DOI: 10.7251/QOL2403137S
UDC: 662.665-042.55:622.771
Original scientific paper

Reduction of Hexavalent Chromium by Nano Zero-Valent Iron

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ABSTRACT: Hexavalent chromium is a toxic form of chromium that has significant health and environmental implications. Reducing hexavalent chromium to trivalent chromium is a crucial step in immobilizing and removing Cr(VI) from water resources. Nano zero-valent iron (nZVI) as an electron-donating agent was used for Cr(VI) reduction in aqueous solution. The effect of contact time and initial concentration of nano zero-valent iron on Cr(VI) reduction was studied. The process of Cr(VI) reduction was designed and optimized using response surface methodology. The results indicated an enhancement in the Cr(VI) reduction ratio with increasing initial concentration of nano zero-valent iron and contact time. A second-order polynomial equation was used to model the correlation between the independent and dependent variables. The utilized model effectively predicted the response variable based on the input variables with a high coefficient of determination (R^2) of 0.9475 and a correlation coefficient (R) of 0.9734. Additionally, the accuracy of the fitted model was demonstrated by the low values of the mean squared error (MSE) at 0.04315 and the sum of squared errors (SSE) at 0.06562. The optimal conditions for reducing Cr(VI) in aqueous solution using nano zero-valent iron were determined to be an initial nZVI concentration of 15 mg/L and a contact time of 209 min.

Keywords: hexavalent chromium Cr(VI), nano zero-valent iron (nZVI), reduction, process design and optimization

INTRODUCTION

Pollution of the environment and water resources by inorganic pollutants, particularly heavy metals and metalloids, poses a significant challenge and risk to the environmental integrity and human health. Chromium is a potentially hazardous metal found in surface and groundwater, originating from both natural processes and human activities (Mitra et al, 2022). Chromium is utilized in various industrial processes, including galvanization, electroplating, production of stainless steel, pigments, paints, and other industrial applications. Significant quantities of chromium-based compounds are released and dumped from industrial establishments into the environment through liquid, solid, and gaseous wastes (Ayele et al, 2021). Chromium can exist in several oxidation states in water resources, however, hexavalent chromium and trivalent chromium are the most common and stable forms that are found (Kotaś & Stasicka, 2000).

Hexavalent chromium Cr(VI) is highly soluble and mobile in aqueous solution and typically does not form insoluble compounds in water. It is more toxic and carcinogenic to humans and animals than trivalent chromium Cr(III). Cr(III) tends to form insoluble compounds or complexes with organic matter in water, reducing its mobility and bioavailability. In an aqueous solution at neutral pH, Cr(III) generally forms insoluble hydroxide precipitates (Barrera-Díaz et al, 2012; Ölmez, 2009). In this context, the reduction of Cr(VI) to Cr(III) is considered a feasible method and essential phase in the immobilization and ultimately the removal of Cr(VI) from the water contaminated with this hazardous pollutant (Dehghani et al, 2016).

Different methods for reducing Cr(VI), including chemical, electrochemical, and biological techniques, are employed to convert Cr(VI) into less toxic and mobile forms (Bandara et al, 2020; Butter et al, 2021; Wang et al, 2010). The selection of a specific method depends on various factors, such as the type of contaminated water (surface, underground, or industrial), the volume of water to be treated, the process effectiveness, the goal efficiency, etc (Saravanan et al, 2021). Iron(II) chloride, iron(II) sulfate, sodium bisulfite, sulfur dioxide, ascorbic acid, and citric acid are frequently used as chemical agents for Cr(VI) reduction in aqueous solution. Each reducing agent has its advantages and limitations (Asgari et al, 2020; Pettine et al, 1998; Zaib et al, 2021).

