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Analysis of Response Surface and Artificial Neural Network for Cr(VI) Removal Column Experiment

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Abstract: In this study, inexpensive, environmentally friendly, and biodegradable cellulose filter paper was used to load nano zero-valent iron (nZVI), effectively improving the dispersibility of nZVI and successfully preparing the supported modified cellulose filter paper (FP-nZVI). Subsequently, the capacity of FP-nZVI to remove Cr(VI) in a flow system was explored. FP-nZVI was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Traditional single-factor experiments often require a large number of repeated experiments when analyzing the interactions among multiple variables, resulting in a long experimental cycle and high consumption of experimental materials. This research used the Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD) and the Artificial Neural Network (ANN) to optimize and predict the removal process of Cr(VI). This RSM investigated the interactions between the response variable (Cr(VI) removal rate) and the independent variables (Cr(VI) concentration, pH value, and flow rate). A highly significant quadratic regression model was constructed, which was proven by a high F value (93.92), an extremely low p -value (<0.0001), and a high determination coefficient ($R^2 = 0.9918$). An ANN model was established to forecast the correlation between independent variables and the removal rate of Cr(VI). Both models demonstrate remarkable consistency with the experimental data; however, from the perspective of statistical parameters, the ANN model has more significant advantages; the coefficient of determination R^2 reaches 0.9937, which is higher than that of RSM (0.9918); the values of indicators such as MSE, RMSE, MAE, MAPE, AAD, and SEP are all smaller than those of RSM. The ANN exhibits greater excellence in prediction error, value fluctuation, and closeness to the actual value and has a more excellent prediction ability. The experiment for treating Cr(VI) with FP-nZVI was optimized, achieving good results. Meanwhile, it also provides a valuable reference for similar experimental studies.



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Keywords: nZVI; cellulose filter paper; response surface methodology; artificial neural network; Cr(VI) removal

1. Introduction

Groundwater is not only a vital source of drinking water but also a key factor in maintaining the stability of the ecosystem, playing a crucial role in ensuring human life and ecological balance. In recent years, with the accelerated global industrialization process, the problem of groundwater pollution has become increasingly severe. Among various pollutants, chromium pollution has become a major concern in the environmental field because of its high toxicity and wide distribution [1]. Cr(VI) has been leaked and discharged irrationally, leading to a large amount of chromium entering groundwater

and surface water bodies, causing serious damage to the ecological environment [2,3]. The forms of chromium's existence are usually Cr(III) and Cr(VI) [4–7]. Cr(VI) is more harmful, highly water-soluble and mobile, and is carcinogenic and teratogenic [8–11]. Therefore, the treatment of Cr(VI) pollution has become a crucial issue in the field of environmental protection.

In previous studies, scholars have put forward a variety of treatment methods (physical [12], chemical [13], and biological methods [14]) to remove Cr(VI). Physical methods include adsorption [15,16], ion exchange [17,18], and membrane separation [19]; chemical methods include coagulation-sedimentation [20], oxidation-reduction [21], electrochemical methods [22–24], and photocatalytic technology [25,26]. However, all these methods have certain limitations. Some physical and chemical methods are often costly [27,28] and generate secondary chemical sludge [29]. Biological methods have strict requirements for environmental conditions, and it is difficult to effectively translate laboratory results into practical applications [30,31]. Owing to its benefits like wide applicability, affordability, and environmental friendliness, the adsorption methodology ranks among the most effective approaches for heavy metal elimination [32].

nZVI is an environmentally friendly material characterized by a large specific surface area and strong reducibility [33]. In comparison with other nanomaterials, iron has the advantages of low cost and simplicity in preparation and modification [34]. nZVI also has the performance of removing heavy metals [35,36], and some studies have confirmed that nZVI can effectively remove Cr(VI) [37]. However, nZVI has problems such as easy agglomeration and easy oxidation in practical applications [38], resulting in a relatively low effective utilization rate of the material. In order to overcome the above problems, scholars have carried out a series of modification studies, mainly using technologies such as porous material loading [39], surfactant modification [40], and bimetallic modification [41–43]. However, these methods have certain defects. For example, bimetallic materials are costly, and heavy metals may be released during the process of introducing another metal [44], causing secondary pollution. Surfactant modification may block the reaction channels and electron transfer [45,46], weakening the ability to remove pollutants. The porous material loading technology can not only retain the advantages of bimetallic composite and surface modification but also further enhance the dispersion degree of nZVI and the adsorption and reduction ability of pollutants through the synergistic effect between the carrier and nZVI. Currently, in relevant studies, microspherical or powdery materials such as bentonite and biochar are often used as carriers for nZVI. However, this type of carrier material has the problem of difficult separation in practical applications, and some materials may also cause secondary pollution [47]. Therefore, developing a new type of insoluble, environmentally friendly carrier that will not block the flow system to fix nZVI is of great significance for the efficient application of nZVI.

Cellulose is a natural polymer compound with biodegradable properties and is an environmentally friendly material. Due to its low cost, good stability, abundant reserves, and renewability, it has been widely used in many fields. Cellulose filter paper (FP), as a cellulose product, is often used as an adsorbent or an adsorbent carrier and is applied in the sphere of water pollution control [48,49]. The FP material contains rich functional groups, such as -COOH, -OH, etc. These functional groups can serve as binding ligands to combine with metal ions, creating favorable conditions for the adsorption and modification of the material [50]. Therefore, cellulose filter paper can be considered a good carrier for nano zero-valent iron.

In terms of experimental design and optimization, traditional experiments adopted the single-factor variable control method, where only one parameter was changed while the remaining parameters were kept constant. This requires a large number of repeated

experiments, consuming a great deal of time and chemical reagents, and it is difficult to analyze the interactions among multiple variables [51]. The RSM is a powerful predictive modeling technique that can optimize multiple independent variables simultaneously and evaluate the interactions among them, thus determining the optimal experimental conditions. It shortens the experimental cycle, reduces the consumption of experimental materials [52], and has been extensively applied in the realm of scientific inquiry [53–57]. The BBD is a frequently employed experimental design approach within response surface methodology. Compared with the central composite design [58], it can effectively explore the response surface with a relatively small number of experiments. In addition, due to its powerful modeling ability, the ANN can capture the highly complex relationships between variables, establish accurate connections between input and output parameters, have excellent self-learning ability, and can be widely applied in the field of scientific research [59–63]. In this study, the ANN model introduced increases the number of hidden layers. Compared with studies that use fewer hidden layers, the coefficient of determination has been improved, and key error indicators have decreased. More combinations of neurons can extract the deep-seated features of the data, bolstering the model's capacity to simulate and forecast data.

