

Optimization of hexavalent chromium removal from aqueous solution using acid-modified granular activated carbon as adsorbent through response surface methodology

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Abstract—Response surface methodology (RSM) was applied to evaluate the effect of the main operational variables, including initial pH, initial chromium ion concentration, bulk density of GAC and time on the removal of hexavalent chromium Cr(VI) from contaminated groundwater by permeable reactive barriers (PRB) with acid-modified granular activated carbon (GAC) as an adsorbent material. The removal rates of Cr(VI) under different values of these parameters were investigated and results indicated high adsorption capacity at low pH and low initial metal ion concentration of Cr(VI), but the bulk density of GAC slightly influenced the process efficiency. According to the ANOVA (analysis of variance) results, the model presents high R^2 values of 94.35% for Cr(VI) removal efficiency, which indicates that the accuracy of the polynomial models was good. Also, quadratic regression models with estimated coefficients were developed to describe the pollutant removals.

Keywords: Permeable Reactive Barriers, Polluted Groundwater, Hexavalent Chromium, Granular Activated Carbon, Response Surface Methodology

INTRODUCTION

The presence of heavy metals in aquatic ecosystems has received widespread attention due to their potential human health risks and harmful effect on living organisms.

Chromium is one of the most toxic and important heavy metals commonly found in wastewater and generally exists in water with two stable oxidation states: hexavalent Cr(VI) and trivalent Cr(III) [1]. Hexavalent chromium Cr(VI) is toxic; in contrast, trivalent chromium Cr(III) is much less toxic and immobile and can be used as a nutriment for humans and animals [2]. Also, at trace level, the trivalent form of chromium is considered as an essential nutrient [3], whereas the hexavalent form is about 500 times more toxic [4]. Cr(VI) is also highly mobile in soil and aquatic systems, and also is a strong oxidant capable of being adsorbed by skin [5]; it is toxic to plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage [6]. The maximum levels permitted for Cr(III) in wastewater are 5 mg/L and for Cr(VI) as 0.05 mg/L [7]. Chromium, which is on the top priority list of toxic pollutants as defined by the US Environmental Protection Agency (EPA), is present in electro-plating, metallurgy, and chemical engineering wastewater as Cr(VI) in the form of oxidized species, such as chromates (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and bichromate (HCrO_4^-), depending on pH and Cr(VI) concentration [8].

Permeable reactive barriers (PRB) are one of the most promis-

ing passive treatment technologies, due to their effectiveness regarding various contaminants, and low cost compared to other in situ technologies. The principle of the treatment of contaminated groundwater with the PRB method lies in digging out a trench (perpendicularly to the groundwater flow), which is afterwards filled with suitable reactive media as shown in Fig. 1; the contaminated groundwater flows through the reactive media where treatment processes occur [9].

Several investigators have used different adsorbents for the removal of Cr(VI) ions such as activated carbon [10], chitosan [11], biosorbents [12], and polymeric compounds [13].

Activated carbon (AC), either in powder or in granular form, can offer a relatively efficient technology for removal of Cr(VI). The ion exchange mechanism is dominant for the removal of Cr(VI) at low concentrations [14]. The ion exchange mechanism of activated carbon is due to the presence of surface functional groups, such as carboxylic, hydroxyl, and lactones, which have a high affinity for the metal ion adsorption. The nature and amount of these acidic functional groups depend on the nature of the carbon and the history of its formation. It is commonly known that oxidation of activated carbon can significantly enhance the adsorption capacity of Cr(VI) on AC [15]. Oxidative treatment in a reaction with a strong acid such as HCl can increase the total amount of acidic functional groups on AC, leading to increased adsorption capacity for Cr(VI) [15-17].

Conventional and classical methods of studying a process in which factors involved are maintained at an unspecified constant level do not depict the combined effect of all those factors. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable [20]. These limitations

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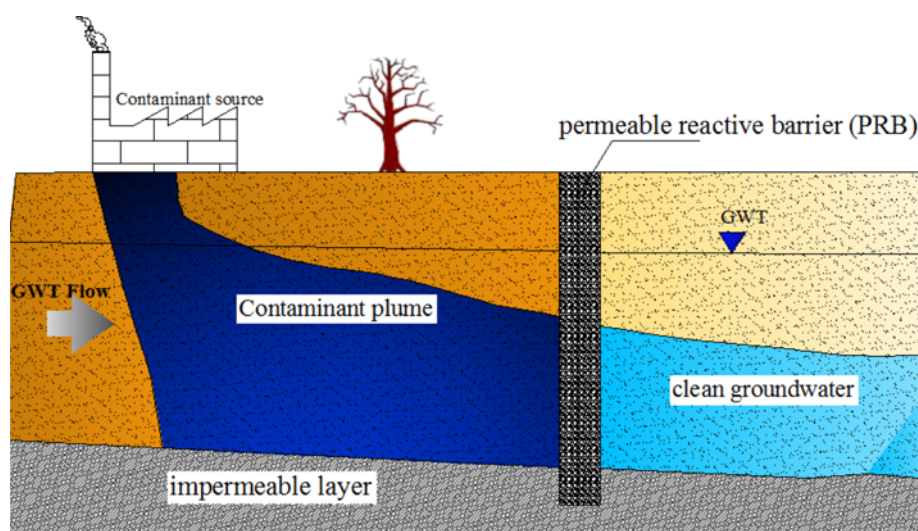


Fig. 1. Schematic of a permeable reactive barrier (PRB).

of a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) [21]. RSM is a combination of mathematical and statistical techniques for designing experiments, building models, evaluating the effects of several factors and searching the optimum conditions for specified responses [22].

A number of researches have been made in recent years for sorption of Cr(VI) from aqueous solution involving batch type experiments to investigate the effects of some parameters on adsorption process and the evaluation of optimum conditions [18,19].