In recent years, nano zero-valent iron (nZVI) has gained significant attention for its effectiveness in removing various pollutions from water resources and soil. This is primarily due to its high specific surface area and reactivity that enhance its ability to rapidly reduce or immobilize pollutants through reduction, adsorption, or catalytic processes. nZVI is a low-cost, environmental-friendly, and efficient solution for the remediation of contaminated groundwater (Wang et al, 2021). It can be applied in permeable reactive barriers or in-situ remediation of various contaminants in groundwater, including Cr(VI) (Zafar et al, 2021). Reducing Cr(VI) by nano zero-valent iron in an aqueous solution involves the adsorption of Cr(VI) on the surface of nanoparticles and the transfer of electrons from the nZVI to Cr(VI) (Qiu et al, 2020). Contact time, nZVI concentration, Cr(VI) concentration, temperature, pH of the solution, the chemical composition of the aqueous solution, and physicochemical properties of the used nZVI influence the reduction of Cr(VI) by nZVI. In general, the effect of operating parameters on the efficiency of the Cr(VI) reduction has mainly been conventionally analyzed and defined. Conventional methods of process optimization typically involve analysis of the influence of one factor at a time while keeping all other factors constant. The main limitation of this approach is the inability to determine the influence of interactions between independent variables (Gao et al, 2022; Niu et al, 2005; Zhang et al, 2020). Advanced statistical methods such as response surface methodology (RSM) can be used to determine the interaction between factors and identify optimal process conditions.

The response surface methodology is a statistical technique used for designing experiments, developing predictive models, and optimizing complex processes based on a limited number of experiments. This technique is established to explore the effects of multiple variables on one or more responses of interest. The primary objective of RSM is the development of predictive polynomial models that accurately describe the behavior of studied processes. One of the key advantages of RSM is its ability to efficiently identify the optimal combination of factor levels that maximize or minimize the response variable. Additionally, the RSM allows the visualization of the predictive models by creating response contour and surface plots (Hadiyat et al, 2022; Kumar & Reji, 2023; Yolmeh & Jafari, 2017).

In the presented study, nano zero-valent iron was used to reduce Cr(VI) in the model aqueous solution. The effect of contact time and initial nZVI concentration on the Cr(VI) reduction ratio was researched. The process was optimized using response surface methodology. Within the framework of this work, a specific system was designed for the highly efficient removal of Cr(VI) through its reduction to Cr(III), coupled with the subsequent optimization of process parameters. A predictive mathematical model for accurately calculating the efficiency of Cr(VI) reduction by nZVI in pH-neutral aqueous solutions contaminated with the pollutant at concentrations around 0.5 mg/L was developed. Additionally, the influence of the studied working parameters and their interaction on the response and optimal reduction region were determined.

MATERIALS AND METHODS

Reduction Of Cr(Vi) By Nano Zero-Valent Iron

The reduction of Cr(VI) to Cr(III) in an aqueous solution was performed in a 2000 mL laboratory glass beaker. Nano zero-valent iron used in this study was synthesized by reducing Fe(III) ions with sodium borohydride. For this purpose, 1.5 g of iron(III) chloride hexahydrate (for analysis, Merck) was dissolved in

83 mL of ethanol 77 %. The ethanol 77 % was prepared using ethanol 96 % (Ph.Eur., Alkaloid) and deionized water. The conductivity of the deionized water was less than 0.5 µS/cm. Then, 93 mL of 0.3 M sodium borohydride solution was prepared and added dropwise to the Fe(III) solution (2 drops per second). During the reaction process, the mixture was stirred in a 1000 mL glass beaker at a mixing speed of 300 rpm. After adding the entire borohydride solution, the mixture was stirred for an additional 15 minutes. Solid zero-valent iron nanoparticles were separated on filter paper (Macherey-Nagel MN640 DE) using vacuum filtration. The particles were washed with 250 mL of ethanol 96 %. The synthesized nZVI was dried in a vacuum desiccator at a pressure of 20 kPa and a temperature of 50°C for 7 h. Dried nZVI was stored in a vacuum bag.