In this study, An environmentally friendly cellulose filter paper with nZVI incorporated into it was fabricated, which effectively improved the dispersibility of nZVI. SEM, FTIR, and XRD were used to characterize FP-nZVI, and the microstructure, functional group composition, and crystal structure characteristics of FP-nZVI were analyzed. Subsequently, a column experiment was carried out to eliminate Cr(VI) from water using FP-nZVI, and Cr(VI) removal efficiency by FP-nZVI was calculated at varying concentrations (10, 20, 30 mg/L), flow rates (1, 3, 5 mL/min), and pH levels (3, 5, 7). In order to avoid conducting plenty of repetitive experiments, which are time-consuming and consume a lot of materials, and to explore the interactions among various variables, RSM and ANN were employed to optimize and forecast the removal efficiency. Through important indicators such as the goodness of fit, MSE, RMSE, MAE, MAPE, AAD, and SEP, the prediction performances of ANN and RSM were compared, and the prediction results of the two models were compared and analyzed with the experimental data. Finally, the advantages and disadvantages of the existing models were discussed, the deficiencies of this study were summarized, and suggestions for future research were put forward so as to provide guidance for the prediction, optimization, and large-scale application of FP-nZVI in water treatment.

2. Materials and Methods

2.1. Materials and Reagents

The ashless cellulose filter paper (FP) was sourced from Whatman in the UK. Key chemicals, including sodium hydroxide (NaOH) and hydrochloric acid (HCl), were procured from Beijing Chemical Works. Additional reagents—ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), sodium borohydride (NaBH_4), and acetone ($\text{C}_3\text{H}_6\text{O}$)—were supplied by Fuchen Chemical Reagent Factory in Tianjin. All chemicals used were of analytical grade purity.

2.2. Material Preparation

First, dissolve 8.6495 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ into 40 mL of ethanol to make a 0.8 M iron solution. Then, dissolve 0.4 g of NaOH in 100 mL of deionized water. Immerse four pieces of ashless cellulose filter papers (FP, from Whatman, Maidstone, Kent, UK) in this solution. After 30 min, take out the filter papers and rinse them using deionized water until the rinse's pH level approaches neutral. Submerge the cleaned filter papers in the iron bath for

40 min, then remove them and allow them to air-dry to yield yellow filter papers. Dissolve 1.9 g of Sodium Borohydride within 100 mL of distilled water to create a reducing reagent. Immerse the yellow filter papers directly into the NaBH_4 solution for 45 min to synthesize black magnetic papers (FP-nZVI). Thoroughly wash the composite material (FP-nZVI) with absolute ethanol. Finally, transfer it to a freeze-drying oven for 600 min of vacuum drying.

2.3. Characterization

The material was characterized using a JEM-7001M produced by JEOL (Tokyo, Japan), an IRAffinity-1S manufactured by Shimadzu Corporation (Tokyo, Japan), and a D8 Advance made by Bruker (Karlsruhe, Germany).

2.4. Experiment Design

To evaluate the ability of the FP-nZVI composite material to remove Cr(VI), column experiments were carried out. An acrylic plexiglass column was used in the experiment, with dimensions of 18 cm in length, 3 cm in inner diameter, and 0.3 cm in wall thickness. The column was filled with FP-nZVI and quartz sand. Specifically, the base of the column featured 2-cm-tall glass beads, followed by quartz sand and FP-nZVI (placed in the central position), as shown in Figure 1. Finally, glass beads with a dimension of 2 cm in height were filled at the top of the column to stabilize the effluent. The glass beads have the property of making the adsorbate solution evenly distributed. During the whole operation, the consistency of the packing material in the column was guaranteed. A variable-speed peristaltic pump was employed to link the Cr(VI) solution at a known concentration to the glass column using latex tubing, enabling the quantitative injection of the solution into the glass column. The Cr(VI) liquid streams from the base to the summit of the column. All experimental procedures were executed at ambient temperature.

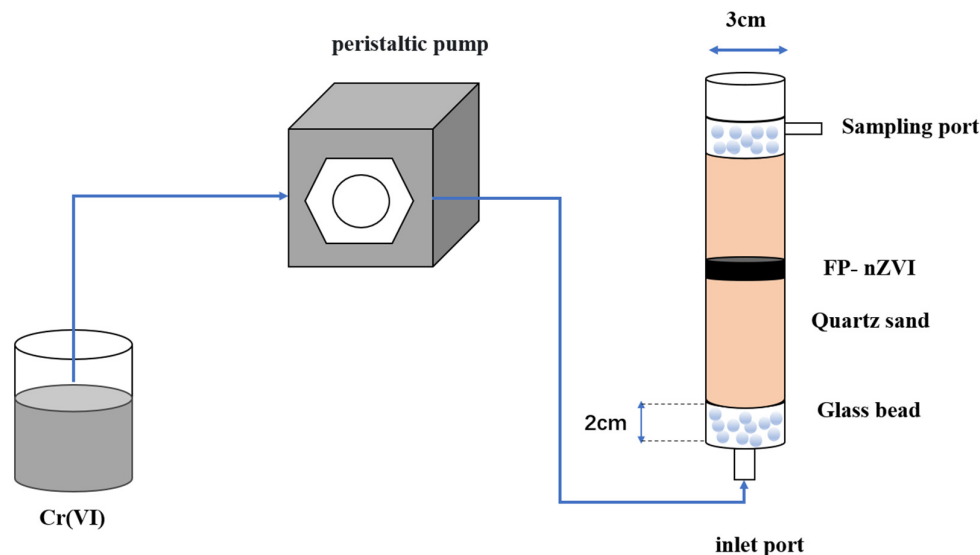


Figure 1. Diagram of the sand column experiment device.

Studies were performed using the experimental configuration presented in Figure 1 under various conditions of pH values (3, 5, and 7), Cr(VI) concentrations (10, 20, and 30 mg/L), and flow rates (1, 3, and 5 mL/min). The column was rinsed with deionized water until it was saturated, and then the Cr(VI) solution was pumped in. Measure the concentration of the effluent at the same time intervals and then plot the breakthrough curve for subsequent analysis. In the experimental process, three parallel tests were conducted on the concentration of the collected effluent. The average value of the obtained data was

taken as the measured value of this sampling point so as to reduce experimental errors and ensure the accuracy of the data.

2.5. Analysis of Experimental Data

2.5.1. Column Experiment Analysis

The total removal amount (q_{total}) of Cr(VI) on the adsorbent and the equilibrium adsorption capacity (q_{eq}) could be computed from the area beneath the breakthrough curve (Figure 2) via the integration approach. The specific calculation formulas are as follows:

