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Optimization and Response Surface Modeling of Chromium Removal from Aqueous Solution using Nano Zero Valent Iron (NZVI)

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***Abstract* – The ability use of NZVI for the removal of Heavy Metal such as Chromium from aqueous solution has been investigated in batch mode examinations. Amount removal of Chromium is found to be 98.87% at pH:4, amount of adsorbent dosage of 0.01 g in 20 minutes and 5 ppm Chromium solution. Influences of parameters like initial Chromium concentration (5-15 mg/L), time (20-150), and NZVI dosage (0.005-0.02 g) on Chromium adsorption were examinated using response surface methodology. The Box-Behnken experimental design in response surface methodology was used for designing the experiments were run as well as for full response surface estimation and 15 trials as per the model. The optimum conditions for maximum removal of Chromium from an aqueous solution of 10 mg/L were as follows: adsorbent dosage (0.005 g), and 20 minutes initial Chromium concentration (5 ppm) in pH: 4. The high correlation coefficient (*R*2:0.971) between the model and the experimental data showed that the Box-Behnken experimental design was able to predict the removal of Chromium using NZVI from aqueous solution effectually.**

***Keywords* – Adsorption, Box-Behnken Design (BBD), NZVI, Chromium.**

I. Introduction

Water contamination with heavy metals is a very severe problem all over world [1],[2]. The world production of chromite ore is several millions of tons in a year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the Aluminuteothermic process) or by electrolysis of either CrO_3 or chrome alum solutions.

Chromium and its compounds are extensively used in metal finishing, leather tanning, electroplating, textile industries, and chromate preparation [3]. In aqueous phase chromium mostly exists in two oxidation states, namely, trivalent chromium (Cr^{3+} and $Cr(OH)^{2+}$) and hexavalent chromium ($HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example, it was reported that $Cr_2O_7^{2-}$ can cause lung cancer [4, 5]. Chromium (III) and Chromium (VI) have major environmental significance because of their stability in the natural environment. Cr (VI) is known to have 100 fold more toxicity than Cr (III) because of its high water solubility and mobility as well as easy reduction [6].

International agency for research on cancer has determinated that Cr (VI) is carcinogenic to humans. The toxicological effect of Cr (VI) originates due to oxidizing nature as well as the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [8]. Therefore, the World Health Organization (WHO) recommends that the toxic limits of chromium (VI) in waste water at the level of 0.05 mg/L, while total Chromium containing Cr (III), Cr (VI) and other species of chromium is regulated to be discharged below 2 mg/L [7].

Several methods are used to remove chromium from the industrial wastewater. These include reduction followed by chemical precipitation [9], ion exchange [10], reduction [11], electrochemical precipitation way of purifying industrial [12], solvent extraction [13], membrane separation [14], evaporation [15] and foam separation [16]. Above cited conventional chromium elimination processes are costly or ineffective at small concentrations. In recent years biosorption research is focused on using readily available nano particles that can remove heavy metals. This process involves the use of nano materials that form complexes with metal ions using their ligands or functional groups. This process can be applied as a cost effective waste water whereby drinking water quality can be attained. A lot of research was focused on nano-adsorbent materials which can efficiently remove heavy metals from aqueous bodies[17], [18].

Among new method that have been well accepted in recent years, Application of nanotechnology in the removal of heavy metals from metal nanoparticles. Iron nanoparticles because of their ability to reduce heavy metals, and resulting in a clean environment are suitable for many applications. So many studies by researchers on this particles for removal of heavy metals has been carried out. In this work, (removal of chromium from aqueous solution by Nano Zero Valent Iron) The influence of several operating parameters, such as initial chromium concentration, time, and adsorbent dosage were investigated in batch mode. The conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. The conventional technique for the optimization of a multivariable system usually defines one-factor at a time. Such a technique needs to perform a lot of experiments and could not reveal the alternative effects between components. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable.

Recently many statistical experimental design methods have been employed in chemical process optimization. Experimental design technique is a very useful tool for this purpose as it provides statistical models, which helps in understanding the interactions among parameters that have been optimized [19].