The chromate aqueous solution with an initial Cr(VI) concentration of 0.5 mg/L was prepared and transferred into the beaker. The initial solution pH was adjusted to 7.0 using a 0.1 M solution of NaOH. Then, the nZVI was introduced into the solution. The reaction solution was stirred at a mixing speed of 1000 rpm and a temperature of 20°C. The effect of contact time and initial nZVI concentration on the Cr(VI) reduction was studied. The contact time was changed from 0 to 240 min, and the initial nZVI concentration was 5 to 15 mg/L. Cr(VI) reduction ratio was calculated following the equation:

$$\text{Cr(VI) reduction ratio} = C/C_0 \tag{1}$$

where C is the concentration of Cr(VI) at a specific time [mg/L], and C_0 is the initial Cr(VI) concentration [mg/L]. After each predetermined time interval, a 5 mL sample was withdrawn from the reactive solution and immediately filtered using a syringe filter with a pore size of 0.2 µm. The Cr(VI) concentration was determined with 1,5-diphenylcarbazide using a spectrophotometer (Spectroquant Prove 600) at 540 nm. The chromate test (Spectroquant, chromium (VI) method: photometric 0.010 - 3.00 mg/L) for the determination of Cr(VI) was employed. Each solution was prepared in accordance with the manufacturer's instructions described in the 1.14758.0001 procedure. A rectangular quartz glass cuvette with a path length of 10 mm was utilized for the analysis. A preprogrammed method (114758) in the spectrophotometer Prove 600 was used to measure the concentration of Cr(VI) in the samples.

Process Design and Optimization

A multilevel factorial design was used to optimize the process of Cr(VI) reduction in aqueous solution by nZVI. The contact time (t) and the initial nZVI concentration (C_{nZVI}) were selected as the most important independent factors that have a significant influence on the Cr(VI) reduction. Hence, these two parameters were used as experimental factors. The reduction ratio of Cr(VI) was employed as a response variable. The Statgraphics Centurion XV statistical software was introduced to fit the chosen model to the experimental data. A mathematical model was created to define the relationships between input variables and the response variable. The second-order polynomial equation was employed to find the critical point (minimum), following the equation:

$$y_{C/C0} = k_0 + k_1 t + k_2 C_{nZVI} + k_3 C_{nZVI} t + k_4 t^2 + k_5 {C_{nZVI}}^2 \tag{2}$$

where $y_{C/C0}$ is a predicted Cr(VI) reduction ratio, t is a contact time [min], C_{nZVI} is an initial nZVI concentration [mg/L], k_0, k_1, k_2, k_3, k_4, and k_5 are regression coefficients. The predictive accuracy of the model was estimated through the values of the mean absolute error (MAE), the standard error of estimate (SEE), the coefficient of correlation (R), and the coefficient of determination (R^2). Lower values of MAE and SEE and higher values of R and R^2 indicate better predictive performance.

RESULTS AND DISCUSSION

Rsm Design of Cr(VI) Reduction by Nano Zero-Valent Iron

The efficiency of the Cr(VI) reduction in aqueous solution by zero-valent iron nanoparticles depends on several parameters: contact time, the concentration of Cr(VI), the concentration of nZVI, the pH of the solution, the temperature, etc. In this study, the effect of contact time and initial nZVI concentration on Cr(VI) reduction was investigated. Three different concentrations of nZVI were employed, while the initial Cr(VI) concentration was fixed at 0.5 mg/L. The reduction ratio of Cr(VI) in aqueous solution at different initial nZVI concentrations is illustrated in Figure 1.