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000} \int_0^{t_{total}} (C_0 - C_t) dt \quad (1)$$

$$q_{eq} = \frac{q_{total}}{m} = \frac{QC_0 \int_0^{t_{total}} \left(1 - \frac{C_t}{C_0}\right) dt}{1000m} \quad (2)$$

where A is the area above the breakthrough curve; q_{eq} is the mass of Cr(VI) (mg/g) adsorbed and reduced per unit mass of FP-nZVI in the column; m is the mass of the adsorbent (mg). The total mass of the influent Cr(VI) is determined by the following Formula (3):

$$W_{total} = \frac{C_0 Q t_{total}}{1000} \quad (3)$$

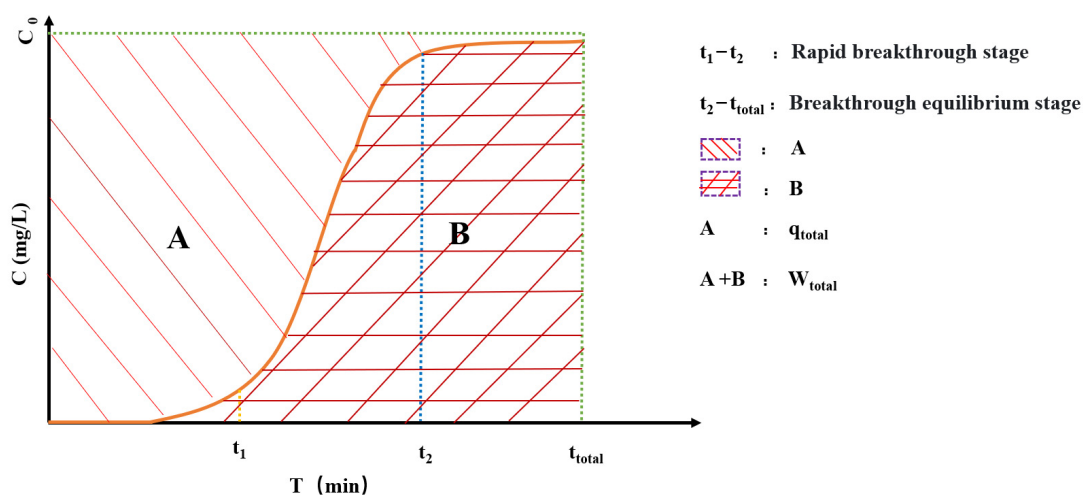


Figure 2. Schematic diagram of the breakthrough curve.

The total removal rate of Cr(VI) is derived from Formula (4):

$$r = \frac{100q_{total}}{W_{total}} \% = \frac{100 \int_0^{t_{total}} \left(1 - \frac{C_t}{C_0}\right) dt}{t_{total}} \% \quad (4)$$

2.5.2. Response Surface Methodology

RSM represents a statistical and mathematical approach applied to efficiently address and resolve multivariate issues [64]. RSM carries out data fitting analysis through a series of rationally designed experiments and multiple regression analysis methods to estimate the functional relationship between the studied response variables and the independent variables concerned with the single factor test [65]. The testing process is defined as the conversion of the input independent variables into the response variables of several outputs, and the statistical model is established by the response surface method [66].

In this study, the independent variables include the pumping flow rate of the peristaltic pump, pH value, and Cr(VI) concentration; the response variable is the removal rate of

Cr(VI). The BBD method using Design Expert software version 13 was employed to analyze, compare, and optimize the studied response variable by combining the independent variables, so as to obtain the influence of this combination on the response variable under different conditions.

Subsequently, single-factor experiments were carried out, and on this basis, the BBD was further adopted for exploration. In this BBD, three levels (−1, 0, +1) were set for each research factor. To accurately estimate the experimental error, five repeated experiments were conducted at the central point ($Q = 3$ mL/min, $pH = 5$, $C_0 = 20$ mg/L). The objective of this investigation was to assess the precise impacts of the pumping flow rate of the peristaltic pump, the starting Cr(VI) concentration, and the solution pH on the Cr(VI) elimination rate when 0.38 g of adsorbent was deployed. The factors, values, and coded levels are as follows: the starting concentration of Cr(VI) (A): 10 (−1), 20 (0), 30 (+1); the flow rate (B): 1 (−1), 3 (0), 5 (+1); the pH value (C): 3 (−1), 5 (0), 7 (+1) (Table 1). The specific experimental design is in Table 2.

Table 1. Factors and corresponding levels for experimental design optimization via BBD.

Factor	Units	Levels		
		−1	0	+1
Flow rate	mL/min	1	3	5
pH	-	3	5	7
Concentration of Cr(VI)	mg/L	10	20	30

Table 2. Cr(VI) removal rate under optimized trivariate conditions when the amount of adsorbent is 0.38 g.

Experiment No.	C_0 (mg/L)	Q (mL/min)	pH	r Experimental (%)	r RSM (%)	r ANN (%)
1	20	5	3	27.85	27.48	27.85
2	30	1	5	31.38	31.35	31.38
3	20	3	5	36.12	37.12	36.93
4	10	1	5	32.56	32.39	32.56
5	10	3	3	35.83	36.17	35.83
6	20	3	5	37.65	37.12	36.93
7	20	1	7	24.19	24.56	24.36
8	20	3	5	37.74	37.12	36.93
9	10	3	7	30.04	29.84	30.08
10	30	3	7	28.61	28.27	28.61
11	30	5	5	27.25	27.42	27.25
12	30	3	3	31.94	32.14	31.94
13	10	5	5	31.94	31.97	31.94
14	20	3	5	36.96	37.12	36.93
15	20	5	7	29.31	29.48	29.31
16	20	1	3	36.92	36.75	37.11
17	20	3	5	37.15	37.12	36.93

The optimization of the response performance of FP-nZVI for Cr(VI) in this experiment was based on the response level, process optimization, and analysis of variance (ANOVA) under a second-order polynomial equation. The optimization analysis of the independent

variables and response variables was performed by the obtained fitted model with the equations shown below.

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k b_{ij} x_i x_j \quad (5)$$

where Y is the estimated response value of Cr(VI) removal, b_0 , b_i , b_{ii} , b_{ij} denote coefficients, and x_i , x_j signifies independent variable factors.

2.5.3. Artificial Neural Network

ANN, with its excellent data-processing capabilities, is widely used in the fields of data simulation and prediction [67–69]. In this study, the hyperbolic tangent sigmoid activation function (tansig) and the identity activation function (purelin) were employed to link the hidden layer and the output layer of the neural network. A three-layer feedforward-backpropagation network was used to train the model network (the network structure's schematic illustration is presented in Figure 3). The transfer function shown in Equation (6) was used to simulate the ability of FP-nZVI to remove Cr(VI). In total, 17 experimental data were employed in the ANN modeling. To eliminate the impact of data magnitude differences on the model, the data were normalized. We partitioned the dataset into training, validation, and test subsets, allocating 70%, 15%, and 15% of the data, respectively. The numbers of data used in the network training, validation, and test stages were 11, 3, and 3, respectively. The Levenberg–Marquardt backpropagation algorithm was employed to conduct the network training of the model. The network topology was set with three input nodes, corresponding to the initial concentration of Cr(VI), the pH value, and the inflow rate, respectively; the output node was the removal rate of Cr(VI). In this study, Matlab R2021b was used for ANN modeling, and various statistical parameters were utilized to evaluate the model performance of RSM and ANN. The specific calculation equations are shown in Table 3.

