Optimization Modeling of \( \text{nFe}^0 / \text{Cu-PRB} \) Design for Cr(VI) Removal from Groundwater

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Abstract—Hexavalent chromium is one of the highly toxic heavy metals which could lead to severe health issues when it is discharged into aquifers as industrial wastewater. In the current study \( \text{nFe}^0 / \text{Cu} \) was successfully employed in PRB technology for Cr(VI) removal from groundwater. Batch and column experiments confirmed the high reactive performance of \( \text{nFe}^0 / \text{Cu} \) towards Cr(VI) removal by around 85% removal efficiency. The main pathways for Cr-species removal by \( \text{nFe}^0 / \text{Cu} \) were determined as the reduction of Cr(VI) to Cr(III) by both \( \text{nFe}^0 \) and Cu0 and the precipitation/co-precipitation of Cr(III) with the released iron oxides on the \( \text{nFe}^0 / \text{Cu} \) surface. The developed 3D-surface response optimization model confirmed the reciprocal relation between the residence time, barrier thickness and hydraulic conductivity. The interaction and sensitivity analysis between the model’s parameters were significantly crucial for defining the optimal design conditions of the \( \text{nFe}^0 / \text{Cu-PRB} \). Generally, the current study could represent a great contribution in scaling-up the PRB technology towards the real field applications.

Index Terms—Bimetallic nanoscale zero valent iron (\( \text{nFe}^0 / \text{Cu} \)), hexavalent chromium (Cr(VI)), optimization, permeable reactive barrier (PRB).

I. INTRODUCTION

Groundwater contamination with chromium (Cr) has grown a great concern due to the severe and toxic impacts on environment and human. The presence of Cr in groundwater is mainly derived from the industrial wastewater discharge into the aquatic environment which causes elevated concentrations of Cr in water bodies [1]. The two main oxidation states of Cr, which are commonly found in water, are Cr(VI) and Cr(III). The trivalent form is, less soluble in water, less toxic, and crucial for human nutrition [2]. However, when it is oxidized to Cr(VI), it becomes highly toxic and more mobile in both groundwater and surface water. The dominant Cr(VI)-species in aqueous solutions are dichromate (Cr\( \text{O}_7^2- \)) and hydrogen dichromate (HCr\( \text{O}_7^- \)) [3], [4]. The presence of these compounds is mainly pH-dependent, where Cr\( \text{O}_7^2- \) dominates in the alkaline conditions unlike HCr\( \text{O}_7^- \) which prefers the acidic medium. The exposure to such Cr(VI) compounds could affect the human health severely by causing lethal diseases the brain and the nervous system [5]. Accordingly, the World Health Organization (WHO) set the maximum permissible concentration of Cr in drinking water to be 50 \( \mu \text{g}/\text{L} \) [6]. Hence, developing an efficient remediation technology for groundwater from Cr(VI) contamination is crucial to meet the permissible limits.

Among the different approaches that have been considered in the literature for the removal of Cr(VI) from water, adsorption is considered to be the most commonly used [7]–[9]. However, reducing the toxic Cr(VI) to Cr(III) within the aquatic environments could be the simplest and the most economic methodology for Cr(VI) removal from water bodies [10]. Such process can be induced by the presence of other materials which have the ability of electron-donation to enhance the reduction process [11]–[14]. In this regard, nanoscale zero-valent iron (\( \text{nFe}^0 \)) is a perfect candidate for Cr(VI) removal from aqueous solutions. \( \text{nFe}^0 \), as an electron donor, can reduce Cr(VI) to Cr(III) in addition to the possibility of Cr(III) immobilization by either adsorption on the passivation film on \( \text{nFe}^0 \) surface or co-precipitation with the released iron oxides from the core. These iron nanoparticles have unique reactive features, such as the nanoscale which provides large specific surface area of the material and the high reactive performance and induces the passivation film on \( \text{nFe}^0 \) surface. These iron nanoparticles have unique reactive features, such as the nanoscale which provides large specific surface area of the material and the high reactive performance and induces the passivation film on \( \text{nFe}^0 \) surface.

