Taguchi design for optimization of the removal of chromium(VI) by impregnated bentonite (K+) from aqueous solution

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ABSTRACT

Adsorption of very toxic Cr(VI) was studied by liquid–solid extraction by natural bentonite impregnated with potassium hydroxide (KOH). The optimization procedure was performed using L9 Taguchi design. The combined effect of the two process parameters are the initial Cr(VI) concentrations in aqueous solutions (10^{-4} – 8×10^{-4} M) and the amount of bentonite (K+) (0.1–0.4 g). The optimum conditions for adsorption are the initial Cr(VI) concentrations 10^{-4} (M) (level 1) and the amount of bentonite (K+) 0.4 (g) (level 3). Analysis of the signal-to-noise ratio was used to determine important parameters that help in the adsorption process. Several kinetics and isotherms were evaluated using non-linear models such as pseudo-first-order and pseudo-second-order; Langmuir and Freundlich models. Langmuir isotherm and pseudo-second-order model explained the removal mechanism among the models evaluated, which infers that the removal followed chemisorption. The results show that the removal of chromium is mainly affected by the initial Cr(VI) concentrations, followed by the adsorbent amount 7.41 mg/g removal of Cr(VI) under optimal conditions with the removal of 10^{-4} M of chromium at pH 5.02 with 0.4 g bentonite (K+) for 30 min and 300 rpm. The optimization procedure performed using the L9 Taguchi design provides access to industrial-scale Cr(VI) rejection processing.

Keywords: Liquid–solid extraction; Bentonite (K+); Cr(VI); Taguchi design; L9 array

1. Introduction

Water pollution is a major global problem which requires methods for planning and executing solutions [1]. Increase in industrial wastewater discharge of heavy metals in the environment has been the result of rapid industrial intensification.This is a critical issue due to the high levels of heavy metals; the concentration is toxic and can lead to hazards on the human body environment and human health [2]. Effluent wood preservation, electroplating, dyes, leather, cement, photography, and many other industries contain chromium as electroplating, leather tanning and textile industries [3,4]. Therefore, finding an efficient and cost-effective adsorbent is persuasive elimination of heavy metals from the environment. Chromium is an important metallic element, known for high and low-temperature corrosion and oxidation-resistance properties [5]. Cr(VI) exists as an anion such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} which are highly mobile in subterranean environments. These chromium anions are bioaccumulative because of their high fluidity and oxidation potential across biological cell membranes. All hexavalent chromium compounds are toxic (due to their oxidizing power) as well as carcinogenic, especially if airborne

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and inhaled where they cause lung cancer. Problematic exposure is known to occur among workers who handle chromate-containing products and those who grind and/or weld stainless steel. Workers who are exposed to hexavalent chromium are at increased risk of developing lung cancer, asthma, or damage to the nasal epithelia and skin [6]. Therefore, the chromium content in the discharge wastewater should be reduced. Its concentration in industrial wastewater ranges from 0.5 to 270 mg/L. Therefore, it is important to remove Cr(VI) from industrial wastewater before releasing them into the aquatic environment [7,8].

Until now, various methods have been reported to remove hexavalent chromium from aqueous solutions industrial waste and polluted water such as: membrane-based technologies [8–10], liquid phase extraction [11–14], solid-phase extraction [15–18], ion exchange [19], non-dispersive [20,21].

Many researchers have studied pollutants adsorption using natural and modified clays, which are good adsorbents, mainly due to their morphology, high surface area and their ion-exchange process [22].

The objective of our work focuses on the removal of very toxic Cr(VI) by solid-phase extraction by impregnated bentonite by potassium hydroxide (KOH). Compared to other sorbents (resins, biosorbents, etc.), the bentonite available in our state is economically the least expensive. A review of relevant literature reveals that there are no studies of the basic activation of this clay, therefore, this aspect has been studied and detailed in this paper. The influence of time of the contact, pH of initial concentration of Cr(VI) on the extraction were studied. The influence of function variables such as chromium concentration (10^{-4} – 8×10^{-4}) M and bentonite mass (0.1–0.4) g by Taguchi design L9 (3^2) on the extraction yield was investigated.

2. Materials and methods

2.1. Materials

The natural bentonite used in this study was obtained from deposits in the area of Maghnia, Algeria and supplied by ENOF Ltd., (Algeria). The chemical composition determined by X-ray fluorescence was found to be as follows: 62.4% SiO_2, 17.33% Al_2O_3, 1.2% Fe_2O_3, 3.56% MgO, 0.8% K_2O, 0.81% CaO, 0.2% TiO_2, 0.33% Na_2O and 13.0% loss on ignition at 900°C [23,24].

The mineralogical analysis, achieved through quantitative measurements by DRX showed that the native crude clay mineral contains preponderantly Montmorillonite, in a proportion exceeding 85 wt.%. The clay composition also includes quartz (10%), cristobalite (4.0%) and beidellite (less than 1%) [25,26].