$$f(x) = \frac{1}{1 + \exp(-x)} \quad (6)$$

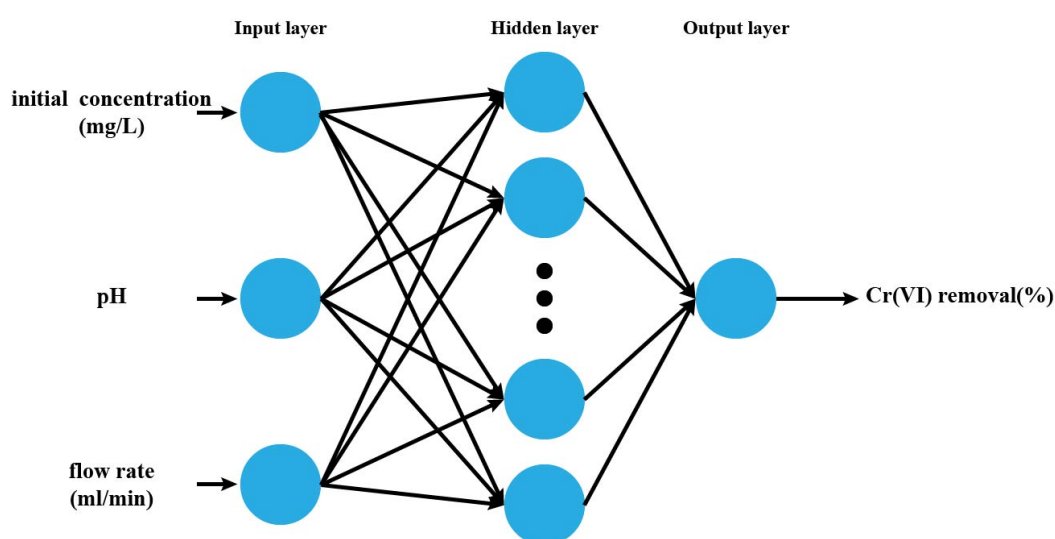


Figure 3. Schematic illustration of the structure of an artificial neural network.

Table 3. Various statistical parameters and their mathematical expressions.

Statistical Parameter	Mathematical Expression
Root Mean Square Error (RMSE)	$\sqrt{\frac{1}{n} \sum_{i=1}^n (y_{i,exp} - y_{i,pred})^2}$
Mean square errors (MSE)	$\frac{1}{n} \sum_{i=1}^n (y_{i,exp} - y_{i,pred})^2$
Mean Absolute Percentage Error (MAPE)	$\frac{100\%}{n} \sum_{i=1}^n \frac{ y_{i,exp} - y_{i,pred} }{ y_{i,exp} }$
Mean Absolute Error (MAE)	$\frac{1}{n} \sum_{i=1}^n y_{i,exp} - y_{i,pred} $
Absolute Average Deviation (AAD)	$\frac{1}{n} \sum_{i=1}^n y_{i,exp} - y_{i,pred} * 100$
Standard Error of Prediction (SEP)	$\frac{y_{i,exp} RMSE}{y_{i,exp}}$

3. Results and Discussion

3.1. Characterizations

3.1.1. SEM Analysis

Scanning electron microscopy (SEM) was employed to characterize the surface morphologies of the filter paper, unmodified nZVI, and the modified FP-nZVI. As shown in Figure 4a,b, the surface of the fiber strips of the filter paper is slightly rough. The interconnections between them form fiber channels, which are conducive to the loading of nanoiron particles. Besides, the intrusion of nanoiron particles into fiber channels' inner space effectively retards oxidation. Figure 4c reveals substantial agglomeration of unmodified nZVI. Van der Waals forces and magnetic effects primarily drive this agglomeration [70]. Figure 4d,e indicates that the nanoiron particles of the modified composite material FP-nZVI are distributed in chains or exist as separate dispersions. The particles are irregular spheres with a uniform particle size of about 50–80 nm. This shows that the ethanol solution added during the preparation process has a certain dispersing effect on the nanoiron particles. Ethanol molecules contain a large number of hydroxyl groups. The strong polarity of the hydroxyl functional groups can combine with iron ions to form chelate bonds, constructing a certain spatial structure that prevents the aggregation phenomenon caused by magnetism and intermolecular forces during the formation of nanoiron particles [71]. This structure enables the nanoiron particles to be dispersed on the surface of the cellulose filter paper and prevents large-scale agglomeration, which is also consistent with relevant research [72].

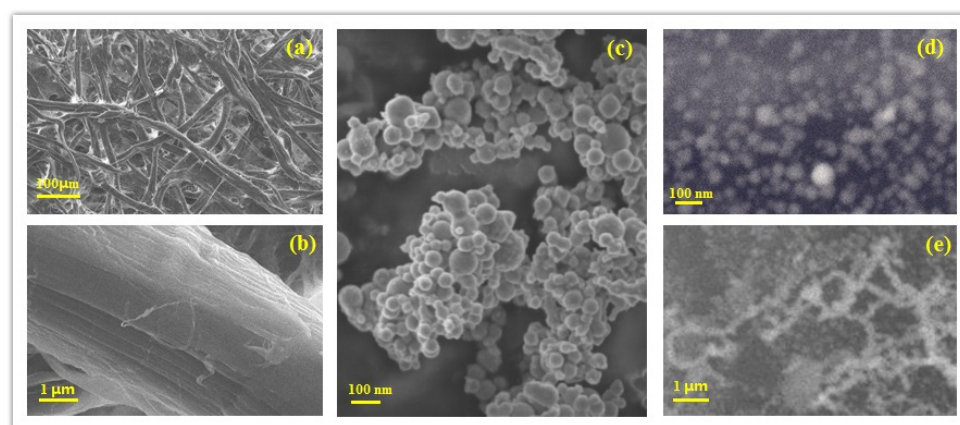


Figure 4. (a,b) SEM images of untreated filter paper; (c) SEM image of unmodified nano zero-valent iron; (d,e) SEM images of the composite FP-nZVI.

3.1.2. FTIR Analysis

Fourier transform infrared (FTIR) spectroscopy was employed to analyze FP and FP-nZVI. As shown in Figure 5, characteristic peaks were manifested at 3317 cm^{-1} , 2893 cm^{-1} , 1653 cm^{-1} , and 1049 cm^{-1} . These characteristic peaks were attributed to the stretching of -OH, -CH₂, H-O-H, and the stretching of C-O and C-C, respectively [73,74]. However, when nZVI was loaded onto FP, the peak at 1653 cm^{-1} in the spectrum of FP-nZVI almost disappeared. New peaks appeared at 1743 cm^{-1} and 1691 cm^{-1} , which could be regarded as the asymmetric stretching of carboxyl groups. Therefore, the FTIR results indicated that nZVI had been successfully embedded in FP. Nevertheless, the C-O and C-C stretching bonds of cellulose at 1049 cm^{-1} remained almost unchanged, suggesting that there was no substantial change in the ring structure of the cellulose filter paper.