\[ \text{Fe}^0 + \text{CrO}_7^{2-} + \text{Cu}^2+ \rightarrow \text{Fe}^{2+} + \text{Cr}^{3+} + \text{Cu}^0 \]  

Different studies have been previously reported on the use of \( \text{nFe}^0 / \text{Cu} \) for Cr(VI) removal from water [25], [26]. It has been reported that loading \( \text{nFe}^0 \) surface with Cu resulted in the retardation of the core oxidation and accelerating the reduction rate of Cr(VI) to Cr(III) in the contaminated groundwater [27].

In this study, \( \text{nFe}^0 / \text{Cu} \) was considered as a reactive material for permeable reactive barrier (PRB) technology for Cr(VI) removal from groundwater. Batch and column experiments were conducted to evaluate the removal performance of the reactive material. Optimization model was developed considering the reactive/hydraulic/economic representative parameters of the PRBs performance; residence time (RT), reactive-mass ratio corresponding to the treated sectional area (RMR), and the cost of \( \text{nFe}^0 / \text{Cu} \) (Cost), and their relation with the design parameters of the barrier: thickness (b) and hydraulic conductivity (Kc). The interaction and sensitivity analysis between the model’s parameters were significantly crucial for defining the optimal design conditions of the \( \text{nFe}^0 / \text{Cu-PRB} \).
II. METHODOLOGY

A. Reactive Material Preparation

nFe\(^0\)/Cu was prepared on two consecutive stages. Firstly, nFe\(^0\) particles were synthesized by the chemical reduction methodology of ferric-precursor/copper-chloride mixture (with an optimized mixing mass ratio of 20) by borohydride-reductant in, following the previously reported synthesis conditions [28], [29]. The synthesized nFe\(^0\)/Cu was separated from the synthesis solution by vacuum filtration to be used directly in the experiments without any further modification.

B. Batch and Column Experiments

Batch experiments were conducted to determine the removal efficiency of the prepared nFe\(^0\)/Cu for Cr(VI). Solution volume of 200 mL was used with an initial Cr(VI) concentration of 20 mg/L. The reactive mass inside the solution was 0.2 g which was selected based on a previous investigation as the optimal dosage for efficient removal and reasonable cost. All batch experiments were conducted at 25 ± 1.0 °C, neutral pH conditions, and mixing speed of 300 RPM (magnetic mixing). Samples were withdrawn over 3 hours reaction time to be analyzed for Cr(VI) concentration using UV-Vis spectrophotometer (DR-2800, HACH, USA).

Column experiments were conducted in order to simulate the reactive performance of nFe\(^0\)/Cu in Cr(VI) removal within groundwater applications. The schematic diagram in Fig. 1 shows the column experimental setup as well as the PRB conditions which will be considered for developing the optimization model. The column’s dimensions were 20 cm and 2.5 cm in length and inner diameter, respectively. The column was filled with nFe\(^0\)/Cu with the addition of thin layer of glass beads (4 mm diameter) at the top and the bottom. The influent solution with 20 mg/L initial Cr(VI) concentration was pumped downward at 3.3 mL/min into the column and effluent samples were collected over 3 hours experiment for Cr(VI) concentration analysis.

Cr(VI) removal efficiency was calculated in batch and column effluent samples considering the following formula [30]:

\[
R(\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100
\]  

(1)

All experiments were duplicated for accurate investigation of the Cr(VI) removal performance.