The aim of this study is to optimize and model Cr(VI) removal from aqueous solution by acid-modified (GAC), which was used as adsorbent for the removal of Cr(VI) from contaminated groundwater using a continuous setup for the simulation of permeable reactive barriers (PRB). The adsorption capacity of acid-modified (GAC) was evaluated for the effective removal of Cr(VI) from the solution by varying initial pH, initial Cr(VI) concentration, bulk density of GAC and time. It is worthwhile to consider that no or few published researches are available in which the bench-scaled laboratory setup has been used. The relationship between the response and four quantitative variables is determined by a second-order polynomial model for a setup experiment according to central composite design (CCD).

MATERIALS AND METHODS

1. Materials and Characterizations

Distilled water was used in all preparations. Potassium dichromate ($K_2Cr_2O_7$) and deionized water were used to prepare synthetic chromium; the solution pH was adjusted to the desired value by adding H_2SO_4 or NaOH.

GAC is widely considered as a suitable adsorbent for on-site or off-site treatment of polluted groundwater. Carbon presents a high adsorption capacity for many organic and inorganic contaminants for its high surface area, due to the micro-porous structure, and a high degree of surface reactivity caused by surface oxide groups

Table 1. The main characteristics of media

Material	Washed sand	Granular activated carbon
Characteristics	<ul style="list-style-type: none"> $D_{50}=0.65\pm 2$ mm $\rho=2.62$ (g/cm³) Porosity $n=0.35$ 	<ul style="list-style-type: none"> $D_{50}=1.85\pm 2$ mm $\rho=1.43$ (g/cm³) in water Porosity $n=0.4$

and inorganic impurities [23], using GAC has a grain-size distribution of 0.3–2.36 mm, and it was selected for this study. Its properties are shown in Table 1, with the density ($r_s=1.43$ g/cm³).

Uncontaminated sand with non-uniform size (mean diameter $d_{50}=0.65\pm 2$ mm) was used as porous medium; the properties of sand are shown in Table 1, with the bulk density ($r_b=1.703$ g/cm³), particle density ($r_s=2.62$ g/cm³), average porosity of sand ($n=0.35$), and average saturated hydraulic conductivity ($K=0.52$ cm/s). In the control runs with no addition of activated carbons, no removal of Cr(VI) was found over the time period of typical experiments.

2. Methods

2-1. Preparation of the Solution of Chromium

A stock solution of 1.0 g/L was prepared by dissolving 2.8298 g of potassium dichromate ($K_2Cr_2O_7$) in 1.0 L of double-distilled water, which was further diluted for the preparation of test solutions. Several solutions with different initial concentrations of potassium dichromate were prepared. The required pH was adjusted by drop addition of 0.4 N H_2SO_4 , depending on the acidity of the sample.

2-2. Activated Carbon Preparation

The activated samples were washed with distilled water to remove surface impurities and dried at 100 °C, then poured into 0.1 mol/L HCl (50 g of raw GAC was added into 250 mL of acid solution) and stirred for 1 h to eliminate the residual alkali [24]. Then, the samples were washed with hot distilled water until the pH of the filtrating solution was neutral (pH~6.5) and to eliminate activating agent residues and other inorganic species formed during the process [25]. The produced GAC was then dried at 105 °C overnight.

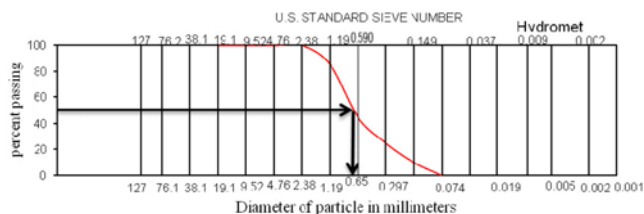


Fig. 2. Grain size distribution of sand.

2-3. Preparation of the Uncontaminated Sand

Sand was soaked in water for 24 h to dissolve the lumps and then washed on the No 200 sieve until the wash water coming through the sieve was clear, and then dried at 105 °C; the sand used in this study was poorly graded sand. The grain size distribution is shown in Fig. 2.

2-4. Apparatus and Instrumentation

The pH values of the solutions were measured by Hanna pH meter using a combined glass electrode; the pH meter was standardized using buffer solutions of pH values: 4, 7 and 10.

The metal ion Cr(VI) was determined by UV-vis spectrophotometer (UV-1601 Shimadzu) using the diphenylcarbazide method.

EXPERIMENTAL SET-UP

The continuous adsorption studies for removing Cr(VI) by GAC were conducted in a bench-scaled laboratory set-up as shown in Fig. 3, schematically. Uncontaminated sand with non-uniform size (mean diameter $d_{50}=0.65\pm 2$ mm) was used as a porous medium. The length of the porous medium before and after the PRB position was 10 and 35 cm, respectively. There are several empty compartments separated by movable and perforated walls, one of them before the position of PRB and other after it for monitoring pH, concentration of Cr(VI) in these reservoirs during the experimental periods.

The laboratory model was made of Plexiglas; a main reservoir was provided to supply influent water with certain Cr(VI) concentration into porous medium. A reservoir in up-stream and one in down-stream of porous medium were considered to create a steady-state condition of flow through sand. A certain pore velocity through sand was made with regulation of water level in these reservoirs.

EXPERIMENTAL PROCEDURE

The simulated polluted groundwater with a Cr(VI) was prepared from a stock solution using deionized water and the range of solution pH (1-8), with the initial Cr(VI) concentration varying from 5 to 33 mg/L. This is then supplied to the entrance compartment, and then collected at an exit compartment at the appropriate interval where it is analyzed for Cr(VI) concentration and PH solution. The temperature during the operation was 25 ± 5 °C.

The percentage of Cr(VI) adsorption from aqueous solution was computed by the following equation:

$$\text{Removal (R (\%))} = [(C_0 - C)/C_0] \times 100$$

where C_0 and C are the initial and final Cr(VI) concentrations, respectively.

The effects of several parameters, such as initial concentration, initial pH, bulk density of activated carbon in PRB and time on the adsorption of Cr(VI) ions onto activated carbon were studied.