These methods involve mathematical models for designing chemical processes and analyzing the process results. Among them, response surface methodology (RSM) is one suitable method utilized in many fields. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determinate the optimum operational conditions for the system or to determinate a region that satisfies the operating specifications [20].

In the present investigation, batch experimental studies were carried out for the removal of chromium (VI) from aqueous solution using Nano Zero Valent Iron. The experimental data points were used to obtain experimental model from Box-Behnken design. The input parameters for the percentage removal of chromium (VI) are initial chromium (VI) concentration, adsorbent dosage and PH. The process optimization has been carried out using BBD to optimize the input parameters to the process for maximum chromium (VI) removal.

II. Material and Methods

A. Preparation of the Adsorbent (Zero Valent Iron Nano Particles)

Firstly, iron nano particles were synthesized by chemical reduction method and the reduction Fe by $NaBH_4$ in the laboratory. During thereaction, thelidis closed**,** and there action was carried out in the presence of nitrogen gas to prevent oxidation of the particles. The synthesized nano-particles were sent to the laboratory for Amirkabir University of XRD and SEM.

B. Preparation of Chromium Stock Solution

First, was used as the initial solution 1000 ppm (Manufacturing of Merck Germany), to prepare a solution of chromium. Then in pH:4, the solution was diluted to 5, 10 and 15 ppm in experiments.

C. Preparation of Chromium Stock Solution and Removal Test

Next**,** Provided the initial concentrations of 5, 10 and 15 mg per liter of the chromium, the effect of iron nano particles in reducing chromium, to experiment with values 0.005, 0.01, 0.02 gr of ironnanoparticles. During the experiment, the contents of the container by mixing in a mixer speed of 150 rpm. Was measured by atomic absorption after deposition solution and passes the rest of the membrane filter.

D. Batch Mode Adsorption Studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dosage, absorption time and pH. The solution containing adsorbate and adsorbent was taken in 250 mL capacity conical flasks and agitated at 180 rpm in a mechanical shaker at pre determinated time intervals. The adsorbate was decanted and separated from the adsorbent using filter paper.

E. Metal analysis

Residual metal concentration after adsorption Was measured by atomic absorption. To estimate the percentage removal of chromium (VI) from aqueous solution, the following equation was used.

Cr (VI) Percentage removal = $\tilde{C}_{\text{int}} C_{fin} / C_{\text{int}}$ (1)

where, C_{int} and C_{fin} are the concentrations of chromium (VI) at the beginning and at the end of the adsorption process.

F. Experimental Design and Procedure

A standard RSM design called Box-Behnken Design (BBD) was applied in this research to study the variables for adsorption of chromium from aqueous solution using in a batch process. RSM or Response surface methodology is a statistical method that uses quantitative data from appropriate experiments to operating conditions and determinate regression model equations. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [20]. BBD for three variables (adsorbate concentration, adsorbent dosage, absorption time), each with two levels (the minimum and maximum), was used as experimental design model. The model has advantage that it permitsthe use of relatively few combinations of variables for determinating the complex response function [21]. A total of 15 experiments are needed to be conducted to determinate 10 coefficients of second order polynomial equation [22]. In the experimental design model, initial chromium(VI) concentration (5-15 mg/L), time (20-150)minute and NZVI dosage (0.005-0.02g) were taken as input variables. Percentage removal of chromium (VI) was taken as the response of the system.Theexperimental design matrix derived from BBD is given in Table II.

This optimization process involves 3 major steps, which are, performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model.

$$Y = f\,(X_1, X_2, X_3, X_4, \ldots X_n) \qquad (2)$$

Y is the response of the system and X_i is the variables of action called factors. The goal is to optimize the response variable (Y). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors and required to find a suitable approximation for the true functional relationship between the response surfaces and independent variables.