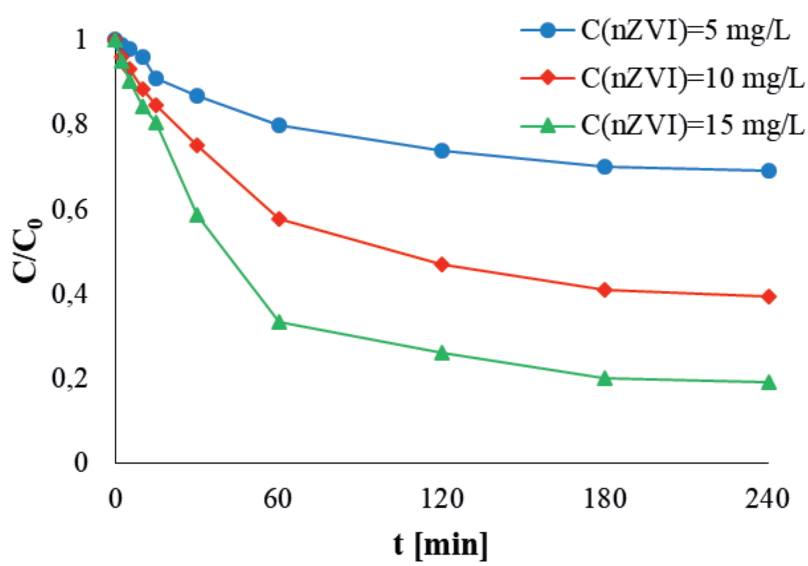

Figure 1. Reduction of Cr(VI) by nZVI at different initial nZVI concentrations

pH=7.0, T=20°C

Results showed that increasing the initial nZVI concentration leads to a significant improvement in the efficacy of Cr(VI) reduction and suggests a strong positive correlation between nZVI concentration and reduction efficiency. When 10 mg nZVI was introduced in the solution, the Cr(VI) reduction efficiency was 26.0 % at a contact time of 120 min and 31.0 % for 240 min. However, when the initial concentration of nZVI was increased to 15 mg/L, the Cr(VI) reduction increased to 81.0% after 240 min. Figure 1 shows that the reduction efficiency increases by increasing contact time.

The relationship between the independent variables and the dependent variable was determined using a second-order polynomial equation based on the experimental data. The model equation is presented in Equation 3:

$$y_{C/C0} = 1.12055 - 0.02235\, C_{nZVI} - 0.00021\, C_{nZVI}\, t + 0.00002\, t^2 + 0.00052\, C_{nZVI}^{\;2} \quad (3)$$

The magnitude of the regression coefficient in the equation of the fitted model represented that the initial nZVI concentration and the contact time have a stronger influence on Cr(VI) reduction than contact time-squared, initial nZVI concentration-squared, and interaction between contact time and initial nZVI concentration. The initial nZVI concentration was determined to be the most important factor for the reduction of Cr(VI) by nZVI in aqueous solution. The analysis of variance (ANOVA) for the studied process is presented in Table 1.

Table 1. Analysis of variance for the response surface quadratic model

Source	Sum of Squares (SS)	Degrees of Freedom (Df)	Mean Square	F-ratio	P-value
A: Contact time	0.773371	1	0.773371	179.63	0.0000
B: Initial nZVI concentration	0.475582	1	0.475582	110.46	0.0000
AA	0.212776	1	0.212776	49.42	0.0000
AB	0.142784	1	0.142784	33.16	0.0000
BB	0.00112667	1	0.00112667	0.26	0.6136
Total error	0.103329	24	0.00430538		
Total (corr.)	1.96679	29			

The ANOVA table showed that 4 effects have P-values less than 0.05, indicating that they significantly differed from zero at the 95.0% confidence level. Several authors have reported developed mathematical models for the reduction and removal of Cr(VI) from aqueous solution by the implementation of nZVI-based material (Jing et al, 2021; Singh et al, 2011; Tong et al, 2022). The model reported in this article depicts the closed system: properties of pure nZVI-Cr(VI) and resulting 3D-RSM area. The interpretation of the obtained results strongly confirms the introduced novelty compared to already reported research: nZVI-based redox system and adequate optimization methodology. The response contour and surface plot were employed to visualize the predictive model and estimated response. The contour plot and response surface plot are given in Figures 2 and 3.

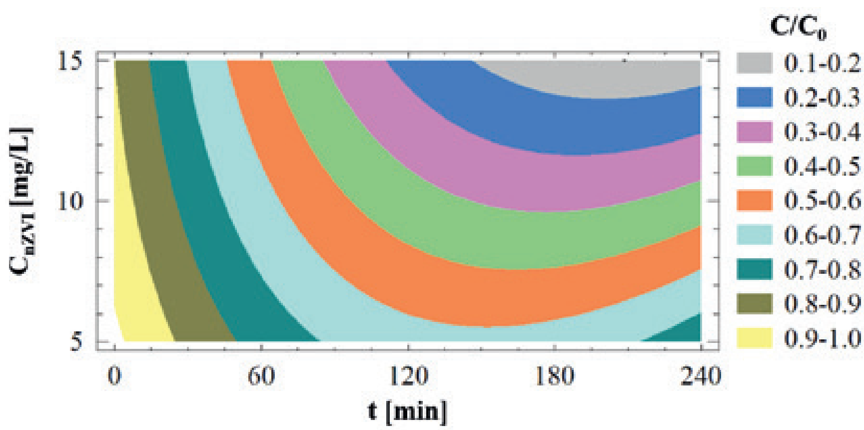

Figure 2. Couture plot for the effect of experimental factors on Cr(VI) reduction by nZVI