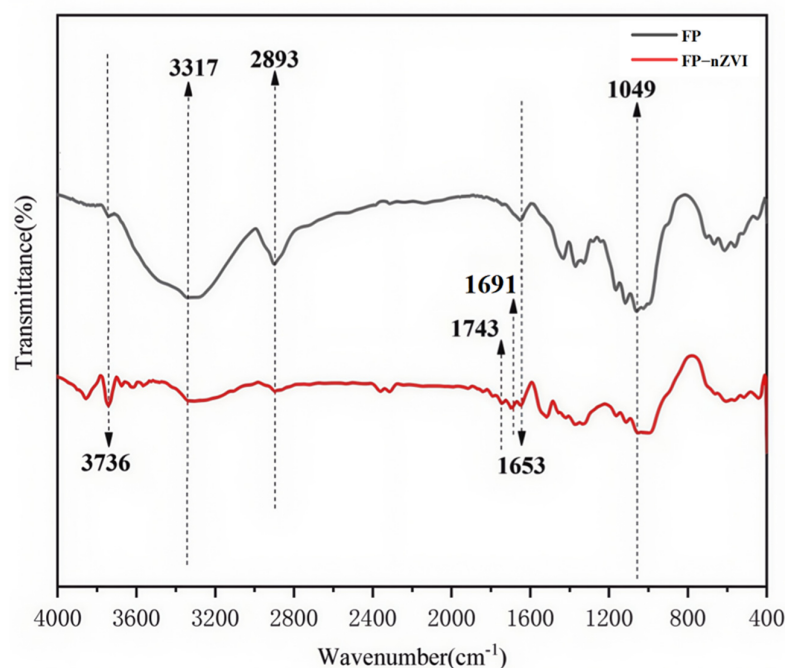


Figure 5. FTIR image of FP and FP-nZVI.

3.1.3. XRD Analysis

Figure 6 depicts the XRD patterns of the FP and FP-nZVI. The picture on the right is an enlarged view of the area within the dashed box in the left picture. At diffraction angles of $2\theta = 14.8^\circ$, 16.6° and 23.1° , these angles correspond to the $(1\bar{1}0)$, (110) , and (200) diffraction peaks of cellulose, respectively [75]. As can be observed from the patterns, for the fabricated composite material FP-nZVI, a diffraction peak corresponding to the (110) crystal plane of α -Fe emerges at $2\theta = 44.68^\circ$, which suggests that the synthesized iron exists in the form of zero-valent iron [76]. However, a characteristic peak of FeOOH appears around $2\theta = 39.21^\circ$, suggesting that the prepared nano zero-valent iron has undergone a certain degree of oxidation.

3.2. Response Surface Analysis

A BBD design was performed using three independent variables, flow rate, concentration, and pH, and statistically significant nonlinear regression equations were established by Expert Design version 13 using the conventional analysis of variance (ANOVA) method. The ANOVA results showed that the reductive adsorption effect of Cr(VI) on FP-nZVI was better explained using a quadratic model containing the interaction parameters, and the obtained quadratic equations were as follows.

$$\text{Cr(VI) removal} = 37.12 - 1.40 \cdot A - 1.09 \cdot B - 2.55 \cdot C - 0.88 \cdot AB + 0.61 \cdot AC + 3.55 \cdot BC - 2.15 \cdot A^2 - 4.19 \cdot B^2 - 3.37 \cdot C^2$$

where A is the Cr(VI) initial concentration, B is the flow rate, and C is the pH value.

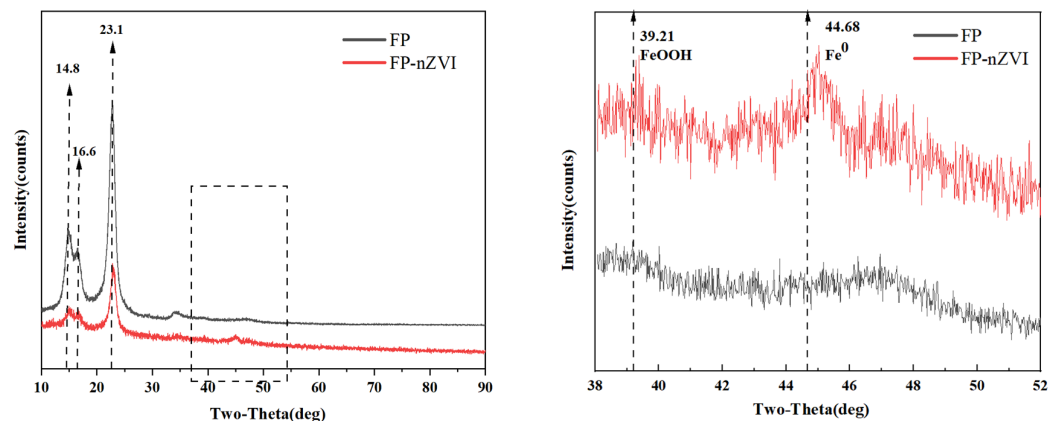


Figure 6. XRD characterization of FP and FP-nZVI.

An analysis of variance was conducted on the second-order model, and the results are presented in Table 4. With an F-value of 93.92 and a *p*-value less than 0.05, the model and all its terms are statistically significant [77]. This means that the initial concentration of Cr(VI), pH, and flow rate have a significant influence on the experimental results. The R^2 and adj. R^2 of the model are 0.9812 and 0.9526, respectively, suggesting that the model has a good fit [78]. The fitting situation between the experimental values and the model-predicted values can be visually compared in Figure 7. The Lack-of-Fit F-value is 0.55, indicating that the lack-of-fit factors have an insignificant impact on the model. There is a 67.55% probability that an F-value higher than the current level of 93.92 may occur due to noise interference [79]. However, based on a comprehensive assessment of various indicators, the model remains stable and reliable overall and can effectively predict and analyze the experimental results.

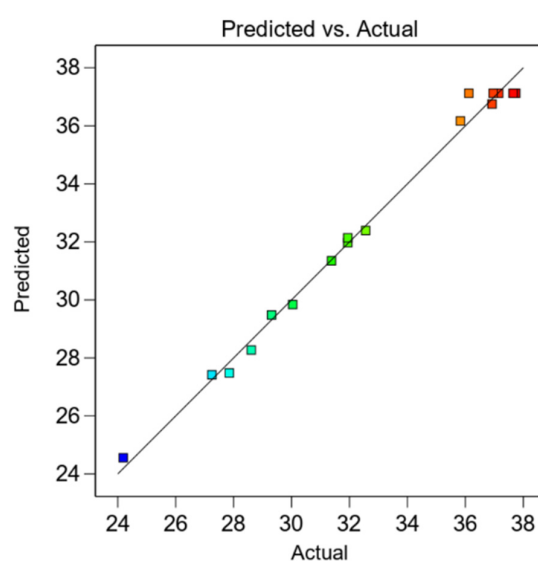
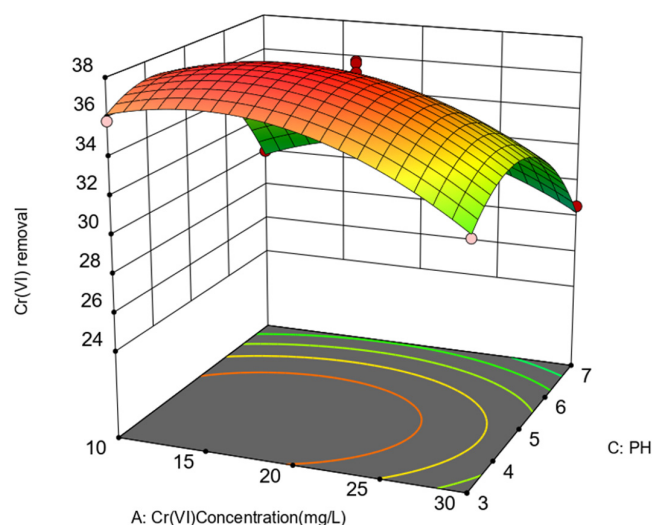


Figure 7. Scatter plot of actual and predicted values of Cr(VI) removal by FP-nZVI.