C. Optimization Model

For developing the optimization model of the PRB design, the sectional area of the treated plume (A) was assumed as 20 m\(^2\) and the PRB depth (d) was considered 2.5 m, as shown in Fig. 1. The main focus in this optimization was on defining the suitable PRB thickness (b) for efficient Cr(VI) removal without the concern with the width (w), as it is the main determinant for the reactive flow within the groundwater. In order to consider the reactive, hydraulic, and economic aspects within the optimization of the PRB design, the three representative parameters which were chosen as dependent factors were: residence time of the plume within the barrier (RT), reactive-mass ratio corresponding to the treated sectional area (RMR), and the cost of nFe\(^0\)/Cu (Cost). Those factors were represented by the following formulas:

\[
RT(\text{day}) = (b \times R) / (v_r \times S_p)
\]  

(2)

\[
RMR(\text{g/m}^2) = (\text{density} \times \text{volume}) / A
\]  

(3)

\[
Cost($) = (\text{Cost per 1 m}^3) \times \text{volume}
\]  

(4)

where, in Equation 2, \(b \ (m)\) is the PRB thickness, \(R\) is the retardation factor of the plume within the barrier which is a function of the density of nFe\(^0\)/Cu \((\text{g/m}^3)\), Cr(VI) solid concentration \((q_s \ (\text{mg/g}))\), Cr(VI) aqueous concentration \((C_e \ (\text{mg/L}))\), and effective porosity of the barrier \((n)\); \(R = 1 + (\text{density} \times q_s) / (n \times C_e)\). Moreover, \(v_r \ (\text{m/day})\) is the average water velocity inside the barrier which can be calculated from the hydraulic conductivity of nFe\(^0\)/Cu \((\text{m/day})\), hydraulic gradient \((i)\), and \(n:\ v_r = (K_r \times i) / n\). Finally, the safety factor \((S_p)\) was considered based on previously reported values in the literature to be around 0.37 [31]–[33].

In Equation 3, RMR was a function of the designed volume of PRB \((\text{m}^3)\), nFe\(^0\)/Cu density \((\text{g/m}^3)\), and sectional area of the treated plume \((\text{m}^2)\). Lastly, in Equation 4, the cost of the reactive material was represented by the cost per 1 m\(^3\) volume of nFe\(^0\)/Cu (neglecting the construction cost) multiplied by the designed PRB volume. Hence, the cost of 1 m\(^3\)-nFe\(^0\)/Cu was considered around 520 $, based on the estimation of the experimental costs for the synthesis process.

The value of the barrier width \((w)\) was estimated as a function of the relative hydraulic conductivity between barrier material and aquifer medium \((K_r / K_{aq})\) considering the following formula [6]:

\[
w(\text{m}) = [(A \times S_p)/d] / (K_r / K_{aq})
\]  

(5)

| Table 1: Experimental Values of PRB-Parameters |
|---------------------------------------------|
| Parameter | Unit  | Value  |
| Retardation factor (R) | — | 57.26 |
| Average water velocity \((v_r)\) | (m/day) | 3.76 |
| Density \((\text{g/m}^3)\) | — | 3100 |
| Cr(VI) solid concentration \((q_s)\) | (mg/g) | 17.94 |
| Cr(VI) aqueous concentration \((C_e)\) | (mg/L) | 3.182 |
| Hydraulic conductivity \((K_r)\) | (m/day) | 3.697 |
| Effective porosity \((n)\) | — | 0.310 |

The relative hydraulic conductivity ratio was assumed within a reasonable range between 1-10, as previously
reported [34]. Table 1 displays all the experimentally estimated parameters for developing the optimization model.

III. RESULTS

A. Cr(VI) Removal

Results of batch experiments revealed that 1 g/L dosage of nFe\(^0\)/Cu showed around 85% removal efficiency towards 20 mg/L Cr(VI) initial concentration after 3 hours reaction time (Fig. 2a). Moreover, the removal efficiency from the column experiment was in perfect correlation with the batch results by reaching around 80% after only 5 min from the beginning of the experiment and continuing in a good agreement till the end of the two experiments (Fig. 2b). These results revealed the consistency of nFe\(^0\)/Cu in Cr(VI) removal without the possibility of the desorption to occur.