EXPERIMENTAL DESIGN AND DATA ANALYSIS

In this study, the central composite design (CCD), which is a widely used form of RSM, was selected for the optimization of the effective parameters with minimum number of experiments, and also used to determine the regression model equations. This method is suitable for fitting a quadratic surface and it helps as well to analyze the interaction between parameters [26]. Four factors, including initial metal ion concentration, initial pH, bulk density of activated carbon in PRB and time with five-levels, were employed for response surface modeling in the adsorption process. A total of 31 experiments were carried out according to a 24 full factorial CCD, consisting of 16 factorial experiments, 8 axial experiments on the axis at a distance of $\pm\alpha$ from the center, and 7 replicates at the center of the experimental domain to obtain orthogonally and is variance by rotation properties.

The value of α depends on the number of points in the factorial portion of the design, which is given in Eq. (1)

$$\alpha = (N_f)^{1/4} \quad (1)$$

where N_f is the number of points in the cube portion of the design

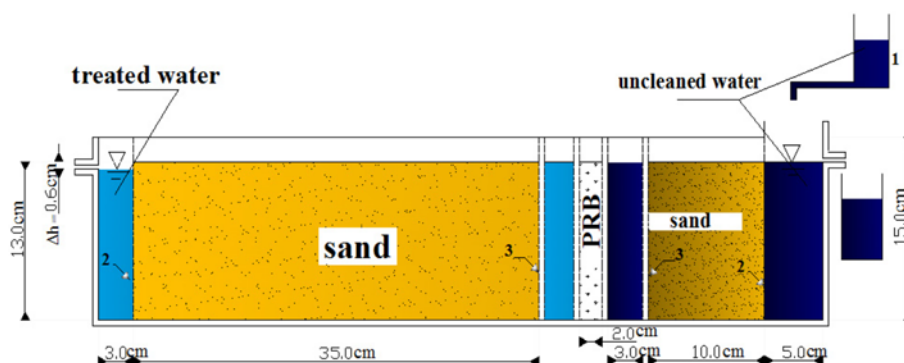


Fig. 3. Schematic laboratory setup.

1. Water tank 2. Plastic mesh 3. Perforated walls

($N_f=2^k$, k is the number of factors) [27]. Therefore, α is equal to $(2^4)^{1/4}=2$ according to Eq. (1).

For statistical calculations, the levels for the four main variables X_i (X_1 (initial pH), X_2 (initial concentration), X_3 (bulk density of activated carbon in PRB), X_4 (time)) were coded as X_i according to Eq. (2):

$$X_i = (X_i - X_0) / \Delta X \quad (2)$$

where X_0 is the value of the X_i at the center point and ΔX presents the step change. The equally spaced values of X_i designated as $-\alpha$, -1 , 0 , 1 , α . Variables, experimental ranges and levels are presented in Table 2.

Experimental data were analyzed using Minitab v 16, and fitted to a second-order polynomial model, and then regression coefficients were obtained. Two-dimensional contour plots, three-dimensional curves of the response surfaces and residual plots were developed using the same program. The generalized second-order polynomial model used in the response (Y) surface analysis is:

Table 2. Experimental range and levels of the test variables

Variables, units	Factors	Range and levels (coded)				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Initial pH	X_1	1	2.75	4.5	6.25	8
Bulk density (g/cm ³)	X_2	0.44	0.48	0.52	0.56	0.6
Initial concentration (mg/L)	X_3	5	12	19	26	33
Time	X_4	0	22.5	45	67.5	90

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (3)$$

where Y is the percentage of Cr(VI) removal, b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients and X_i , X_j are the coded values of the variables. A system with several variables was conducted primarily by some of the main effects and low-order interactions. It can be assumed that the higher order interactions are small relative to the

Table 3. RSM design and its observed and predicted values

Run order	pH	Bulk density of GAC (g/cm ³)	Initial concentration (mg/L)	Time (h)	Cr(VI) removal efficiency (R (%))	
					Observed	Predicted
1	6.25	0.48	12	22.5	90.600	92.718
2	6.25	0.56	26	67.5	42.700	46.081
3	2.75	0.48	12	67.5	99.100	97.479
4	6.25	0.56	12	67.5	68.800	71.801
5	2.75	0.48	12	22.5	99.600	97.058
6	2.75	0.48	26	22.5	99.500	98.563
7	2.75	0.56	12	22.5	99.900	93.896
8	4.50	0.52	19	45.0	87.100	86.804
9	4.50	0.52	19	45.0	86.500	86.804
10	6.25	0.48	26	67.5	30.700	38.768
11	4.50	0.52	19	90.0	75.200	72.257
12	6.25	0.56	26	22.5	67.200	70.885
13	4.50	0.52	5	45.0	90.000	94.007
14	2.75	0.48	26	67.5	97.100	95.558
15	4.50	0.44	19	45.0	85.500	82.874
16	4.50	0.52	19	45.0	86.700	86.804
17	6.25	0.56	12	22.5	90.800	93.181
18	6.25	0.48	26	22.5	62.000	65.947
19	4.50	0.52	19	45.0	87.400	86.804
20	4.50	0.52	19	45.0	86.400	86.804
21	4.50	0.52	19	45.0	86.632	86.804
22	8.00	0.52	19	45.0	63.800	51.629
23	2.75	0.56	26	67.5	99.300	99.246
24	4.50	0.60	19	45.0	87.300	87.024
25	2.75	0.56	12	67.5	99.800	96.692
26	6.25	0.48	12	67.5	68.300	68.964
27	4.50	0.52	19	45.0	86.895	86.804
28	1.00	0.52	19	45.0	99.867	109.135
29	2.75	0.56	26	22.5	99.700	99.875
30	4.50	0.52	33	45.0	76.700	69.790
31	4.50	0.52	19	0.0	96.600	96.640

low-order interactions. Therefore, only two way interactions have been considered in the present work. The statistical significance of the models was justified through analysis of variance (ANOVA) for polynomial model with 89.40% confidence level, and residual plots were used to examine the goodness of models fit. The quality of the fit polynomial model was also expressed by the coefficient of determination R^2 . Finally, optimum values of factors were obtained by determining a target in dedicated RSM program (response optimizer).