Potassium chromate (K_2CrO_4) is used to prepare chromate solution (from Sigma-Aldrich). Potassium hydroxide (KOH) was supplied by Sigma-Aldrich. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to control the pH of Cr(VI) solutions (from Sigma-Aldrich).

2.2. Impregnation process

Naturel bentonite was washed with distilled water for 2 h. It was then filtered and dried at 60°C for 24 h. In a bi-column flask equipped with a refrigerant. 15 g of natural bentonite was impregnated in 150 mL of KOH at 3 N. The mixture was heated at 100°C in a water bath for 4 h and then we have filtered the mixture and dried the bentonite in the oven at 105°C for 4 h. Further, the dried bentonite was crushed using a jaw crusher and ground to pass through a 75 μm sieve (200 mesh ASTM) using a porcelain mill.

2.3. Batch adsorption experiments

The agitating contact time varied from 1 to 150 min. An amount of bentonite (K+) (0.4 g) was augmented in 20 mL Cr(VI) solution at different concentrations between 10^{-4} and 8×10^{-4} M. The study of the effect of pH on the extraction of Cr(VI) by bentonite impregnated with KOH was carried out using a Cr(VI) solution at a concentration of 8×10^{-4} M brought into contact for 30 min, at room temperature, with 0.4 g of adsorbent at a pH varying between 2.09 and 5.25. The pH of the solution was fixed by adding HCl or NaOH, with stirring at 300 rpm.

A solution of 2 mL of H_2SO_4 at 16 M was added to 2 mL of Cr(VI) ions sample before and after extraction. The UV-Vis absorbance of solutions of Cr(VI) was measured using SP-UV 200S UV-Visible spectrophotometer at 446 nm. pH meter Adwa was used for pH measurements. The removal efficiency (%) of Cr(VI) and the capacity of adsorption (q_e, mg/g) were calculated by:

$$\text{Removal}\left(\%\right) = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q_e\left(\text{mg/g}\right) = \frac{\left(C_i - C_e\right)V}{m} \tag{2}$$

where C_i and C_e are the initial concentration and equilibrium concentration of Cr(VI) respectively, V is the volume (L); and m is mass (g) of treated bentonite.

2.4. Taguchi experimental design

The Taguchi method of experimental design and multiple regression analysis are some of the important tools used for robust design to produce high-quality products efficiently [27]. Taguchi method is based on testing the sensitivity of a set of response variables to a set of control parameters (or independent variables) by considering experiments in an "orthogonal array" to attain the optimum setting of the control parameters. Orthogonal matrices provide a good set of well-rounded but minimal experiments. Log functions of the desired production. Known as the signal-to-noise ratios (S/N). Serve as the objective function for optimization [28].

The quality of the product can be quantified depending on the noise factor and the signal factor. It can also be enhanced by maximizing the signal/noise ratio for the product concerned. The calculation of the signal-to-noise ratio can be carried out by Taguchi design of the experimental design module. The S/N ratio for any design operation can be worked out resulting in the design value available in the experimental design module [29].

The signal-to-noise ratio may also be considered a reversal of the variance and maximization of the signal-to-noise ratio to reduce process variation from unintended changes in the adjacent environment (also called uncontrollable factor or noise factor) [30]. The obtained experimental data are processed with the "Larger is Better" (LB) quality characteristic (as given by Eq. (3)) to determine the optimum conditions and identify the significance of individual parameters in Cr removal.

$$\frac{S}{N_{LB}} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{R_i^2}\right] \tag{3}$$

where "larger-the-better" is expressed by the subscript LB,' n is the number of repetitions under the same experimental conditions and R_i expresses the measurement performance [31].

The controllable factors considered in this study are the amount of bentonite (K+) and initial Cr(VI) concentration. They are denoted by A and B respectively. The minimal, medium and maximal levels of each variable in called forms 1, 2, and 3, respectively are presented in Table 1. These two experimental factors with their levels were considered in the statistical optimization of Cr(VI) extraction by bentonite (K+) using Taguchi's methodology with an orthogonal array L9(3²). The required experiments number was given by the L9 matrix design (Table 1).

3. Results and discussion

3.1. Adsorption studies

3.1.1. Effect of contact time on extraction

Effect of contact time for removal of Cr(VI) onto bentonite (K+) was studied in the time interval of 1 to 150 min at initial metal ion concentration constant (8×10^{-4} M). From Fig. 1, the removal capacity increased very rapidly in the early stages of time and then became slow until equilibrium was reached. This is due to the disponibility of sites on our adsorbant. After gradual utilization of these sites, the adsorbant became less efficient.

In view of the curves obtained from Fig. 1, it can be seen that the removal yield of Cr(VI) has a maximum of 41.84% corresponding to 5.62 mg/g after 30 min of stirring time. Then, equilibrium time is 30 min. These results are more better than the adsorption behavior of Cr(VI) removal from water using granular ferric hydroxide adsorbents [5].