Out by three chosen independent process variables using Box-Behnken design with 12 unique runs including 3-replicates at center points.The quadratic equation model for predicting the optimal point was expressed according toEq(2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta x_i x_j + \varepsilon \qquad (3)$$

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3 factors are given in Table I, were studied and their low and high levels. Percentage adsorption was studied with a standard RSM design called Box-Behnken Design (BBD). 15 experiments were conducted in duplicate according in Table II to the scheme mentioned. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability in dependent variables was explained by the multiple coefficient of determination, *R*2 and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range [20].

Table I: Coded and actual values of variables of the experimental design

Factor		*Coded levels of variables*		
		-1	*0*	*1*
adsorbent dosage(gr)	x_1	*0.005*	*0.01*	*0.02*
Absorptiontime(minute)	x_2	*20*	*90*	*150*
adsorbate concentration (ppm)	x_3	*5*	*10*	*15*

Table II: Experimental design & results for the chromium removal &PH after contact time

Run Order	*Coded values*			*Actual values*			*Percentage removal*	
	x_1	x_2	x_3	*A*	*B*	*C*	*observed*	*predicted*
1	1	-1	0	0.01	90	10	91.6535	91.6535
2	-1	1	0	0.01	150	15	92.2372	92.596
3	-1	-1	0	0.005	20	10	94.778	95.186
4	1	1	0	0.01	20	5	98.8705	98.512
5	-1	0	-1	0.01	90	10	91.6535	91.653
6	1	0	-1	0.005	90	5	94.916	94.867
7	-1	0	1	0.01	20	15	93.805	93.392
8	1	0	1	0.02	90	5	93.3744	93.369
9	0	-1	-1	0.005	90	15	94.327	94.333
10	0	1	-1	0.01	150	5	93.855	94.268
11	0	-1	1	0.02	20	10	91.4699	91.834
12	0	1	1	0.02	150	10	88.714	88.306
13	0	0	0	0.01	90	10	91.6535	91.653
14	0	0	0	0.005	150	10	94.0385	93.674

III. Results and Discussion

A. Characteristics of NZVI

1. SEM

The (SEM) Scanning Electron MicrographNZVI showed in Figure 1. The results showed that the particle size of approximately 50 nm. (refer to figure 1)

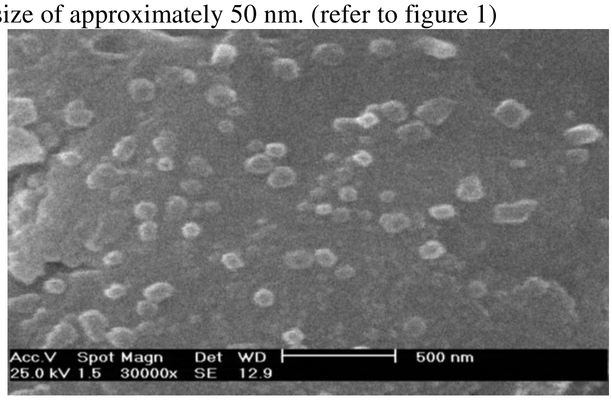

Fig.1. SEM images of NZVI

2. XRD

To determine the sex of nanoparticles produced using data obtained from X-ray diffraction technology (XRD). The results show that (Figure 2), due to peak in the range 45 = θ2 XRD, there Fe0 is evident in the final product.

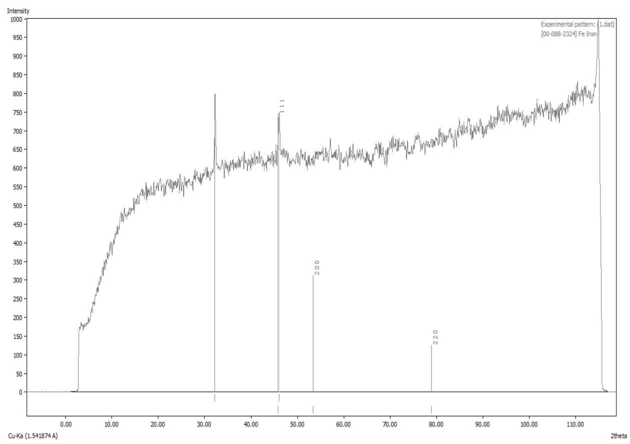

Fig.2. SEM images of NZVI

B. Results of Bbd Experiments

The each experiments results performed as per the software are given in Table II.