RESULTS AND DISCUSSION

1. Development of Regression Model Equation and Validation of the Model

We used a four-factorial and a five-level central composite experimental design (± 1 for the factorial points, 0 for the center points, and $\pm \alpha$ for the axial points), with two replicas at the center point leading to a total number of thirty one experiments for response surface modeling. The variables (independent factors) were the initial pH (X_1), bulk density of GAC (g/cm^3) (X_2), initial concentration (mg/L) (X_3) and time (X_4). Cr(VI) removal efficiency (Y) was considered as the dependent factor (response).

Table 4. Estimated regression coefficients for Cr(VI) removal efficiency (%) in coded units

Term	Coef	SE coef	t	P
Constant	86.804	2.108	41.183	0.000
X_1	-14.376	1.138	-12.630	0.000
X_2	1.038	1.138	0.911	0.376
X_3	-6.054	1.138	-5.319	0.000
X_4	-6.096	1.138	-5.355	0.000
X_1^2	-1.605	1.043	-1.539	0.143
X_2^2	-0.464	1.043	-0.445	0.662
X_3^2	-1.226	1.043	-1.176	0.257
X_4^2	-0.589	1.043	-0.565	0.580
X_1X_2	0.906	1.394	0.650	0.525
X_1X_3	-7.069	1.394	-5.070	0.000
X_1X_4	-6.044	1.394	-4.335	0.001
X_2X_3	1.119	1.394	0.802	0.434
X_2X_4	0.594	1.394	0.426	0.676
X_3X_4	-0.856	1.394	-0.614	0.548

Table 5. Analysis of variance (ANOVA) for Cr(VI) removal efficiency (%)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	8301.76	8301.76	592.98	19.07	0.000
Linear	4	6757.68	6757.68	1689.42	54.32	0.000
Square	4	109.64	109.64	27.41	0.88	0.497
Interaction	6	1434.44	1434.44	239.07	7.69	0.001
Residual error	16	497.57	497.57	31.10		
Lack-of-fit	10	496.83	496.83	49.68	398.98	0.000
Pure error	6	0.75	0.75	0.12		
Total	30	8799.34				

Note: $R^2=94.35\%$, $R^2(\text{adj})=89.40\%$

To study the combined effect of these factors, experiments were performed for different combinations of the parameters using statistically designed experiments. The experimental design matrix together with the maximum observed and predicted percentage removal are listed in Table 3. The coefficients of the response function (Eq. (3)), the t and P values for percentage removal are also presented in Table 4. The second-order polynomial equations for Cr(VI) removal efficiency in terms of coded factors are given by Eq. (4):

$$Y = 86.804 - 14.376X_1 + 1.038X_2 - 6.054X_3 - 6.096X_4 - 1.605X_1^2 - 0.464X_2^2 - 1.226X_3^2 - 0.589X_4^2 + 0.906X_1X_2 - 7.069X_1X_3 - 6.044X_1X_4 + 1.119X_2X_3 + 0.594X_2X_4 - 0.857X_3X_4 \quad (4)$$

It was observed in Table 4 that the coefficients for initial pH (X_1), initial concentration (X_3), and time (X_4) ($P=0$ for all) confirm the high significance of these factors. However, bulk density of GAC (X_2), square terms and all interaction terms except X_1X_3 and X_1X_4 (P values of 0.00 and 0.001, respectively) were insignificant to the Cr(VI) removal efficiency.

For a model to be reliable, the response should be predicted with a reasonable accuracy by the model when compared with the experimental data. Fig. 4 compares experimental Cr(VI) removal efficiency (%) with the predicted values obtained from the model. The figure indicates good agreement between the experimental and predicted values of Cr(VI) removal efficiency.

The adequacy of the model was further evaluated through ANOVA

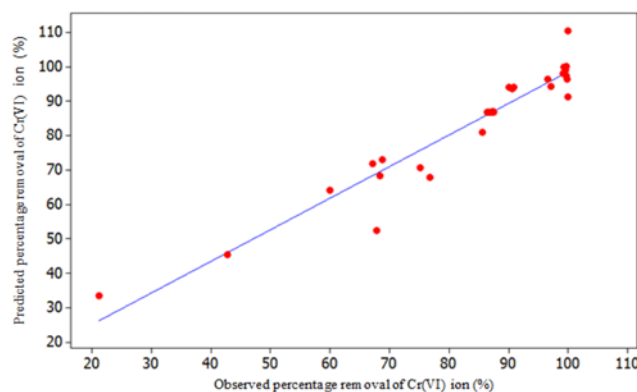


Fig. 4. Parity plot for the observed and predicted value of Cr(VI) removal (%).

(analysis of variance). The results of the ANOVA for Cr(VI) removal are shown in Table 5; in this case, the P-value of 0.000 ($P < 0.05$) for regression model equation implies that the second-order polynomial model fitted to the experimental results well. Additionally, a high R^2 value, close to 1, is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. Also, a reasonable agreement with adjusted R^2 is necessary [28].

According to the ANOVA results (Table 5), the value of $R^2 = 94.35\%$, $R^2(\text{adj}) = 89.40\%$ confirms the accuracy of the model.

The adequacy of the model was also evaluated by the residuals (difference between the observed and the predicted response value). Normal probability plots are a suitable graphical method for judging the normality of the residuals [29]. The plots of residuals versus fitted values and the normal probability plots for Cr(VI) removal efficiency are illustrated in Fig. 5.

As seen in Fig. 5, the normality assumption was relatively satisfied as the points in the plot form a fairly straight line. For a model to be reliable, no series of increasing or decreasing points, patterns such as increasing residuals with increasing fits and a predominance

of positive or negative residuals should be found. All of the plots in Fig. 5 revealed that model is adequate to describe the Cr(VI) removal by RSM.

2. Response Surface and Counter Plotting for Evaluation of Operational Parameters

Generally, the most important parameters that affect the efficiency of Cr(VI) removal using GAC are initial pH, initial metal ions concentration (mg/L), bulk density of GAC (g/cm^3) and time. Main effects plot of each parameter for Cr(VI) removal using GAC are shown in Fig. 6.