Table 1
Design summary

Parameter level	Level	Experimental factors with their units	
		A (g)	B (M)
Minimal	1	0.10	0.0001
Medium	2	0.25	0.0005
Maximal	3	0.40	0.0008

A: Amount of bentonite (K+)
B: Initial concentration of Cr(VI)

3.1.2. Effect of initial pH of solution

The chromate ions may exist in the aqueous phase in different ionic forms ($HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, $Cr_2O_7^{2-}$). Any of these forms will predominate other forms of chromium depending on the total amount of chromium and pH of the aqueous phase. CrO_4^{2-} anion prevails in basic or slightly acidic solution while $Cr_2O_7^{2-}$ anions dominate in acidic aqueous solution. Moreover, $Cr_2O_7^{2-}$ convert into $HCrO_4^-$ anions in acidic aqueous solution at a total Cr(VI) concentration lower than $(1.26–1.74) \times 10^{-2}$ M [32]. Therefore, in this study, the chromate ion will be in the form of $HCrO_4^-$ ($10^{-4} – 8 \times 10^{-4}$ M) as shown in Fig. 3.

To explain the observed behavior of Cr(VI) removal with varying pH, it is necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction, and ion exchange which are responsible for adsorption on sorbent surfaces.

For bentonite clay, the aluminum, calcium, magnesium, iron, and silicium oxides are present in varying amounts in bentonite. The hydroxylated oxide surfaces develop a charge on the surface in an aqueous solution through amphoteric dissociation. The surface is expected to be positively charged at low pH and consequently will favor the adsorption of anionic form as $HCrO_4^-$ [34].

According to Fig. 2, it appears that the extraction yield and the sorption capacity of Cr(VI) are maximum at pH 5.02 but after this value there is a strong reduction in the yield and Cr(VI) sorption capacity of 62.07%–34.48% and 7.41–5.62 mg/g. These results are in excellent agreement with the results of other researchers [2].

3.1.3. Effect of initial concentration of Cr(VI)

The results presented in Fig. 4 shows that the initial concentration of Cr(VI), for a better removal yield, corresponds to a value equal to 2×10^{-4} M.

3.1.4. Removal kinetics

The pseudo-first-order and pseudo-second-order models were applied to test the experimental data in order to evaluate the removal process. The pseudo-first-order model
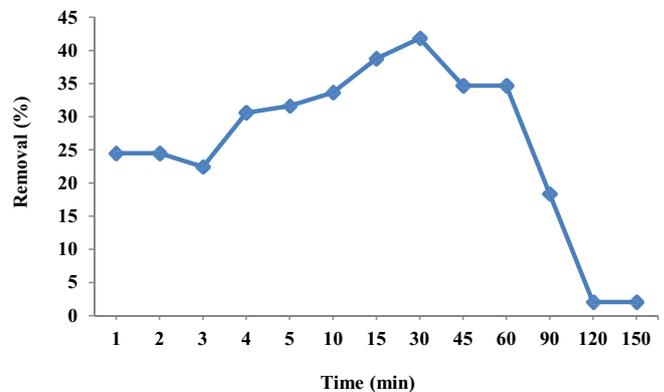
Fig. 1. Effect of contact time for the removal of Cr(VI) onto bentonite (K+); V = 20 mL; m = 0.4 g; [Cr(VI)] = 8×10^{-4} M; pH = 5.02; stirring = 300 rpm.
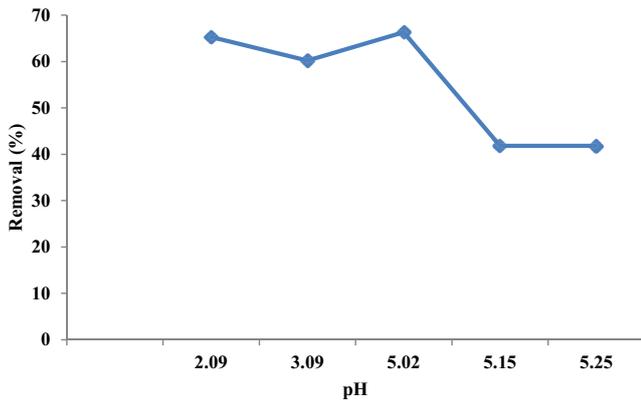
Fig. 2. Effect of pH for the removal of Cr(VI) onto bentonite (K$^+$); V = 20 mL; m = 0.4 g; [Cr(VI)] = 8 × 10^{-4} M; time of the contact = 30 min; stirring = 300 rpm.
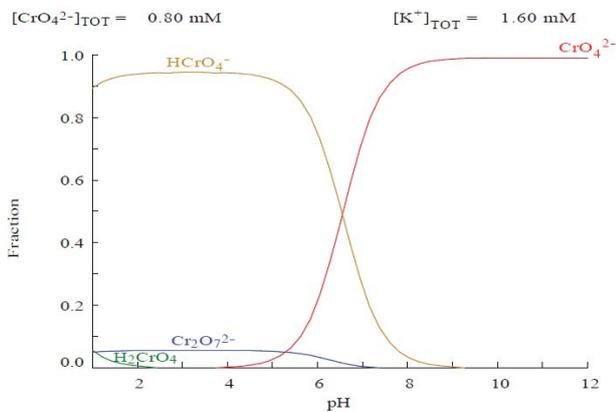
Fig. 3. Distribution diagrams of Cr(VI) in sulfate media using Medusa and Hydra programs [33]; [Cr(VI)] = 8 × 10–4 M.
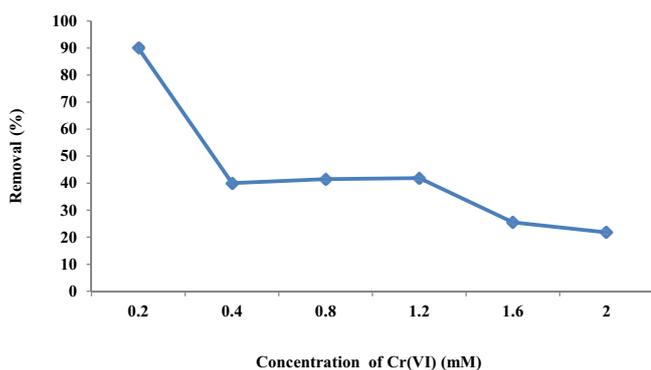
Fig. 4. Effect of initial concentration of Cr(VI) for the removal of Cr(VI) onto bentonite (K$^+$); V = 20 mL; m = 0.4 g; pH = 5.02; time of the contact = 30 min; stirring = 300 rpm.