The main removal pathways of Cr(VI) by nFe\(^0\)/Cu can be summarized in the following equations [35], [36]:

\[
\begin{align*}
3Fe^0 + Cr_2O_7^{2-} + 14H^+ &\rightarrow Cr^{3+} + 3Fe^{2+} + 7H_2O \quad (6) \\
6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ &\rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (7) \\
Fe^0 + Cu^{2+} &\rightarrow Cr^{0} + Fe^{2+} \quad (8) \\
3Cu^0 + Cr_2O_7^{2-} + 14H^+ &\rightarrow Cr^{3+} + 3Cu^{2+} + 7H_2O \quad (9) \\
Cr^{3+} + 3OH^- &\rightarrow Cr(OH)_3 \downarrow \quad (10) \\
Fe^{2+} + 2Cr^{3+} + 8OH^- &\rightarrow FeCr_2O_4 \downarrow + 4H_2O \quad (11)
\end{align*}
\]

As shown in Fig. 3, the main mechanism which is involved in Cr(VI) removal is the reduction of Cr(VI) to Cr(III) by the released electrons from the nFe\(^0\) core or by the Fe(II) ions released within the system (following Equations 6 and 7).

The presence of copper ions in the system (Cu\(^{2+}\)) can cause a redox effect after being reduced to the valent form (Cu\(^0\)) by nFe\(^0\), which later can act as an additional reductant in the system for Cr(VI) (following Equations 8 and 9).

Moreover, the formed Cr(III) could later either precipitate or co-precipitate with Fe(II) to form Cr/Fe (oxy)hydroxides (following Equations 10 and 11).

B. Statistical Regression

ANOVA statistical analysis coupled with multiple regression model was conducted considering three different dependent parameters; residence time (RT), reactive-mass ratio corresponding to the treated sectional area (RMR), and the cost of nFe\(^0\)/Cu (Cost). The response of the formerly mentioned parameters was optimized by maximizing RT and minimizing both of RMR and Cost towards the change in the independent variables; barrier’s thickness (b) and permeability (K\(_r\)) within a changing range of 0.2 - 4.2 m and 0.4 - 8 m/day, respectively.

Statistical analysis results showed that the quadratic model, with the highest correlation (R\(^2\) = 0.998) and adequate precision (107.94), was the best model to describe the multiple-regression relation between the model’s variables. The statistical significance of the proposed model was confirmed by the corresponding low p-values for the three responses cases (<0.0001). Hence, the following mathematical formula was considered to for the multiple regression [37], [38]:

\[
Y = \phi_0 + \sum_{i=1}^{3} \phi_i X_i + \sum_{i=1}^{2} \sum_{j=1}^{2} \phi_{ij} X_i X_j + \sum_{i=j}^{2} \phi_{ij} X_i X_j \quad (12)
\]

where, \(Y\) represents the response of the designated dependent factors, \(\phi_0\) stands for the model constant of interception, \(\phi_i\) is the linear coefficient, \(\phi_{ij}\) is the quadratic coefficient, \(\phi_{ij}\) is the coefficient of the interaction effect, \(X_i\) and \(X_j\) represent the two independent factors. Accordingly, the regression equations to describe the change in RT, RMR, and Cost corresponding to the variance in b and K\(_r\), are as follows:

\[
RT (day) = 14.981 + 1.910 b - 1.450 K_r + 0.201 b K_r + 1.297 b^2 - 0.025 K_r^2 \quad (13)
\]

\[
RMR (g/m^2) = 82.670 + 7.740 b - 1.040 K_r + 0.156 b K_r + 0.590 b^2 - 0.950 K_r^2 \quad (14)
\]
The calculated factor’s coefficients in Equations (13-15) indicate the contribution of each factor towards the change in the responses. The sign of the coefficient and the value represent the type of contribution, in terms of positive or negative, and the extent of the influence, respectively.

For better understanding of this point, the contribution percentage (CP) was estimated for each parameter based on the following equation [37]:

\[
CP(\%) = \frac{\text{Sum of squares for one factor}}{\text{Sum of squares}} \times 100
\]

Fig. 4. Contribution percentage (CP) of the independent variables toward the target responses; a) resident time (RT), b) reactive-mass ratio (RMR), and c) reactive mass cost (Cost).

