	< 0.0001	
X_1X_2	50.77	1	50.77	7.79	0.0163	
X_1X_3	20.33	1	20.33	3.43	0.0889	
X_1X_4	3.33	1	3.33	0.51	0.4883	
X_2X_3	0.016	1	0.016	0.002398	0.9617	
X_2X_4	0.60	1	0.60	0.092	0.7666	
X_3X_4	32.78	1	32.78	5.03	0.0446	
X_1^2	962.13	1	802.24	147.65	< 0.0001	
X_2^2	139.06	1	256.84	21.34	0.0006	
X_3^2	111.94	1	103.94	17.18	0.0014	
X_4^2	280.82	1	268.07	43.10	< 0.0001	
Residual	78.19	12	6.52	–	–	–
Lack of fit	78.05	10	7.81	111.50	0.0089	Significant
Pure error	0.14	2	0.070	–	–	–
Total SS	2431.58	26	–	–	–	–

The thorough awareness of the effect of each factor on the response, as well as their interactions, can be seen in Eq. (3). In the equation, a positive sign denotes a synergistic effect, while a negative sign denotes an antagonistic effect. The comparison of observed and predicted Cr(VI) removal values (Table II) yielded a high correlation coefficient R^2 of 0.8150, which is in good agreement with the adjusted R^2_{adj} value of 0.9303. This is illustrated in Fig. 4, while the plot of the predicted values *vs*. experimental values for the removal percentage of Cr(VI) revealed a good fit, indicating the validity of the regression model.

The relationship between relevant model terms and the three dimensional contours of the optimal response is graphically depicted in Fig. 5. These plots were constructed using fixed and optimum values of other variables for a specific combination of factors.

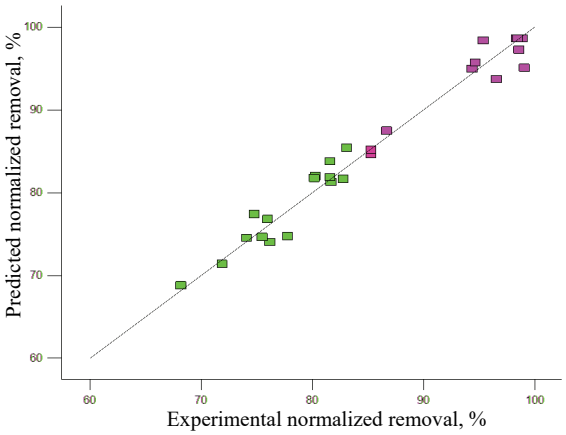

Fig. 4. The experimental data *vs.* the predicted data of normalized removal of Cr(VI).

The interaction of the adsorbent dosage with contact time, temperature and Cr(VI) concentration are presented in Fig. 5a–c, respectively. An increased removal percentage of chromium was observed with increasing adsorbent dosage. This is due to the presence of additional vacant adsorption sites with increasing adsorbent dose, which led to an enhanced caption of metals. At lower amounts of Alg@PANI beads, the removal percentage decreased because of the smaller numbers of active sites.

The 3D curvature of the response surfaces shown in Fig. 5c–e for the Cr(VI) concentration showed changes in the percentage removal as a function of adsorbent dosage and other factors with interaction between them. As can be seen, the removal percentage decreases upon increasing the initial concentration of the Cr(VI) solution. At lower concentrations, the amount of adsorbent used was greater than the amount of metal ions used, and the adsorption sites could easily catch the Cr(VI) ions. On the contrary, at higher concentrations, the decrease in removal percentage was due to a decrease in available adsorption sites, indicating that the entire surface sites on Alg@PANI beads was saturated using a certain Cr(VI) concentration. Furthermore, higher Cr(VI) concentrations may cause more offensive forces within the solid particles and solute molecules, causing a reduction in the removal of metal ions.

The effect of contact time on the removal percentage and the interaction of diffrent factors with it are illustrated in Figs. 5a, d and f. The results showed that the maximum rate of removal percentage was achieved after 30 min. However,

extending the contact time had no affect on the rate of Cr(VI) adsorption because all the active adsorption sites had been saturated after 30 min of contact.