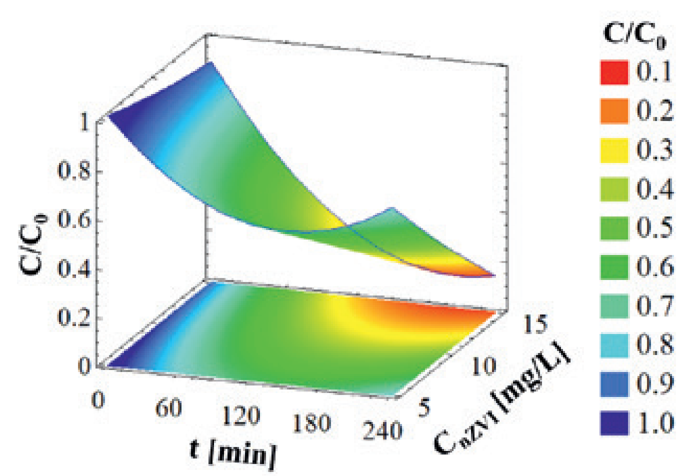

Figure 3. Response surface plot for the effect of experimental factors on Cr(VI) reduction by nZVI

The contour and response surface plots showed that the reduction of Cr(VI) significantly increased with increasing the initial nZVI concentration in the range of 5 to 15 mg/L, especially evidently after 60 min. Furthermore, plots suggested that the Cr(VI) reduction ratio significantly decreased for the process duration from 0 to 120 min, and after 180 min the Cr(VI) reduction asymptotically approaches a stationary state. The interaction effect of contact time and initial nZVI concentration on the response variable visually is given in Figure 4.

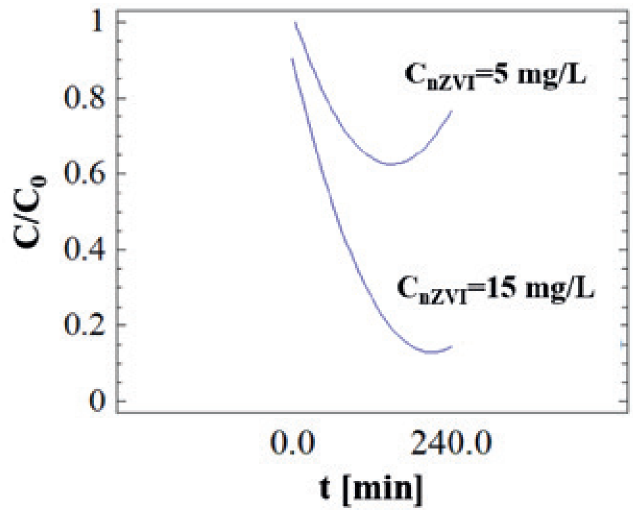

Figure 4. Interaction effect between contact time and initial nZVI concentration on the Cr(VI) reduction

In Figure 4, the x-axis represents contact time, the y-axis represents Cr(VI) reduction ratio, and the lines represent different levels of initial nZVI concentration. The placement of the curves signified that the effect of contact time on Cr(VI) reduction varies depending on the level of initial nZVI concentration, and vice versa.

The established model effectively predicted the reduction of Cr(VI) by nano zero-valent iron (nZVI) in aqueous solutions with a high coefficient of determination of 0.9475 and a correlation coefficient of 0.9734. Low values of MAE (0.04315) and SEE (0.06562) indicated that the model provided a good fit to the experimental data and could be effectively used for optimization purposes. Additionally, the scatter plot (Figure 5) showed that most points were close to the reference line, indicating a good correlation between predicted and observed values. The comparison between actual and predicted responses obtained by the developed model is illustrated in Figure 6.