The contribution percentage (CP) of the independent variables effect on RT, RMR and Cost is presented in Fig. 4. Results depicted that the linear coefficients of \( b \) and \( K_r \) had the highest contribution to the change in all the three dependent variables. However, in case of \( b \) the contribution was positive, unlike the case for \( K_r \) which had negative contribution. For RT, the quadratic coefficient (\( b^2 \)) had a relatively higher contribution comparing with the interaction coefficient and the quadratic one of \( K_r \), with CP value of +10.98. In case of RMR and Cost, the quadratic coefficient of hydraulic conductivity (\( K_r^2 \)) showed higher contribution than that of \( b^2 \) and \( bK_r \), with CP values of -10.17 and -6.19, respectively. Such results indicated the cruciality of the barrier thickness and its effect on RT and the importance of the hydraulic conductivity in case of RMR and material cost.

Fig. 5. Interaction effect on the target responses with respect to the change in independent factors a) resident time (RT), b) reactive-mass ratio (RMR), and c) reactive mass cost (Cost).

The positive effect of \( b \)-coefficients on the three dependent factors was confirmed by the interaction effect charts shown in Fig. 5. Results showed that the values of RT, RMR, and Cost within the nFe\(^{0}\)/Cu-PRB are influenced in a positive way with the increase in \( b \) value. Such trend was followed at both the high and the low changing values of \( K_r \). These findings were in good agreement with the regression
expressions indicating the proportional relationship between the three dependent variables and the barrier thickness.

C. Sensitivity Analysis

Sensitivity analysis was executed to evaluate the sensitivity of the dependent responses to the change of the two independent factors. The experimental estimation of $K_r$ (3.697 m/day) and an assumed starting value of $b$ (0.2 m) were considered as the base-line values for the change in those factors. The corresponding change range was at ±25, ±50, ±75 and ±100% from the base-line values.

Fig. 6. Sensitivity of the target responses to the change (%) in the independent factors; a) PRB-thickness ($b$), and b) PRB-permeability ($K_r$) [the change (%) in the independent variable is represented by the solid-axes lines (—), and the corresponding change in the responses values is represented by the dash-grid lines (---)].

Fig. 6 shows radar-chart of the sensitivity response of RT, RMR, and Cost towards the changes in $b$ and $K_r$. Results depicted that the highest sensitive parameter to the developed nFe$^0$/Cu-PRB model was $K_r$ within the barrier, corresponding to the highest response values in the three parameters; to reach the maximum response values of +8.7, +367.5, and +1233.06 for RT, RMR, and Cost, respectively. The sensitivity of the Cost to the change in both $b$ and $K_r$ was higher than that of RT and RMR. Moreover, both RMR and Cost were more sensitive to the changing ranges lower from the base-line values of $K_r$ than the higher ones. However, in case of $b$, the higher changing ranges resulted in more sensitive performance of RMR and Cost.

D. Optimization

In order to optimize the nFe$^0$/Cu-PRB design parameters with respect to their effect on the dependent variables, the 3D-response surface approach was considered. The interaction effect between the parameters was estimated by the change in the 3D-surface of each response, as shown in Fig. 7. Results indicated the proportional relation between RT, RMR and Cost and $b$ in all charts. On the other hand, the rise in $K_r$ values resulted in a decline trend in the three responses, corresponding to a negative effect. The influence of $K_r$ on RMR and Cost was significantly observed comparing with that in case of RT. Such results were in a great agreement with the formerly mentioned sensitivity analysis findings. Accordingly, its is clear that barrier thickness plays a crucial role in defining the residence time of the plume within the barrier. Furthermore, the decrease of the hydraulic conductivity of the barrier material could cause a depletion in the water velocity within the barrier and thereby more RT.