Table 4. Anova for Response Surface Quadratic model of column system.

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	
Model	288.27	9	32.03	93.92	<0.0001	significant
A-Cr(VI) concentration	15.65	1	15.65	45.89	0.0003	
B-Flow rate	9.46	1	9.46	27.74	0.0012	
C-pH	51.97	1	51.97	152.38	<0.0001	
AB	3.08	1	3.08	9.03	0.0198	
AC	1.51	1	1.51	4.44	0.0732	
BC	50.34	1	50.34	147.60	<0.0001	
A ²	19.50	1	19.50	57.17	0.0001	
B ²	73.90	1	73.90	216.69	<0.0001	
C ²	47.73	1	47.73	139.96	<0.0001	
Residual	2.39	7	0.34			
Lack of Fit	0.70	3	0.23	0.55	0.6755	not significant
Pure Error	1.69	4	0.42			
Cor Total	290.66	16				
R ² = 0.9918						

The 3D surface maps were plotted to observe the interactions of the independent variables, as shown in Figures 8–10. It can be observed that the surfaces of the plotted images are continuously varying and of different shapes, which better describes the different degrees of nonlinear interactions between the independent variables.

**Figure 8.** The 3D response surface plot for the pH and Cr(VI) concentration.

The interaction of chromium solution concentration and pH on chromium removal is shown in Figure 8. It can be observed that at any fixed pH, the removal rate showed a small increasing trend from 10 mg/L to 20 mg/L with increasing concentration and was at a high level, while the removal rate showed a large decreasing trend when the concentration increased from 20 mg/L to 30 mg/L. This is mainly due to the fact that at a concentration of 10 mg/L, the smaller concentration gives the chromium ion and FP-nZVI material sufficient reaction time, while the lower chromium solution concentration makes the reflection time longer, and the FP-nZVI material still maintains a certain reduction and adsorption capacity after the rapid penetration period, which makes the overall reaction time of the column system longer and the calculated removal rate slightly decreases compared with 20 mg/L. At a chromium concentration of 30 mg/L, the larger chromium concentration caused the FP-nZVI material to penetrate in a faster time compared to the other two concentrations,

and a large amount of Cr(VI) at high concentrations did not have time to react with FP-nZVI for adsorption, and the adsorption sites were occupied quickly, and the nZVI was reduced by a more rapid reaction, making the calculated removal rate lower. Secondly, it can be observed that the removal rate shows a decreasing trend with the gradual increase of pH at any fixed concentration. This phenomenon is due to the fact that chromium ions are easily bound by hydroxide in an alkaline environment, which affects the reduction and adsorption of Cr(VI) with FP-nZVI, resulting in a decrease in the removal rate.

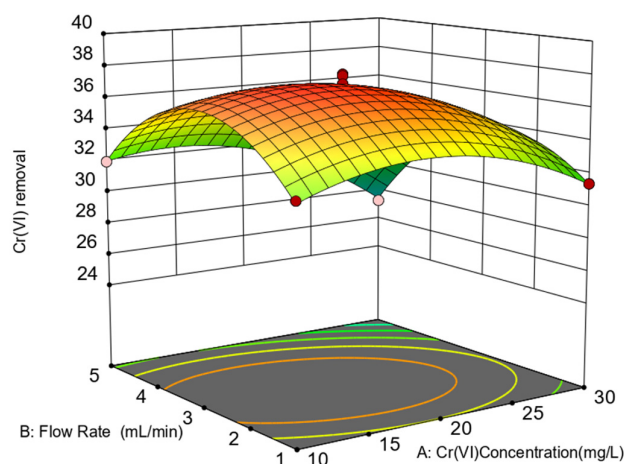


Figure 9. The 3D response surface plot for the flow rate and Cr(VI) concentration.

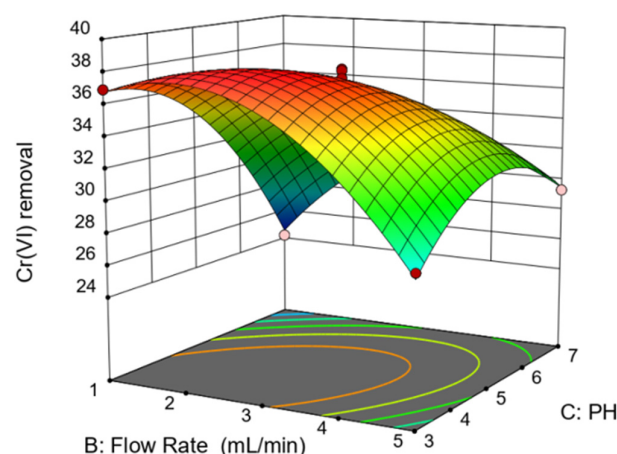


Figure 10. The 3D response surface plot for the pH and flow rate.

The interaction between chromium solution concentration and influent flow rate on chromium removal is shown in Figure 9, where it can be observed that the removal rate tends to increase with decreasing influent flow rate at any fixed concentration, and the Cr(VI) removal rate was higher. When the inlet flow rate increased to 5 mL/min, the faster inlet flow rate made the FP-nZVI material too late to adsorb and react with chromium ions, which made the material adsorption and reaction sites saturated rapidly, resulting in a faster penetration rate and a relatively low overall removal rate. Secondly, when the influent flow rate was controlled at a fixed value, the Cr(VI) removal rate also showed higher at low Cr(VI) concentrations and lower at high Cr(VI) concentrations.

The interaction between pH and influent flow rate on chromium removal is shown in Figure 10. It can be observed that when controlling any variable of pH or influent flow rate, the removal rate showed a similar pattern as above, i.e., the removal rate of Cr(VI) was higher under acidic conditions compared to alkaline conditions, and the removal rate of Cr(VI) was higher at lower influent flow rates compared to higher flow rates.

3.3. ANN Evaluation

The L-M backpropagation algorithm was used to conduct experiments on different numbers of hidden layer neurons. By adjusting the network parameters, a three-layer ANN model was established based on 17 sets of experimental data to obtain the optimal structure that is suitable for the experimental results. To develop and train the model, all 17 datasets underwent random division. Specifically, they were split into a training set, a validation set, and a test set following a ratio of 11:3:3. After multiple rounds of training, it was found that when the number of hidden layer neurons was 8, the model had good fitting performance, and the coefficient of determination R^2 reached 0.9937. The regression plot of the model depicts the linear association between the actual and the predicted values of the ANN model during training, validation, testing, and for the entire dataset. As shown in Figure 11, all experimental results fall on or are close to the parity line, and the R^2 value of each dataset is above 0.99, which well reflects the high consistency and correlation between the ANN model and the experimental results. Secondly, by comparing the predicted values of the model with the actually obtained experimental values, it was found that the predicted values fit well with the actual values. The comparison between the predicted values and the actual values obtained by the model is shown in Figure 12.