assumed that the rate of change of solute uptake over time is directly proportional to the difference in saturation concentration and the amount of solute uptake over time.

The pseudo-second-order is used to investigate the behavior of the entire adsorption process [19]. The

Table 2
Parameters of pseudo-first-order and pseudo-second-order kinetics models

Pseudo-first-order			Pseudo-second-order		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg·min)	R^2
0.514	0.122	0.918	0.981	0.666	0.983

non-linear equations of the two models pseudo-first-order and pseudo-second-order are as follows respectively:

$$q_t = q_e\left(1 - \exp\left(-k_1 t\right)\right) \tag{4}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5}$$

where q_t is the amount of adsorbate adsorbed per gram of adsorbent (mmol/g) at time t, k_1 is the pseudo-first-order rate constant (min^{-1}), t is the shaking time (min) and k_2 is pseudo-second-order rate constant (g/mmol·min).

The removal kinetics involved during Cr(VI) adsorption onto impregnated bentonite was investigated using pseudo-first-order and pseudo-second-order. Table 2 lists the kinetic constants. However, the pseudo-second-order model thoroughly describes the adsorption kinetics with a high correlation coefficient, indicating that chromium(VI) recovery by bentonite (K$^+$) follows the chemisorption (Fig. 5).

3.1.5. Isotherm models

Two known isotherm models namely: the Langmuir and Freundlich models are used in this study to describe the removal process of Cr(VI) onto bentonite (K$^+$).

The Langmuir model assumes one pollutant molecule/ion will only occupy one active site on the homogeneous adsorbent surface [35]. The non-linear Langmuir model equation is as follows:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{6}$$

where q_m is the maximum monolayer coverage capacity (mg/g), k_L is the Langmuir isotherm constant (L/mg) and C_e is the concentration of Cr(VI) at equilibrium (mg/L).

The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surfaces which caused by the presence of different functional groups on the surface and interaction between adsorbent–adsorbate [36]. The non-linear Freundlich isotherm model equation is expressed as follows:

$$q_e = K_f C^{\frac{1}{n}} \tag{7}$$

where K_f ((mg/g)(L/mg)$^{1/n}$) is the adsorption capacity of the adsorbent and n is the Freundlich constant, gives

indication of how favorable the adsorption process (adsorption intensity) is or surface heterogeneity.

The different isotherm constants for adsorption of Cr(VI) onto bentonite (K$^+$) are given in Fig. 6 and the Table 3. Higher R^2 value for Langmuir as compared with Freundlich model indicated the homogeneous adsorbent surface.

3.2. Statistical optimization of Cr(VI)

Taguchi's DOE methodology is established by Gen'ichi Taguchi for industrial purposes that develop the quality of manufactured goods, and it has been extended to the engineering in the recovery of metal ions and organic pollutants from the wastewater. Taguchi's experimental technique presents many advantages; it reduces the cost and improves the quality of the studied process and it provides robust design solutions.