As shown in Fig. 6(a), pH is one of the most important parameters controlling uptake of Cr(VI) from aqueous solutions. The effect pH on the adsorption of Cr(VI) by GAC is attributed to interactions between ions in solution and the complex formed on the adsorbent surface. It appears that the Cr(VI) removal efficiency was sensitive even to small alterations of the initial pH.

The results in Fig. 6(b) indicate that the bulk density of GAC slightly influenced the process efficiency, for which a small increase in the percentage removal of Cr(VI) ions was shown with increase

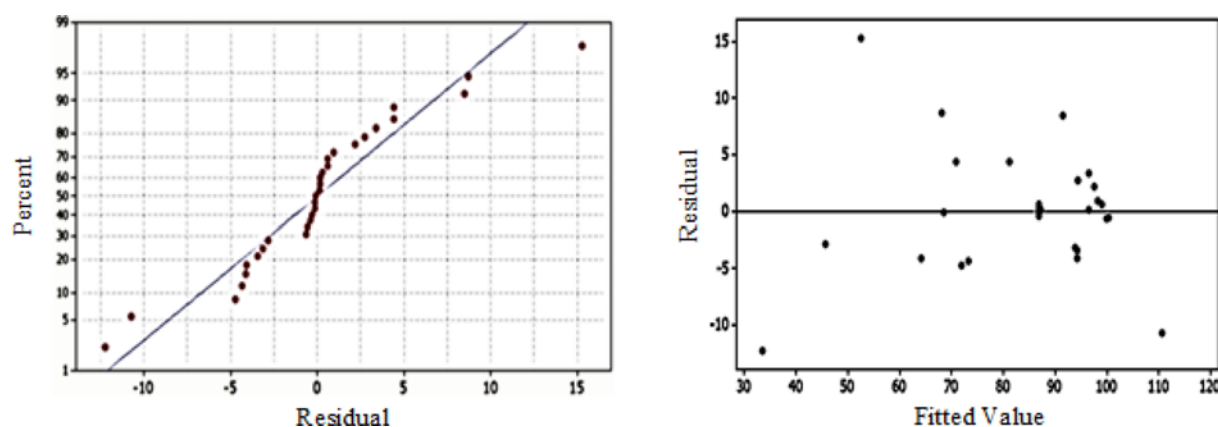


Fig. 5. Normal probability plot and residual versus fit plot for Cr(VI) removal efficiency.

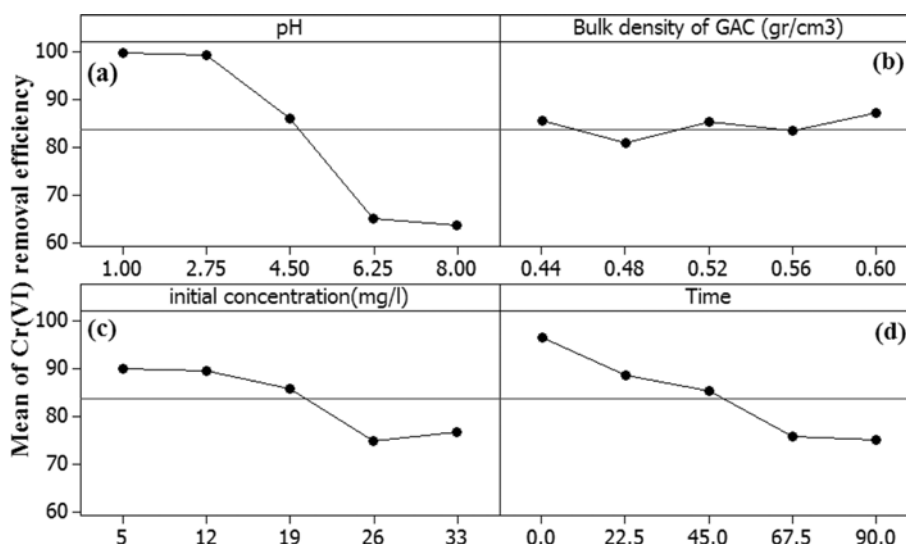


Fig. 6. Main effects plot of (a) initial pH, (b) bulk density of (GAC), (c) initial Cr(VI) concentration and (d) time on Cr(VI) removal efficiency using (GAC).

of bulk density of reactive carbon. Increase in percentage removal of Cr(VI) might be attributed to the decrease of contaminated solution flow rate through reactive media, for which the residence time distribution of influent concentration to the adsorbent is greater in lower flow rate. This in turn leads to the metal ions to interact easily with the sites [30].

Furthermore, from Fig. 6(c), as initial sorbate concentration increased, Cr(VI) removal efficiency decreased, because at lower con-

centration there are sufficient active sites that the sorbate can easily occupy.

Also from Fig. 6(d), the adsorption process proceeds in two stages. High adsorption rates are observed within the first time interval, whereas a decrease in the Cr(VI) adsorption occurs in the second one. The initial rapid adsorption is due to the availability of the positively charged functional groups of the GAC adsorbent; also initially, the adsorption sites are open and the metal ions interact