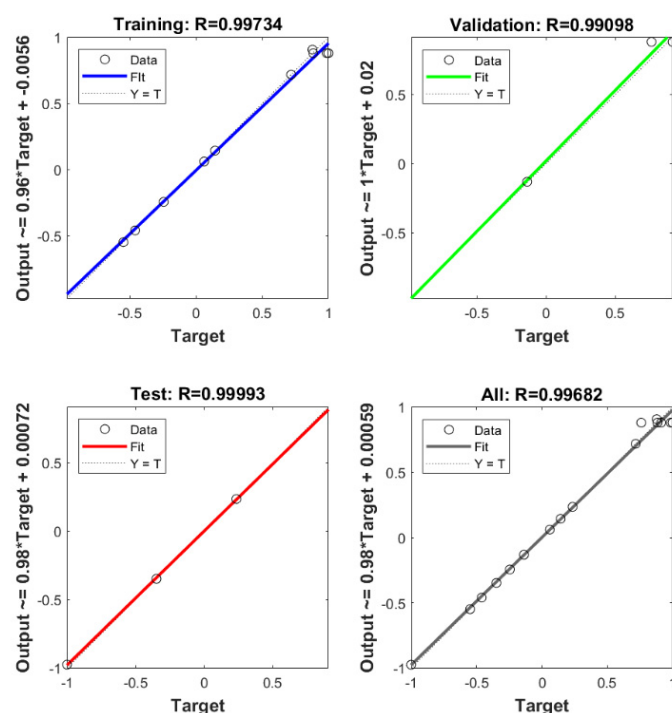


Figure 11. Regression plots of ANN model for Cr(VI) removal using FP-nZVI.

Figure 13a shows the relationship between the mean squared error (MSE) and the number of epochs of the ANN model. At the 4th training epoch, the training stopped, and the validation set achieved the best performance with an MSE of 0.0060782, which is acceptable and significantly lower than those of the validation and test sets, indicating that the model fits well on the training set.

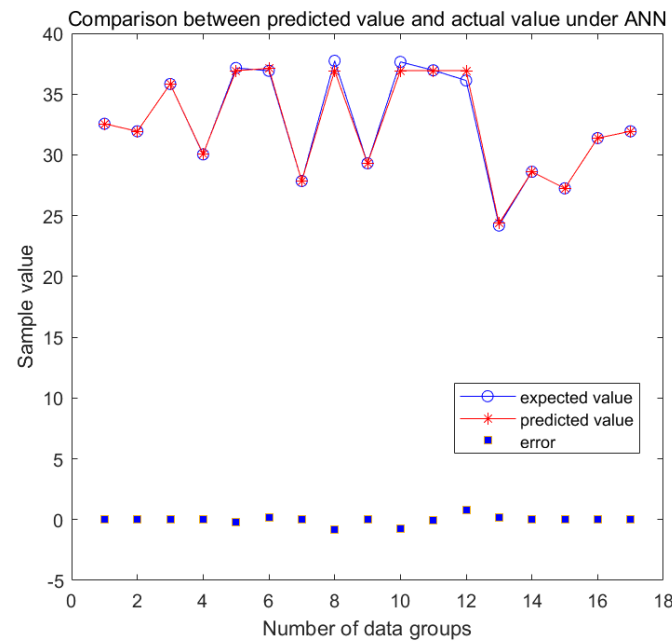


Figure 12. Comparison between predicted and actual value under ANN.

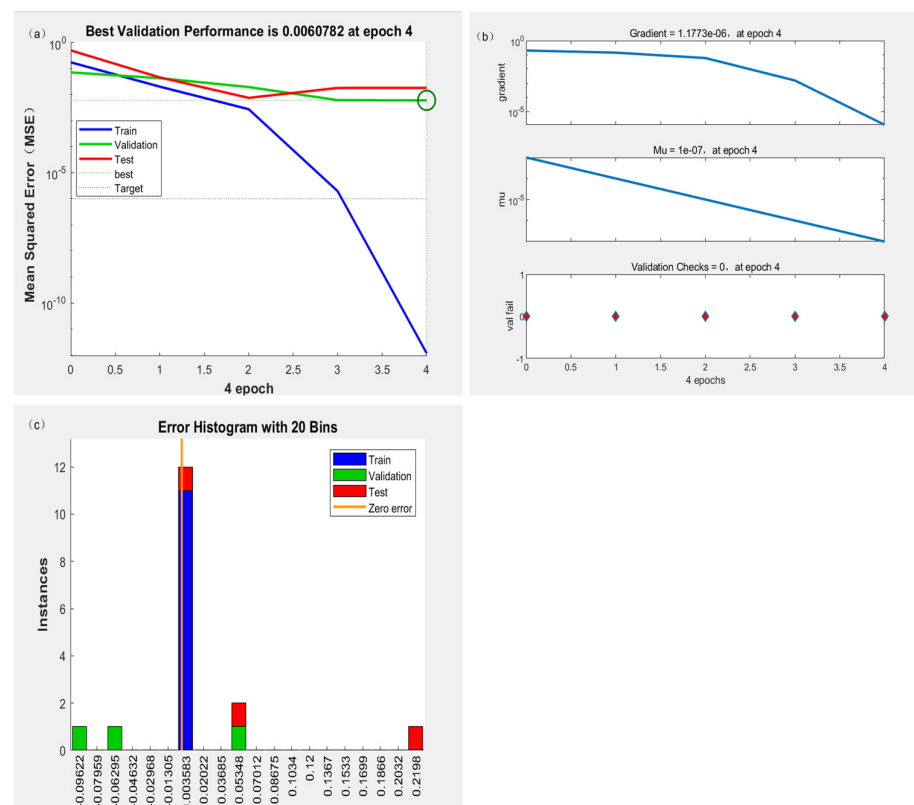


Figure 13. (a) MSE of the training, test, and validation datasets; (b) Curves showing the changes of validation checks, damping factor μ , and gradient with the number of training epochs; (c) Error histogram.

Figure 13b shows the curves of the validation checks, damping factor μ , and gradient changing with the number of training epochs during the training process of the ANN model. At the 4th epoch, the Gradient was 1.1773×10^{-6} , which indicates that the change of the loss function tends to be gentle under the current parameters, and the model is approaching convergence. The damping factor μ was 1×10^{-7} , and its change conforms to the convergence characteristics of the Levenberg–Marquardt algorithm. The Validation

Checks value was 0, indicating that the performance of the validation set did not deteriorate continuously in the current epoch, and the training process was relatively stable.