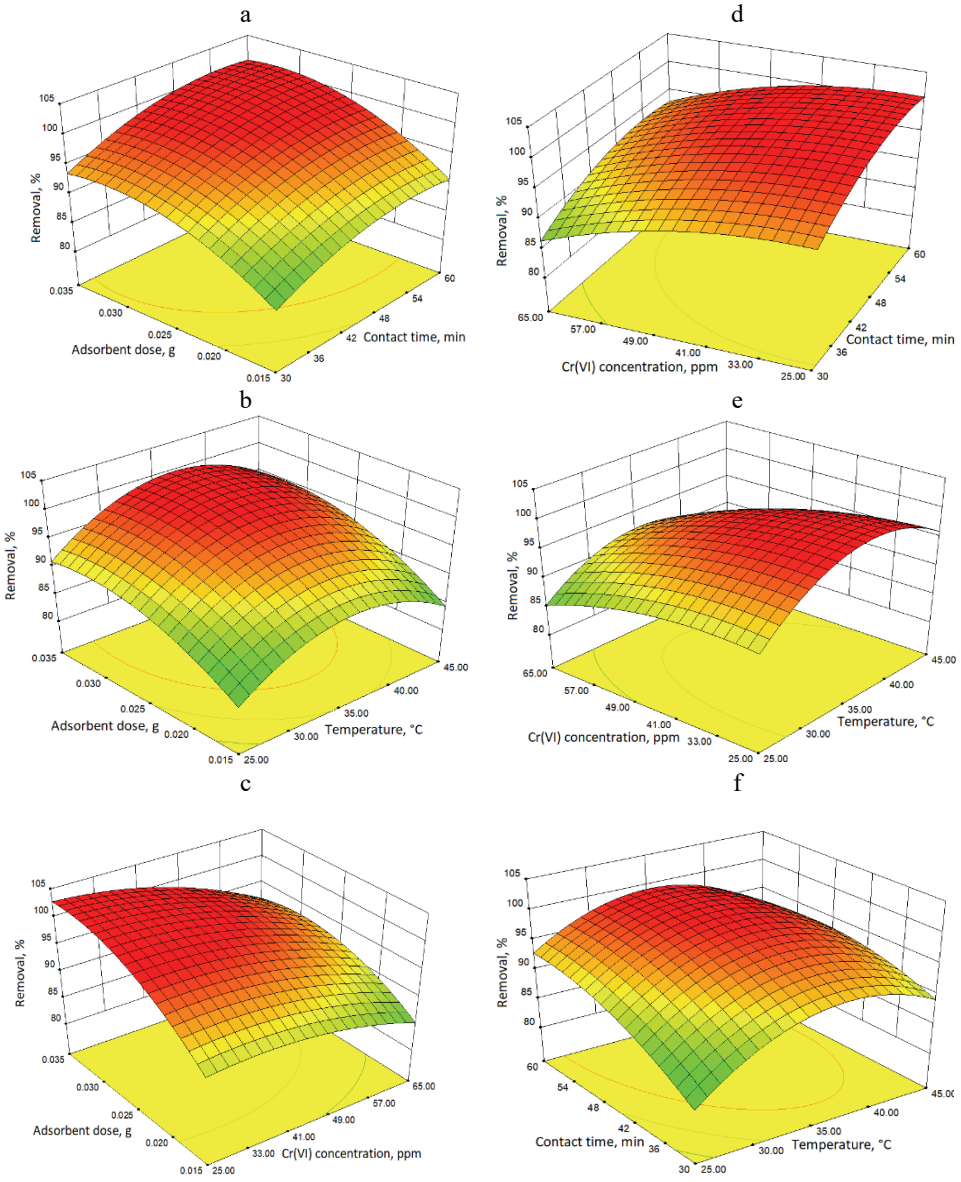

Fig. 5. Response surfaces for the CCD: a) adsorbent dosage–contact time; b) adsorbent dosage–temperature; c) adsorbent dosage–Cr(VI) concentration; d) Cr(VI) concentration–contact time; e) Cr(VI) concentration–temperature; f) contact time–temperature.

The response surfaces plots for the effect of temperature and its interaction with adsorbent dosage, Cr(VI) concentration and contact time are shown in Fig. 5b, e and f, respectively. With rising temperature, the percentage removal of Cr(VI) increased which indicates the endothermic nature of the adsorption process.