Table 4 shows the effects of the 9 experiments concerning the removal of Cr(VI) by bentonite (K$^+$). The removal means is the mean of two repeated experiments. It determines the S/N ratio by Eq. (3). The results show that the Cr(VI) removal means ranged from 27.77% to 89.79% according to the combination of the controllable factors.

3.3. Response table for signal-to-noise ratios and for mean

This statistical method studies the main and interaction effects of process based on the quantitative information that can be collected from a few experimental trials, given by the orthogonal arrays (fractional design). Thus, a numerous factors can be simultaneously optimized. The output of the orthogonal array is optimized by the analysis of mean (ANOM) in function of the signal-to-noise ratio (S/N) of the process responses, which reduces the process variability and makes the difference over the conventional statistical techniques. Taguchi's method allows the identification

of the optimal levels of factors that have more influence on the process by using the analysis of variance (ANOVA) as statistical tool. It included seven steps that are listed in the order such as factors targeting and response(s) choice, orthogonal array design selection (OAD), experiments realization in accordance to OAD, signal-to-noise ratio (S/N), analysis of variance (ANOVA), optimum conditions determination and test validation.

The response table for the S/N ratio (Table 5) and the response table for standard deviations contain a row for the mean S/N ratio for each factor level Delta and Rank (Table 6). The table contains a column for each factor. Delta is the difference between the maximum and minimum mean response (S/N or standard deviation) for the factor. The Rank is the rank of each Delta, where Rank 1 is the largest Delta.

In results, we want to maximize the S/N ratio and the response for the mean.

Concentration of Cr(VI) (Delta = 7.03. Rank = 1) has the largest effect on the S/N ratio. Followed by amount of bentonite (K$^+$) (Delta 0.31. Rank = 2).

Concentration of Cr(VI) (Delta = 42.17. Rank = 1) also has the largest effect on the mean, followed by amount of bentonite (K$^+$) (Delta = 5.37. Rank = 2).

3.4. Main effects plot

Main effects plots show how each factor affects the response characteristic (S/N ratio and means). The main effect exists when different levels of a factor affect the characteristic differently. By comparing the slopes of the lines, we can compare the relative magnitude of the factor effects.

From these results, the main effects plot for the S/N ratio (Fig. 7) and means (Fig. 8) indicates that the concentration of Cr(VI) has the largest effect on the signal-to-noise ratio. On mean, experimental runs with [Cr(VI)] 3 had much higher signal-to-noise ratios than experimental runs with [Cr(VI)] 2 and [Cr(VI)] 1.

The amount of bentonite (K$^+$) had a small effect or no effect on the signal-to-noise ratio.

3.5. Interaction plot

The interaction plots show interactions between the two factors. If the lines are parallel to each other, then there is no interaction between the two factors. If the lines are not parallel to each other, then there is an interaction between the two factors.

For the S/N ratios and means given in Figs. 9 and 10, the lines are not parallel. Amount of bentonite (K$^+$) 3 has a

Table 3
Isotherm parameters for adsorption of Cr(VI) onto bentonite (K$^+$)

	Langmuir			Freundlich		
q_m (mg/g)	k_L (L/mg)	R^2	n	K_f ((mg/g)(L/mg)$^{1/n}$)		R^2
4.44	3.08	0.945	0.7	0.106		0.928

Table 4
Removal of Cr(VI) and S/N ratios

Run	A (g)	B (mM)	E_1	E_2	$\bar{E}$ (%)	S/N ratio
1	0.10	0.1	65.20	65.22	65.21	36.2863
2	0.10	0.5	41.23	39.31	40.27	32.0996
3	0.10	0.8	49.42	41.37	45.39	33.1392
4	0.25	0.1	73.21	73.91	73.56	37.3328
5	0.25	0.5	41.66	26.38	34.02	30.6347
6	0.25	0.8	42.52	45.97	44.24	32.9163
7	0.40	0.1	91.41	88.17	89.79	39.0646
8	0.40	0.5	27.76	27.78	27.77	28.8715
9	0.40	0.8	51.72	47.12	49.42	33.8781