Empirical relationships between the independent variables and the response have been expressed by the quadratic model adsorption Equation 4.

$$Y_{Pb} = 93.80 + 1.3416\,X_1 + 1.0749\,X_2 - 0.3554\,X_3 + 0.6730\,X_1 X_2 - 1.3115\,X_1X_3 + 1.1484\,X_2 X_3 + 2.3125\,X^2_1 - 1.5371\,X_2^2 + 0.9367\,X_3^2 \quad (4)$$

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where Y is the percentage removal of Chromium (VI) X_1 is the scaled initial adsorbate concentration, X_2 is time and X_3 is concentration of Cr (VI) scaled.Regression coefficient of full polynomial model is given in Table III. Analysis of variance has been calculated to analyze the accessibility of the model. The analysis of variance for the response has been predicted in Table IV. To evaluate the goodness of the model, the coefficient of variation (the ratio of the standard error of estimate to the mean value expressed as a percentage) and *F* value tests has also been performed. The *F* distribution is a probability distribution used to compare variances by examinating their ratio.

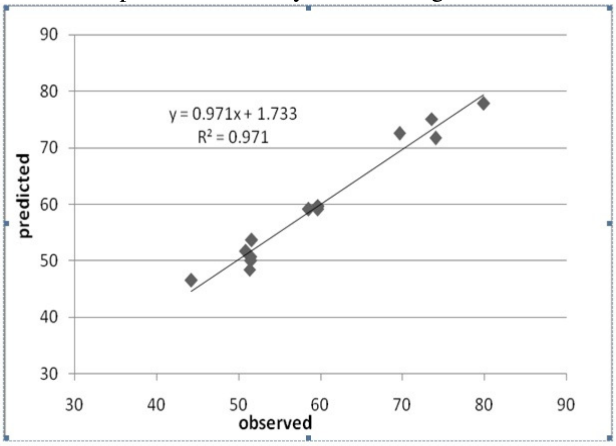

Fig.3. Parity plot showing the distribution of experimental vs predicted values of percentageremoval of chromium (VI)

If they are equal then *F* value would equal to one. The *F* value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the *F* value and the more likely that the variance contributed by the model is significantly larger than random error. As a general rule, if *p*-value is less than 0.05, model parameter is significant (Table IV). On the basis of analysis of variance, the conclusion is that the selected model adequately represents the data for chromium (VI) removal from aqueous solution by NZVI. The Experimental values and the predicted values are in perfect match with *R*2 value of 0.971 (Figure 3).

Table III: Regression coefficient of full polynomial model. (* significant<0.05)

Coefficient	*Parameter Estimate*	*P Value*
Constant	*93.8015*	*0.000*
A	*1.3416*	*-0.05*
B	*1.0749*	*0.094*
C	*-0.3554*	*0.526*
*A*A*	*2.3125*	*0.03*
*B*B*	*-1.5371*	*0.102*
*C*C*	*0.9367*	*0.277*
*A*B*	*0.673*	*0.403*
*A*C*	*-1.3115*	*0.136*
*B*C*	*1.1484*	*0.18*

Table IV: ANOVA test results

Source of variation	*Degrees of freedom*	*Sum of squares*	*Mean square*	*F-value*	*p-value*
Regression	*9*	*72.191*	*8.021*	*3.69*	*0.082*
Residual	*5*	*10.881*	*2.176*		
Total	*14*	*83.082*			

This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in reduction. The optimal values of input variables from regression equations for the adsorption of chromium (VI) were shown in Table V.