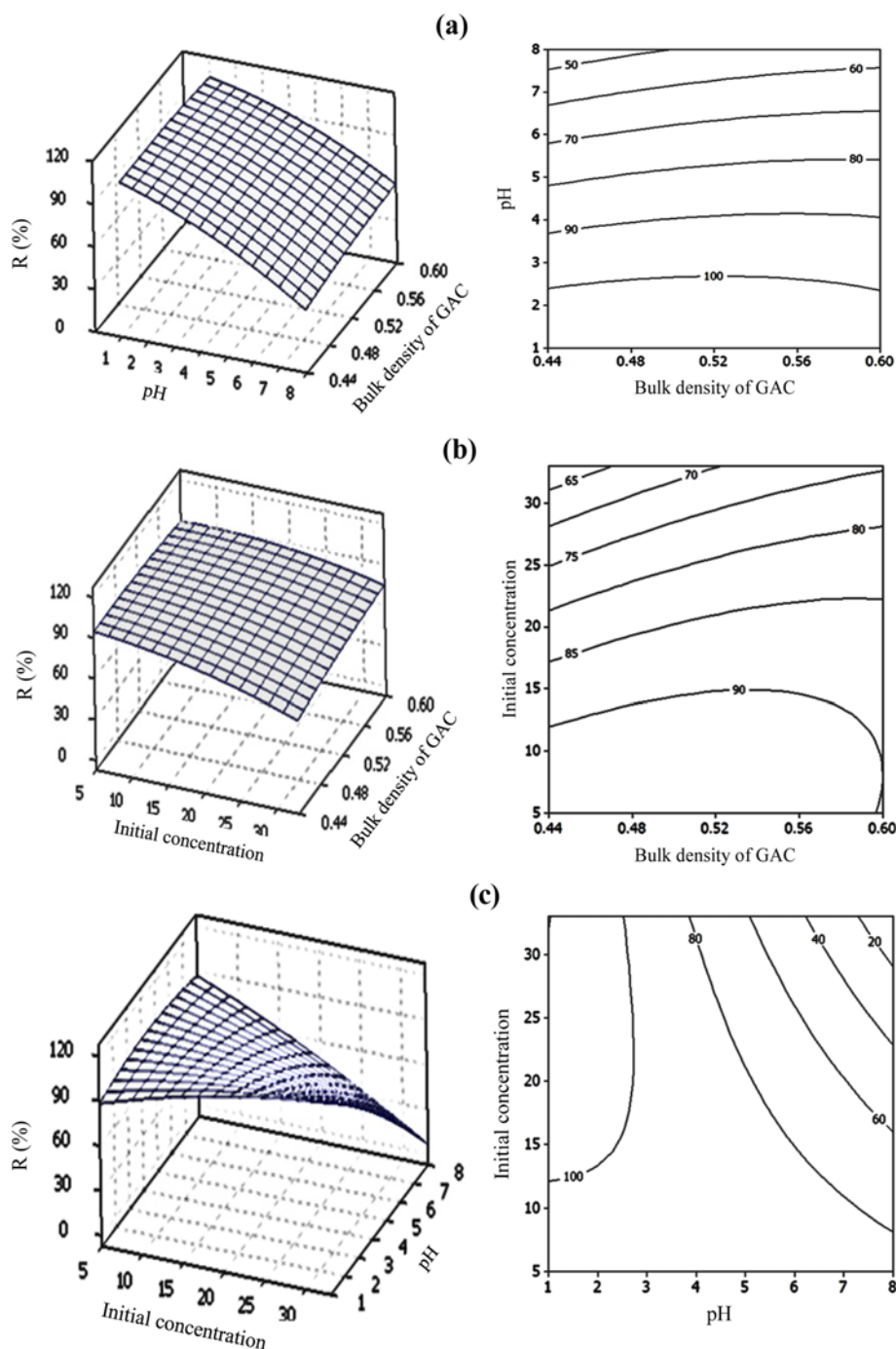


Fig. 7. Surface plots and corresponding contour plots for Cr(VI) removal as a function of: (a) Initial pH and bulk density of GAC at initial Cr(VI) concentration of 19 mg/L; (b) bulk density of GAC and initial Cr(VI) concentration at pH 4.5; (c) initial pH and initial Cr(VI) concentration at bulk density of GAC of 0.52 g/cm³.

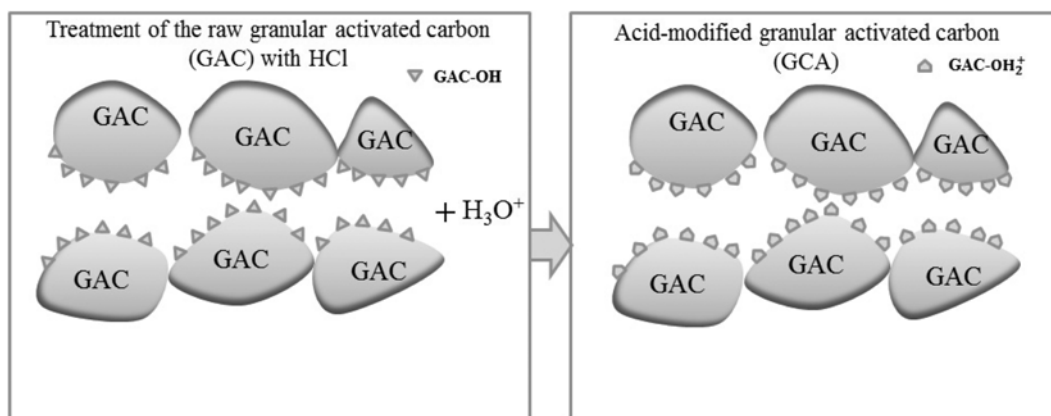
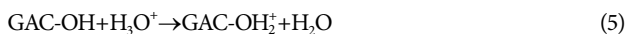


Fig. 8. Schematic diagram illustrating the process of treatment of the raw granular activated carbon (GAC) with HCl.

easily with the sites and hence a higher rate of adsorption is observed. The subsequent slower adsorption can be attributed to changes in GAC surface reactivity, due to continuous diminishing of the number of positively charged functional groups throughout the adsorption experiment. Also, sufficient active sites are occupied by sorbate, so active sorption sites are not sufficiently available for the sorbate to occupy; in addition, the electrostatic repulsion between negative charges of adsorbate ions results in the decrease of the adsorption percentage [31].

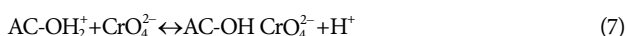
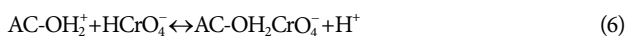
For a better explanation of the independent variables and their interactive effects on the remove Cr(VI), 3D plots and corresponding contour plots are represented in Fig. 7.