| Table II: Optimal Values for PRB-Design Parameters |
|-----------------|-----------------|-----------------|-----------------|
| Variable        | Sol. 1          | Sol. 2          | Sol. 3          |
| Independent factors | $b$ (m) | 0.651           | 0.650           | 0.666           |
| $K_r$ (m/day)    | 0.733           | 0.350           | 0.351           |
| RT (day)         | 15.794          | 16.309          | 16.366          |
| RMR (g/m$^2$)    | 86.761          | 87.514          | 87.464          |
| Cost ($)         | 182.73          | 183.33          | 183.56          |
| Desirability (%) | 0.864           | 0.756           | 0.761           |

Based on the 3D-response surface results, certain constraints were considered for the independent variables; ($b$ = 0.5 – 5 m) and ($K_r$ = 0.3 – 0.9 m/day), to determine the best optimal solutions towards achieving the optimization objectives represented as; maximizing RT, and minimizing both RMR and Cost. The selected optimal values were selected based on the desirability function, which basically transformed the removal efficiency response ($R \%$) into values ranged between 0 and 1, where 1 the most favorable condition [39], [40]. Three optimal solutions were found for the nFe$^0$/Cu-PRB design parameters and presented in Table 2. Considering the same conditions in terms of the initial Cr(VI) concentration and the targeted plume area, the best optimal solution with the highest desirability percentage of 86.4% showed values of the barrier thickness ($b$) and hydraulic conductivity ($K_r$) of 0.651 m and 0.733 m/day, respectively. The optimized responses corresponding to the formerly mentioned values were around 16 days, 87 g/m$^2$, and 183 $ for RT, RMR, and Cost. Such results confirmed the possibility of considering nFe$^0$/Cu-PRB as a feasible technology for groundwater decontamination from Cr(VI).
IV. CONCLUSION

In the current study nFe⁰/Cu was successfully employed in PRB technology for Cr(VI) removal from groundwater. Batch and column experiments were conducted to investigate the reactive performance of nFe⁰/Cu in Cr(VI) removal from aqueous solutions. Statistical optimization model was developed to describe the effect of the PRB design variables on the reactive/hydraulic/economic performance parameters. Detailed sensitivity analysis was conducted to define the most sensitive factors towards the model response. Batch experimental results confirmed the ability of 1 g/L dosage of the synthesized nFe⁰/Cu to remove around 85% of 20 mg/L initial Cr(VI) concentration over 3 hours reaction time without any desorption to occur. Moreover, column experiments depicted the feasibility of nFe⁰/Cu to be used as a reactive material within the PRB to remove Cr(VI) from groundwater by a consistent removal efficiency with that of batch tests. The main pathways for Cr-species removal by nFe⁰/Cu were determined as the reduction of Cr(VI) to Cr(III) by both nFe⁰ and Cu⁰ and the precipitation/co-precipitation of Cr(III) with the released iron oxides on the nFe⁰/Cu surface. ANOVA statistical analysis showed that the quadratic model was the best model to describe the regression relation between the model parameters with correlation percentage of 99.8%. Findings of sensitivity analysis and interaction effects depicted the proportional correlation between residence time of the plume within the barrier and the barrier thickness and confirmed that reactive mass ratio and cost were inversely proportional to the hydraulic conductivity of the barrier’s material. The 3D-surface response optimization model confirmed the cruciality of the preliminary design of PRB in terms of the suitable residence time (RT), thickness (b) and hydraulic conductivity (Kₚ) towards effective remediation performance. The outcome of the current research should be a seed for further studies on investigating the designing factors for PRBs. A crucial aspect which should be considered beyond this work is focusing on the simulation of the real-field conditions by considering field PRB-data to confirm the validity of such optimization techniques in the preliminary PRBs design. Also, employing more PRB materials with different modified reactive features, such as coated nanomaterials and environmentally friendly adsorbents, could be another important direction for further studies. In conclusion, the current work could represent a great contribution and a vital step towards an accurate PRB’s design based on a previously determined optimal conditions.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors have contributed equally to the present work and the final version is approved accordingly.

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