Table V: Optimum values of variables obtained from regression equations for the removal of chromium

S.No	*Parameter*	*Optimum value*	*Maximum predicted value*
1	*NZVI(gr)*	*0.005*	*98.87*
2	*Time*	*20*	
3	*Metal concentration*	*5*	

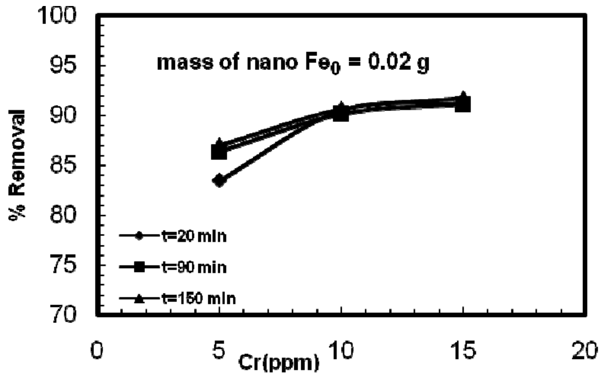

Fig.4. Effect of initial concentration of chromium (VI) and Time on removal of Cr

1. Effect of Initial Concentration of Chromium (VI) and Time on Removal of Cr (VI) by NZVI

The percentage adsorption of Cr (VI) with NZVI was studied by pre-selected range of Time and initial concentration of chromium (VI). The results have been depicted in Figure 4. The results indicated that despite the increase in chromium with increasing the time, removal of chromium (VI) increases.

2. Effect of NZVI Dosage and Adsorbate Concentration on Removal of Cr (VI) by NZVI

The NZVI dosage and adsorbate dosage are most important process parameters for assessing the removal capacity of an adsorbent. Adsorption experiments were carried out as per the selected model with selected range of NZVIdosageand adsorbent dosage.

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The results indicated that removal of chromium (VI) decreases with increasing the adsorbate concentration. (Figure5).

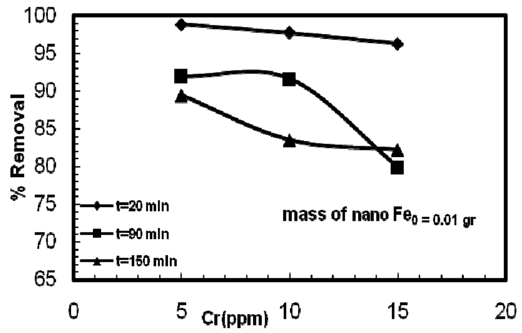

Fig.5. Effect of NZVI dosage and adsorbate concentration on removal of Cr

3. Effect of Time and NZVI Dosage on Removal of Cr (VI) by NZVI

The combined effect of adsorbent dosage and time of test on removal of chromium (VI) has been presented in Figure 6. The results indicated that removal of chromium (VI) increases with increasing the NZVI dosage.

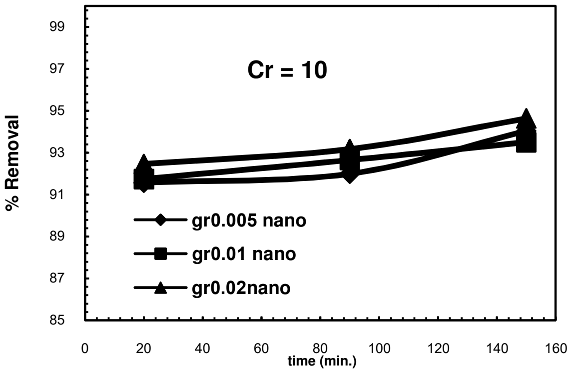

Fig.6. Effect of TIME and NZVI dosage on removal of Cr (VI) by NZVI

IV. Conclusions

A detailed batch experimental study was carried out for the removal of chromium (VI) from aqueous solution by using NZVI. The objective of the present study was to find out the optimum process conditions, using response surface methodological approach for the removal of chromium (VI) from aqueous solution by NZVI as adsorbent.Response surface methodology using Box-Behnken design proved very effective and time saving model for studying the influence of process parameters on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. The Experimental values and the predicted values are in perfect match with R2 value of 0.869. This methodology could therefore be successfully employed to study the importance of individual, cumulative, and interactive effects of the test variables in absorption. The optimal absorption of chromium (VI) was obtained as initial concentration of chromium (VI), time and adsorbent dosage and these were found to be 5 ppm, 20 minutes and 0.005 gr, respectively, resulting in 98.0% of maximum predicted adsorption of chromium (VI).

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