As it can be seen from Fig. 7(a) and (c), it appears that percentage removal efficiency of Cr(VI) ions onto adsorbents increased significantly with decreasing pH value. This observation can lead to the conclusion that the adsorbent has a pH dependent charged surface; as the hydronium ions concentration increases, the majority of adsorbent surface will be positively charged, and the amount of acidic functional groups increase, according to Eq. (5). Therefore, the raw (GAC) is treated with a strong acid such as HCl as shown in Fig. 8, schematically:



That means that at low pH, the sorbent is positively charged because of protonation, whereas the sorbate like dichromate or bichromate ions exists mostly as an anion, leading to an electrostatic attraction between the sorbent and the sorbate. This results in increased adsorption at low pH as shown in Fig. 9. Adsorption of Cr(VI) at pH values greater than 6.0 decreases, which may be due to the competition of both anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent in as much as OH^- predominates. Moreover, when the pH of the solution increases, the sorbent undergoes deprotonation, and the adsorption capacity decreases as shown in Fig. 10.

Adsorption of HCrO_4^- and CrO_4^{2-} on GAC may be explained by the following reactions [32,33]:



The favorable effect at low pH can be attributed to the neutralization

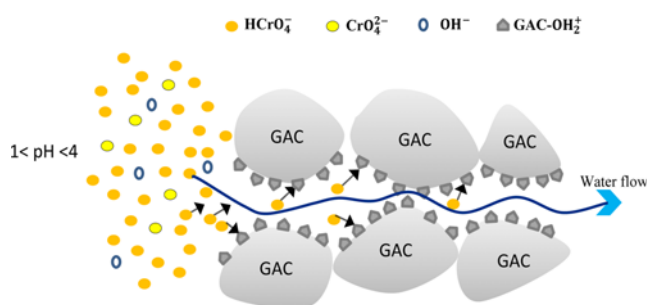


Fig. 9. Schematic diagram summarizing processes responsible for Cr(VI) removal by acid-modified granular activated carbon ($1 < \text{pH} < 4$).

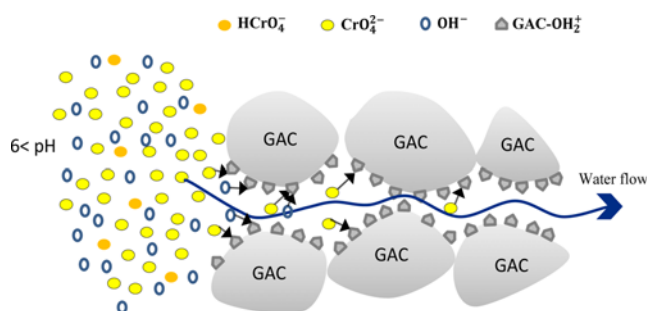


Fig. 10. Schematic diagram summarizing processes responsible for Cr(VI) removal by acid-modified granular activated carbon ($6 < \text{pH}$).

of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of the hydrogen chromate ion (HCrO_4^-) and its subsequent adsorption, because (HCrO_4^-) is the dominant anionic form of Cr(VI) between pH 1.0 and 4.0.

According to Fig. 7(a), at lower initial pH values, the effect of bulk density of GAC on the removal efficiency is not significant. And at high initial pH values, removal efficiency increases with increase bulk density of GAC.

At constant value of the initial Cr(VI) concentration (19 mg/L), when the bulk density of GAC increases and the initial pH of Cr(VI)'s solution decreases, the Cr(VI) removal efficiency increases (Fig.

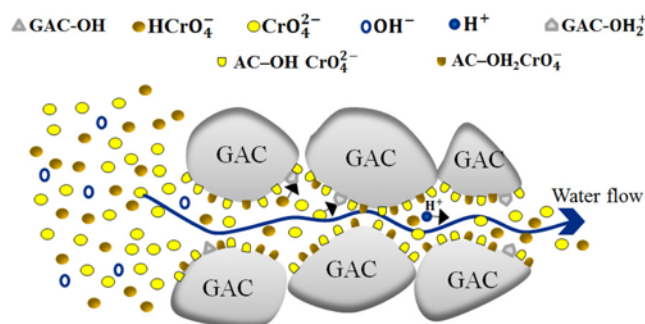
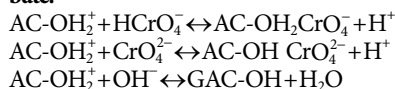


Fig. 11. Schematic representations of the reaction mechanisms for the removal of Cr(VI) by acid-modified granular activated carbon showing the active sites which are occupied by sorbate.



7(a)).

As shown in Fig. 7(b), the bulk density of GAC slightly influenced the process efficiency. However, at a fixed bulk density of GAC, the percentage of Cr(VI) removal decreased with increasing the initial concentration (Fig. 7(b)), because at higher concentrations, active sorption sites are not sufficiently available for the sorbate to occupy. Hence, Cr(VI) ions are not completely adsorbed in solution due to the saturation of adsorption sites. In addition, the electrostatic repulsion between negative charges of adsorbate ions results in the decrease of the adsorption rate [31].

According to the observed results (Fig. 7(c)), at high initial pH values, the percentage of Cr(VI) removal decreased with increasing the initial concentration, and at low initial pH values, initial concentration slightly influenced the process efficiency.

3. Cr(VI) Removal Optimization

The main objective of the optimization is to determine the optimum values of variables for Cr(VI) removal efficiency by GAC using the model obtained from the experimental data.

In optimization, the desired aim in terms of Cr(VI) removal efficiency was defined as a target to achieve 90% removal efficiency. The optimum amounts for variables were obtained with consideration of 7, 12 mg/L, 0.48 mg/cm³ and 22.7 h, as starting values for initial pH, initial concentration, bulk density of GAC and time, respectively. To prevent addition of acid/base into solutions, initial pH of 7 was considered as a starting value in the optimization process. The optimization results of the process variables are shown in

Table 6. Optimum values for Cr(VI) removal from aqueous solution

Variables	Unit	Optimum values (X_i)
Initial pH	-	7
Bulk density of GAC	g/cm ³	0.48
Initial concentration	mg/L	12
Time	h	22.7
Cr(VI) removal efficiency (predicted)	%	90
Cr(VI) removal efficiency (experimental)	%	88.3

Table 6.