Figure 13c shows an error histogram with 20 bins, presenting the error distributions of the training set, validation set, and test set. Most of the error samples in the training set are concentrated near zero error, indicating that the model has a high degree of fitting to the training data. The error distributions of the validation set and test set are more dispersed compared to the training set, but there is still a certain concentration trend, indicating that although there are some errors when the model processes new data, the overall prediction direction is relatively accurate. This may be due to the small size of the dataset, which is also consistent with relevant literature [80].

3.4. Comparison of RSM and ANN

The ANN and the RSM were employed for the study of Cr(VI) removal by the FP-nZVI material. The predicted removal rates were compared with the experimental values, and the results are shown in Figure 14. The predicted data of both models have a good correlation with the actual data, but the ANN model performs better. As can be seen from Table 5, the ANN model has a higher R^2 value. The mean squared error (MSE) of the ANN model is 0.1146, and the root mean squared error (RMSE) is 0.3385, which are much lower than those of the RSM model, indicating that the deviation between its predicted values and the actual values is small and the fluctuation is low. The mean absolute percentage error (MAPE) is 0.4903, which is significantly lower than 0.8895 of the RSM model, suggesting that the proportion of the prediction error in the actual value is small and meets the requirements of high-precision prediction. The mean absolute error (MAE) is 0.1760, the average absolute deviation (AAD) is 0.4903, and the standard error of prediction (SEP) is 1.0399, all of which are at a relatively low level, highlighting the characteristics of low error and high stability of this model.

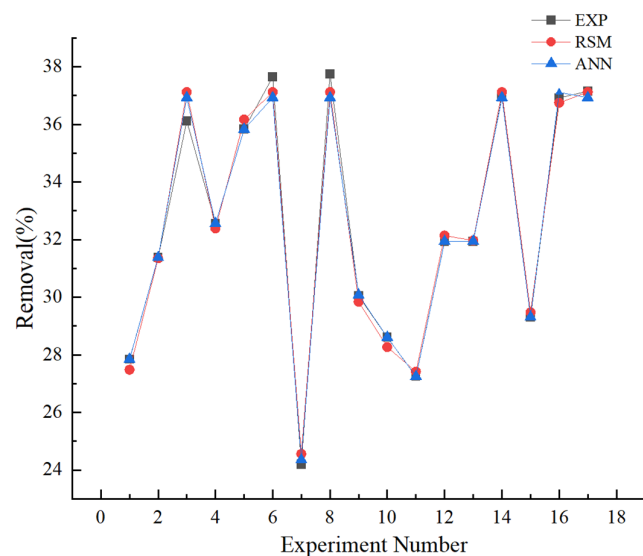


Figure 14. Comparison of experimental values with predicted values obtained by RSM and ANN model for Cr(VI) removal using FP-nZVI.

Table 5. Comparison of statistical parameters of RSM and ANN.

Statistical Parameters	RSM	ANN
R ²	0.9918	0.9937
MSE	0.1404	0.1146
RMSE	0.3747	0.3385
MAE	0.2874	0.1760
MAPE	0.8895%	0.4903%
AAD	0.8795	0.4903
SEP	1.1511	1.0399

Related studies have shown that the ANN model overcomes the limitation of the RSM, which only assumes a quadratic nonlinear correlation because the ANN model itself can capture almost any complex nonlinear process [81]. This is also related to the nature of the model itself. The ANN can better imitate the human brain to learn the properties of the dataset and generalize the complex relationship between the actual response and the predicted response [82]. Similar findings have also been reported in related studies. For example, Kim et al. [83] constructed a model for the NO_x removal system in an LNG receiving terminal, and Hamza et al. [84] used MIL-53(Al) as an adsorbent for the removal of dicamba and MCPA. In these cases, although we used different RSM designs (Box-Behnken Design (BDD) and Central Composite Design (CDD)), the results all showed that the artificial neural network provided more accurate predictions with smaller errors compared to the response surface methodology model.

Although the ANN model has obvious advantages, it still has limitations in practical applications. When the dimensionality of variables is low, and the observed data are scarce, the data-driven ANN model struggles to fully extract data features during the development and training phases. The model converges slowly, requiring repeated parameter adjustments and multiple training sessions. This significantly increases the time consumption and highlights the gap between theory and practice. Therefore, improving this issue requires the collective attention of the academic community to further promote the wide application and optimization of the ANN model in real-world scenarios.

4. Conclusions and Suggestions

In this research, cellulose filter paper, which is inexpensive, environmentally friendly, and biodegradable, was utilized to support nZVI. The FP-nZVI was successfully prepared, which effectively improved the dispersibility of the nZVI. Column experiments for the removal of Cr(VI) were carried out using FP-nZVI. This composite material demonstrated outstanding performance in removing Cr (VI) within a flow system. Subsequently, the RSM was employed for simulation and prediction, and RSM demonstrated good simulation performance. Based on the column experiments and response surface optimization tests, an ANN model was developed and tuned. A comparative analysis showed that both models were in good agreement with the experimental data. However, compared with RSM, the ANN model had a higher R² value, and key indicators such as MSE, RMSE, MAE, MAPE, AAD, and SEP were all smaller than those of RSM. It performed better in terms of prediction error, value fluctuation, and closeness to the actual values. The validation set had excellent performance, the validation checks value was 0, the gradient and damping factor converged, and the error distribution of the test set was concentrated without over-fitting. Therefore, it could simulate the Cr(VI) removal process more accurately.

This research offers a novel material for the removal of Cr (VI) pollution. RSM and ANN overcome the drawbacks of the traditional single-factor variable control method, improve the experimental efficiency and model prediction accuracy, and optimize the

prediction of the Cr(VI) removal process. However, this study also has certain limitations: (1) The cellulose filter paper is in the form of a thin sheet, and its strength decreases to a certain extent after treating chromium pollution, which affects its reusability to some degree. (2) This experiment was conducted under artificially set conditions in the laboratory without taking into account the hydrogeological conditions and hydrochemical characteristics in the field. (3) The scale of the experiment is small, and there is still a certain gap from industrial application. In view of the above-mentioned deficiencies, the following suggestions are put forward: (1) Improve the structural form of the cellulose filter paper. On the premise of ensuring its adsorption performance and structural characteristics, enhance its strength and increase its reusability. (2) In the follow-up, it is advisable to consider combining the hydrogeological conditions and hydrochemical characteristics of the actual polluted site to carry out pilot-scale experiments. (3) Increase the scale of the pilot-scale experiments, optimize the experimental process flow, establish a response model between the treatment rate/treatment capacity and experimental materials, pollutant concentration, pH value, anions and cations, and hydrodynamic conditions, conduct a comprehensive evaluation of the treatment effect, obtain the key treatment parameters for large-scale application, and form a treatment process applicable to industrial applications.

Author Contributions: Z.R.: conceptualization, methodology, resources, supervision, writing—reviewing and editing, and project administration. Z.L.: Methodology, investigation, data curation, writing original draft, formal analysis. H.T.: investigation, writing—reviewing and editing. L.Y.: project administration. J.Z.: project administration. Q.J.: conceptualization, resources, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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