Table 5
Response table for S/N

Level	A (g)	B (M)
1	33.84	33.31
2	33.63	30.54
3	33.94	37.56
Delta	0.31	7.03
Rank	2	1
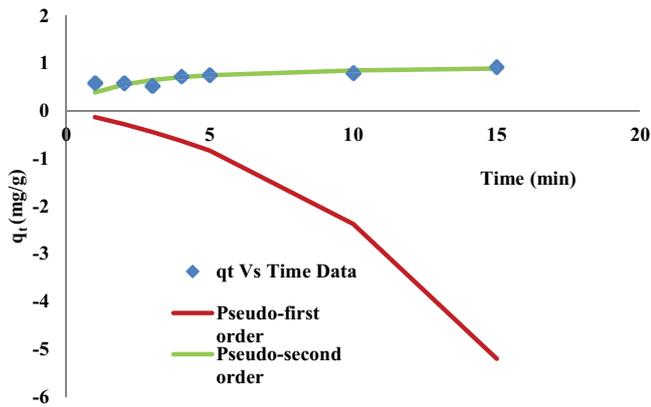
Fig. 5. Pseudo-first-order and pseudo-second-order kinetic profiles of the removal of Cr(VI) onto bentonite (K$^+$).
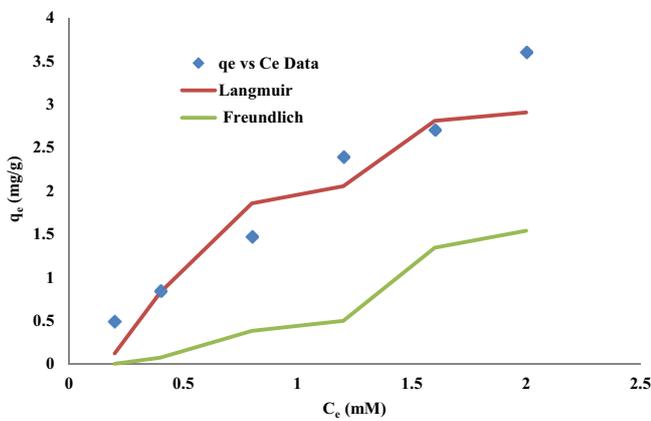
Fig. 6. Isotherm models of the removal of Cr(VI) onto bentonite (K$^+$).

higher S/N ratio than the amount of bentonite (K$^+$) 2 and 1 using both concentrations of chromium(VI) 3; 2 and 1.

3.6. Analysis of variance

ANOVA is used to estimate error variance and to determine the relative importance of various factors. It indicates the effect of each investigated factor on the optimization criterion. ANOVA also demonstrates whether the observed variation in the response is due to the alteration of level adjustments or experimental standard errors [37].

The sum of squares of factor, the total sum of squares, error of sum of squares, error variance, mean of the square and associated *F*-test (*F*-value) of significance (5% of risk) are used in ANOVA [37,38]. The results of the ANOVA are shown in Table 7.

In these results, the main effect for the concentration of Cr(VI) is statistically significant at the significance level of $\alpha = 0.05$ (the *P*-value is less than the significance level α). We can conclude that a change in this variable is associated with a change in the response variable. *S* is measured in the units of the response variable and represents how far the data values fall from the fitted values.