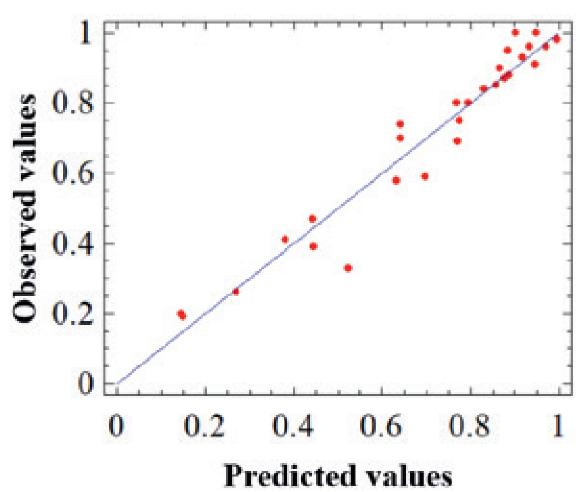

Figure 5. Scatter plot of predicted versus observed values

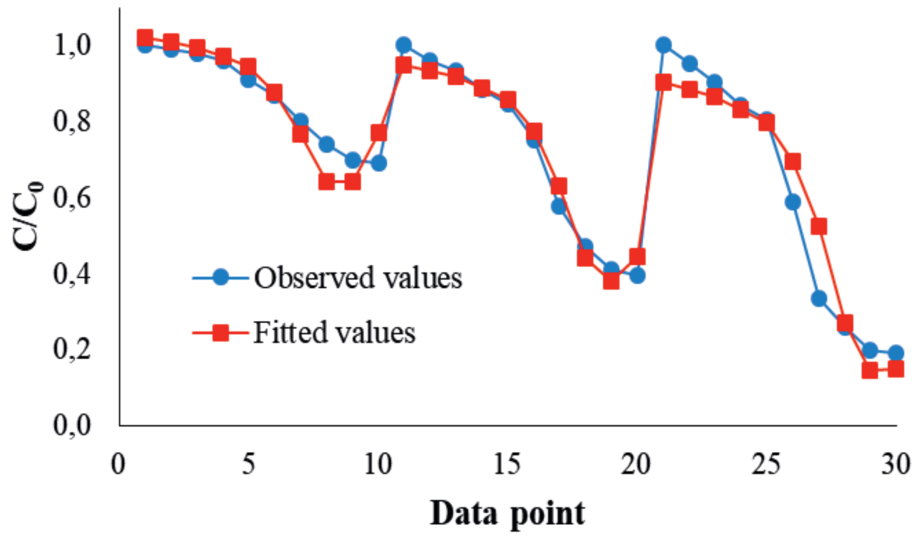

Figure 6. Comparison of model-predicted and actual values of Cr(VI) reduction

The design variables of contact time and initial nZVI concentration were utilized to determine the optimal process parameters as well as the minimal Cr(VI) reduction ratios. The optimal reduction ratio for Cr(VI) using nano-zero valent iron was 0.13, achieved under optimal conditions of 15 mg/L initial nZVI concentration and 209 min of contact time.

CONCLUSION

The study investigated the reduction of hexavalent chromium by nano zero-valent iron (nZVI) in an aqueous solution as a potential remediation technique. The effectiveness of nZVI in reducing Cr(-VI) concentrations was examined under various experimental conditions, including different initial nZVI concentrations and contact times. The reduction process was designed and optimized using response surface methodology to assess the influence of process parameters on the Cr(VI) reduction ratio while minimizing environmental impact and optimizing processing conditions. The applied model adequately fitted the experimental data with a high coefficient of determination (R^2=0.9475) and correlation coefficient (R=0.9734). Furthermore, low values of the mean absolute error (MSE=0.04315) and the sum of squared errors (SSE=0.06562) confirmed the ability and accuracy of the model in representing the relationship between the factors and the response. The results showed that the reduction of Cr(VI) significantly depended on the contact time and initial nZVI concentration. The optimal Cr(VI) reduction ratio was 0.13 at the initial nZVI concentration of 15 mg/L for 209 min.

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Recived: May 12, 2024

Accepted: June 15, 2024