Finally, the optimum values were further validated by actually carrying out the experiment at the optimal condition. The experimental checking in these optimum conditions (88.3% of Cr(VI) removal efficiency) confirms good agreements with RSM results.

CONCLUSIONS

Response surface methodology was employed as an experimental design tool to explain the effect of main operational parameters and their interactions on the removal of Cr(VI) ions from aqueous solutions as a major response. The effects of four main parameters in the removal process including initial pH, initial sorbate concentration, bulk density of GAC and time were evaluated. The results showed that the Cr(VI) ion removal efficiency was severely affected by all the mentioned variables except bulk density of GAC. Additionally, some of the interactions like X_1X_3 , X_1X_4 for Cr(VI) ion removal efficiency influenced the process performance. According to the ANOVA results, the model presents high R^2 values of 94.35% for Cr(VI) ion removal efficiency, which indicates that the accuracy of the polynomial models was good. In the optimization process, the desired removal efficiency was defined as target to achieve 90% removal efficiency. The optimum values of 7, 0.48 g/cm³, 12 mg/L and 22.7 h, as starting values for initial pH, bulk density of GAC, initial concentration and time were obtained, respectively.

An experiment was carried out in optimum conditions and the results showed a close agreement between the model and experimental results (88.3% of Cr(VI) removal efficiency from the experiment compared to 90% from the model). Therefore, RSM is a powerful tool for evaluation and optimization of adsorption of hexavalent chromium Cr(VI) ions using GAC as an adsorbent in PRBs.

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REFERENCES

1. C. H. Weng, Y. T. Lin, T. Y. Lin and C. M. Kao, *J. Hazard. Mater.*, **149**, 292 (2007).
2. G. Rojas, J. Silva, J. A. Flores, A. Rodriguez and L. Maldonado, *Sep. Purif. Technol.*, **44**, 31 (2005).
3. B. J. Alloway, 2nd Ed. London, Blackie Academic and Professional, 368 (1995).
4. Z. Kowalski, *J. Hazard. Mater.*, **37**, 137 (1994).
5. I. B. Singh and D. R. Singh, *Environ. Technol.*, **23**, 85 (2002).
6. M. Cieslak-Golonka, *Polyhedron*, **15**, 3667 (1995).
7. F. N. Acar and E. Malkoc, *Bioresour. Technol.*, **94**, 13 (2004).
8. S. Babel and T. A. Kurniawan, *Chemosphere*, **54**, 951 (2004).
9. U.S. Army Corps of Engineers (USACE). *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents*. Washington, DC., U.S. Department of the Army, CEMP DG 1110-345-117 (1997).

10. A. A. Attia, S. A. Khedr and S. A. Elkholy, *Brazilian J. Chem. Eng.*, **27**, 183 (2010).
11. S. Chatterjee, D. S. Lee, M. W. Lee and S. H. Woo, *Bioresour. Technol.*, **100**, 3862 (2009).
12. E. Thirunavukkarasu and K. Palanivelu, *Indian J. Biotechnol.*, **6**, 359 (2007).
13. M. Yiitulu and M. Arslan, *Polym. Bulletin*, **55**, 259 (2005).
14. S. X. Liu, X. Chen, X. Y. Chen, Z. F. Liu and H. L. Wang, *J. Hazard. Mater.*, **141**, 315 (2007).
15. S. J. Park and Y. S. Jang, *J. Colloid Interface Sci.*, **249**, 458 (2002).
16. S. Babel and T. A. Kurniawan, *Chemosphere*, **54**, 951 (2004).
17. G. Park, J. K. Lee and S. K. Ryu, *Carbon Sci.*, **3**, 219 (2002).
18. K. Selvi, S. Pattabhi and K. Kadirvelu, *Bioresour. Technol.*, **80**, 87 (2001).
19. D. Satapathy, G. S. Natarajanb and S. J. Patil, *J. Chinese Chem. Soc.*, **52**, 35 (2005).
20. A. Aleboyeh, N. Daneshvar and M. B. Kasiri, *Chem. Eng. Process.*, **47**, 827 (2008).
21. Z. Zaroual, H. Chaair, A. H. Essadki, K. El Ass and M. Azzi, *Chem. Eng. J.*, **148**, 488 (2009).
22. S. Zodi, O. Potier, F. Lapique and J. P. Leclerc, *Desalination*, **261**, 186 (2010).
23. M. Arora, I. Snape and G. Stevens, *Cold Regions Sci. Technol.*, **66**, 12 (2011).
24. W. Feng-Chin, T. Ru-Ling and J. Ruey-Shin, *Sep. Purif. Technol.*, **47**, 10 (2005).
25. Z. Hu and M. P. Srinivasan, *Micropor. Mesopor. Mater.*, **27**, 11 (1999).
26. B. H. Hameed, I. A. W. Tan and A. L. Ahmad, *J. Hazard. Mater.*, **164**, 1316 (2009).
27. S. Sadri Moghaddam, M. R. Alavi Moghaddam and M. Arami, *J. Hazard. Mater.*, **175**, 651 (2010).
28. M. Y. Nordin, V. C. Venkatesh, S. Sharif, S. Elting and A. Abdullah, *J. Mater. Process. Technol.*, **145**, 46 (2004).
29. A. R. Khataee, M. Zarei and L. Morad Khannejhad, *Desalination*, **258**, 112 (2010).
30. R. Han, Y. Wang, W. Yu, W. Zou, J. Shi and H. Liu, *J. Hazard. Mater.*, **141**, 713 (2007).
31. N. K. Hamadi, X. D. Chen, M. M. Farid and M. G. Q. Lu, *Chem. Eng. J.*, **84**, 95 (2001).
32. H. Valdes, M. Sanchez and J. Rivera, *Langmuir*, **18**, 2111 (2002).
33. S. J. Park, B. J. Park and S. K. Ryu, *Carbon*, **37**, 1223 (1999).