Table 6
Response table for mean

Level	A	B
1	50.29	46.35
2	50.61	34.02
3	55.66	76.19
Delta	5.37	42.17
Rank	2	1
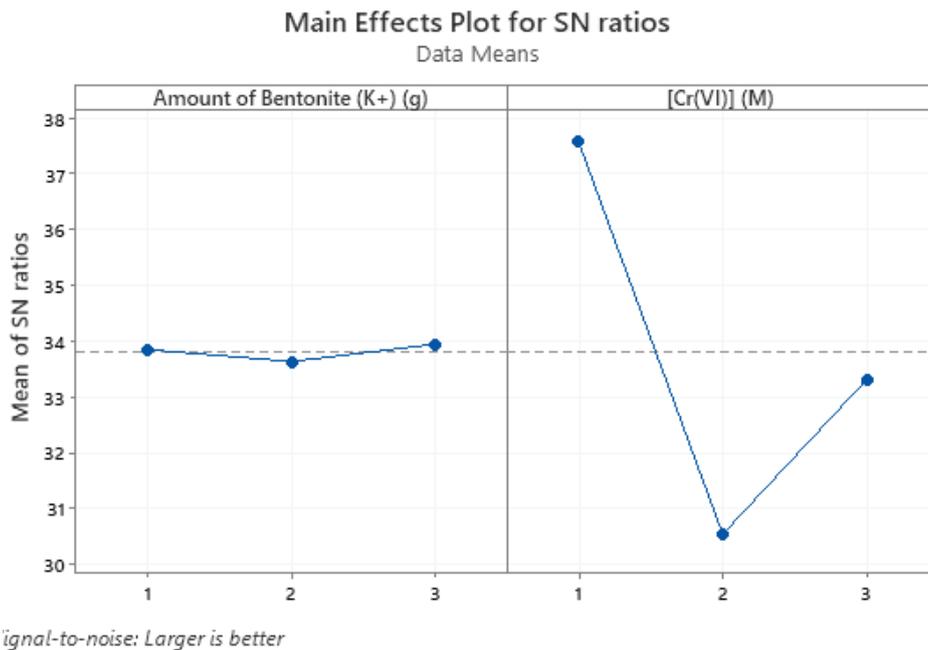
Fig. 7. Response distribution of S/N ratios.
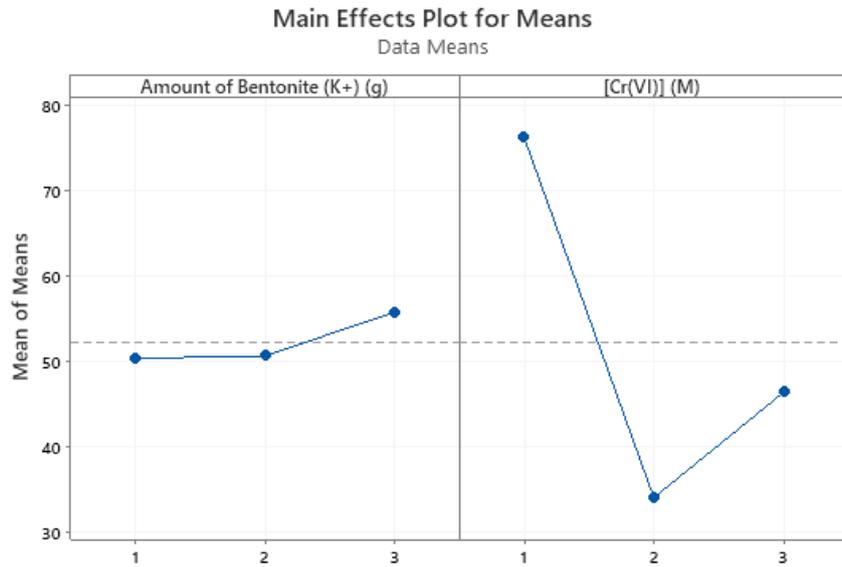
Fig. 8. Response distribution of means.
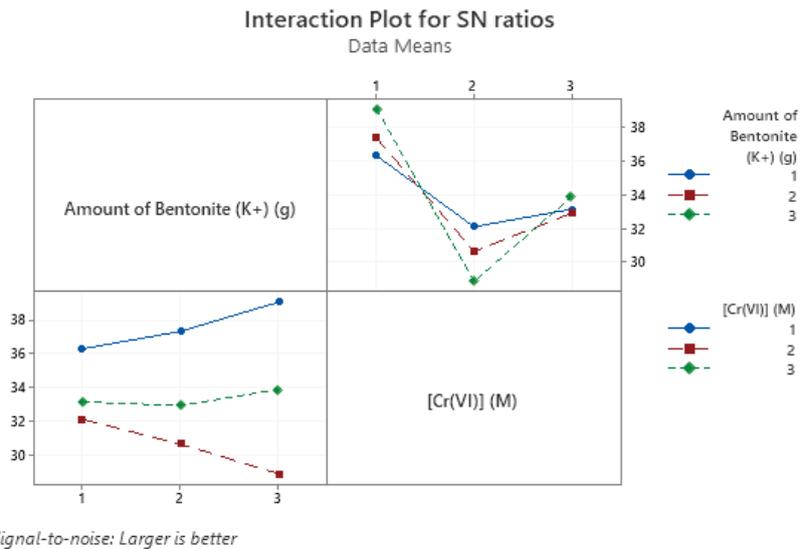
Fig. 9. Interaction plot of S/N ratios.

Table 7
Analysis of variance for the transformed response of % removal data using Minitab 19

Source	DF	Adj. SS	Adj. MS	F-value	P-value
Amount of bentonite (K^+) (g)	2	54.47	27.24	0.31	0.749
[Cr(VI)] (M)	2	2,820.28	1,410.14	16.08	0.012
Error	4	350.89	87.72		
Total	8	3,225.64			
S		9.3660			
R-sq. (%)		89.12			
R-sq. (Adj.) (%)		78.24			

The lower value of S indicates that the model describes the response. Also, the model explains 89.12% of the extraction of Cr(VI) by bentonite (K^+). For these data, the R^2 value indicates that the model provides a good fit to the data (R-sq. (Adj.) = 78.24%).

3.7. Contour plot of extraction yield

This contour plot shows the relationship between the amount of bentonite (K^+) and the [Cr(VI)] settings used for the extraction of the metal (Fig. 11).

Darker regions indicate higher quality. These higher response values seem to form a ridge running from the upper-middle to the lower right of the graph. These graphs represent the amount of bentonite (K^+)-[Cr(VI)]