In this study, design expert software was used to determine the optimal parameter values for the adsorption of Cr(VI) by Alg@PANI beads. In addition, the optimal conditions for total adsorption (Fig. 6) were obtained at optimum conditions set as: adsorbent dose = 0.027 g, pH 2, time = 45 min, temperature = = 38 °C and Cr(VI) concentration = 29.24 ppm. The optimal operating conditions were determined in order to lead to higher yields, with the minimum adsorption mass and maximum concentration.[24] Then, the optimum removal of 88.62 % was achieved with a minimum dose = 0.018 g, contact time = 47 min, temperature = = 31.4 °C and Cr(VI) concentration = 65 ppm.

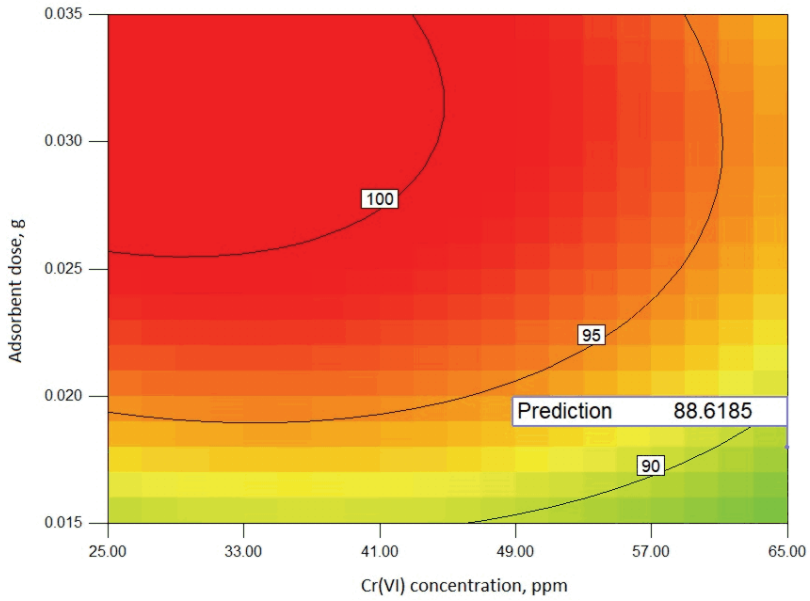

Fig. 6. Optimum removal efficiency (contour plot obtained from RSM optimization).

CONCLUSIONS

The experimental design methodology was used in this study to optimize Cr(VI) removal by Alg@PANI beads. Temperature, contact time, Cr(VI) concentrations, and adsorbent dose were evaluated as operational variables for the optimization of the treatment process and statistical analysis of model response interaction were studied. As a result, the majority of the impacts are substantial, and the *P*-value of the model was less than 0.05 (*P*-value = 0.0089), indicating that composite central design of the model is appropriate for the explored systems.

The total efficiency of Cr(VI) removal was reached under the optimum conditions, *i.e*., adsorbent dose of 0.027 g, pH 2, time 45 min, temperature 38 °C and Cr(VI) initial concentration of 29.24 ppm. Moreover, using the minimum amount of adsorbent (0.018 g) and a high concentration of Cr(VI) (65 ppm), the adsorption rate was 88.62 %. Finally, this strategy of modelization offers a cost-effective way to obtain specific information in a short period with a small number of experiments.

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ИЗВОД

ЕКСПЕРИМЕНТАЛНИ ДИЗАЈН ЗА ИСИТИВАЊЕ АДСОРПЦИЈЕ ХРОМА(VI) НА АЛГИНАТ/ПОЛИАНИЛИН ПЕРЛАМА

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У овом раду су јефтине, натријумом-алгинатне перле са превлаком од полинаилина (Alg@PANI перле) добијене једноставном методом унакрсног повезивања и примењене за адсорпцију Cr(VI) из водених раствора. Испитиван је утицај неколико параметара, укључујући температуру, време контакта, концентрацију Cr(VI) и дозу адсорбента, и оптимизован користећи дизајн централног композита (CCD) применом методологије површине одговора (RSM). Анализа варијансе (ANOVA) квадратног модела и анализираног модела показала је да су модели статистички значајни, са малом *P*-вредношћу (< 0,0001) и већом вредношћу корелационог коефицијента (R^2 = 0,93). Оптимални параметри за тоталну адсорпцију су били: доза адсорбента = 0,027 g, pH 2, време контакта = 45 min, температура = 38 °C, и концентрација Cr(VI) = 29,24 ppm. Резултати овог истраживања указују да припремљене Alg@PANI перле могу бити коришћене за успешно уклањање Cr(VI) јона из водених раствора.

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