Interaction Plot for Means
Data Means
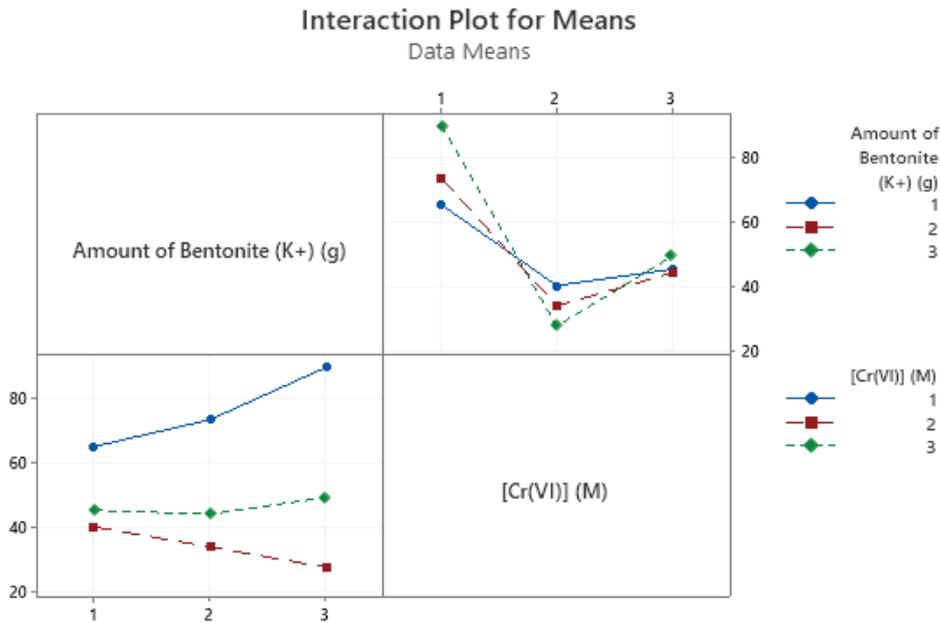
Fig. 10. Interaction plot of means.

Contour Plot of Extraction yield vs Amount of Benton; [Cr(VI)] (M)
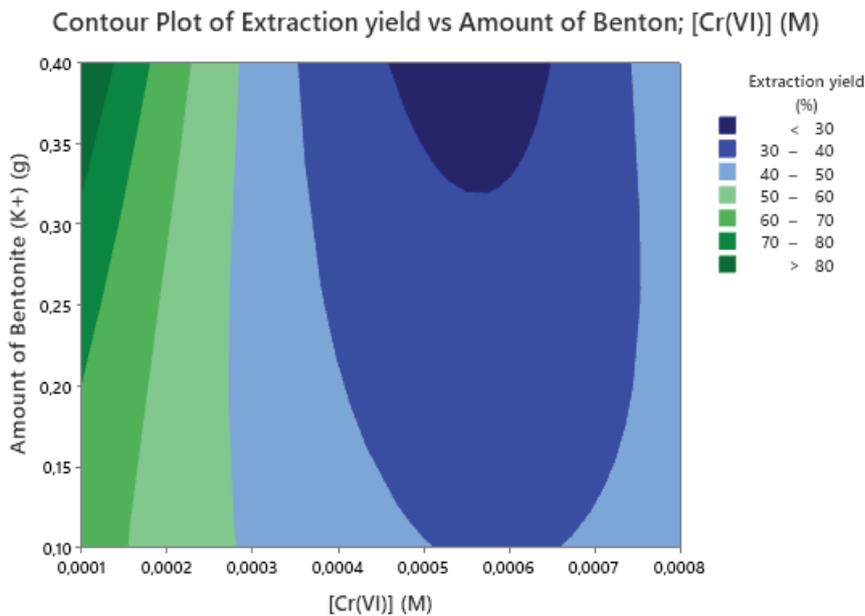
Fig. 11. Contour plot of extraction yield of Cr(VI) by bentonite (K⁺).

combinations. The extraction of Cr(VI) at 10^{-4} M is significant using 0.4 g of bentonite (K⁺).

The Cr(VI) sorption yield was found to be 89.79% with the removal of 10^{-4} M of chromium at pH 5.02 with 0.4 g bentonite (K⁺) for 30 min and 300 rpm.

4. Conclusion

In this study, the adsorption of very toxic Cr(VI) was performed by using basic activated bentonite. The extraction of Cr(VI) was influenced by a number of variables such as the time of the contact, pH of solution and initial concentration of Cr(VI). The chromium(VI) could be selectively extracted within 30 min from natural pH of solutions containing Cr(VI) at 2×10^{-4} M. Pseudo-second-order kinetics described the adsorption satisfactorily. The adsorption of Cr(VI) was adequate for the Langmuir isotherm model.

Taguchi design was used in this study to get the optimum experimental condition for the adsorption of Cr(VI) on impregnated bentonite with potassium hydroxide (K⁺). An

L9 array was used to obtain the experimental matrix using Minitab 19. The optimum condition of the adsorption, considering the effect of the amount of bentonite (K⁺), the initial Cr(VI) concentration in solution, was found to be at *A* (g) of 0.4 (level 3), *B* (M) of 10^{-4} (level 1). A removal of 89.79% was obtained at the optimum condition. Therefore, the statistical study revealed that the Taguchi's method with an L9 orthogonal array design was applied successfully to the experimental optimization refinement of Cr(VI) extraction. Based on the mentioned results, it can be inferred that the impregnated bentonite with potassium hydroxide (K⁺) can be efficiently utilized for the removal of heavy metals from aqueous solution. The results obtained recommend to apply the recovery of Cr(VI) on an industrial scale.

Acknowledgment

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