

# Study on the Preparation of Nano-FeS Loaded on Fly Ash and Its Cr Removal Performance

Xuying Guo,\* Zhiyong Hu, Xinle Gao, Yanrong Dong, and Saiou Fu

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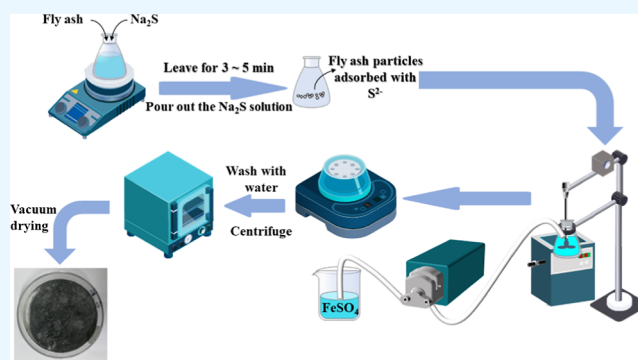
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**ABSTRACT:** Chromium has been considered as one of the most hazardous heavy metals because of its strong and persistent toxicity to the ecosystem and human beings. In this study, fly ash-loaded nano-FeS (nFeS-F) composites were constructed with fly ash as the carrier, and the performance and mechanism of the composites for the removal of Cr(VI) and total chromium from water were investigated. The composite was characterized by X-ray diffraction and transmission electron microscopy. The effects of fly ash size, molarity of FeSO<sub>4</sub>, and flow rate of FeSO<sub>4</sub> solution on the removal of Cr(VI) and total chromium were investigated by a single factor experiment. The interaction of various factors was studied by the Box-Behnken response surface methodology. The optimum conditions of removal of Cr(VI) and total chromium by nFeS-F were determined. The results show that ① the optimal preparation conditions for nFeS-F were an FeSO<sub>4</sub> concentration of 0.45 mol/L, a fly ash particle size of 120–150 mesh, and a flow rate of 0.43 mL/s. ② The response surface model provides reliable predictions for the removal efficiencies of Cr(VI) and total chromium. ③ The removal efficiencies of Cr(VI) and total chromium were 92.87 and 83.53%, respectively, under the optimal preparation conditions by the experimental test. This study provides an effective method for the removal of Cr(VI) and total chromium.



## 1. INTRODUCTION

With the development of modern industry, a large amount of chromium-containing wastewater inevitably enters the water and soil environment, endangering human health. Chromium often exists in water bodies in the state of Cr(III) and Cr(VI), which is highly toxic, difficult to degrade, and difficult to treat.<sup>1,2</sup> Currently, the commonly used treatment methods are adsorption,<sup>3</sup> ion exchange,<sup>4</sup> electrochemical,<sup>5</sup> and reduction precipitation.<sup>6</sup> The reduction precipitation method is widely used to treat highly concentrated acidic chromium-containing wastewater because of its easy operation, stable operation, and low price.<sup>7</sup>

Nano FeS has good adsorption performance, efficient reduction ability, large surface area, and high reactivity, which is considered as an efficient material for treating chromium pollution.<sup>8</sup> Li et al.<sup>9</sup> used a homogeneous precipitation method to prepare FeS nanoparticles to remove Cr(VI) from soil, and the removal rate of Cr(VI) was as high as 98% at a molar ratio of FeS to Cr(VI) of 1.5:1. Due to the high surface energy and susceptibility to oxidative agglomeration of nano-FeS, there is a need to provide a carrier material that enhances its stability.<sup>10</sup> Yao et al.<sup>11</sup> used a novel colloid of polyacrylate compounded with nano-FeS to remove Cr(VI) from water, which improved the dispersion and stability of nano-FeS by increasing the spatial site resistance and

electrostatic repulsion between nano-FeS particles. Park et al.<sup>12</sup> used experiments to compare the adsorption capacity of quartz sand for Cr(VI) before and after loading FeS, and the results showed that the adsorption of Cr(VI) by quartz sand after loading FeS was 25.2 times higher than that of quartz sand. The research group<sup>13</sup> achieved better results using lignite loaded with nano-FeS to treat acidic chromium-containing wastewater in the previous stage. However, the high cost of lignite is not suitable for large-scale application. Therefore, further screening of cheap and stable carrier materials is needed.

Fly ash, as an industrial waste, is produced in China alone at more than 600 million tons per year.<sup>14,15</sup> Because of its good physicochemical properties such as high porosity and large surface area, it is often used as an adsorbent to treat wastewater.<sup>16–18</sup> Ribeiro et al.<sup>19</sup> used fly ash after gasification for the adsorption of Cr(VI), and the results showed that fly

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Table 1. Main Composition of Fuxin Fly Ash

constituent	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
fly ash	67.10	0.12	19.74	3.35	0.34	2.87	4.00	1.08	1.30	0.10

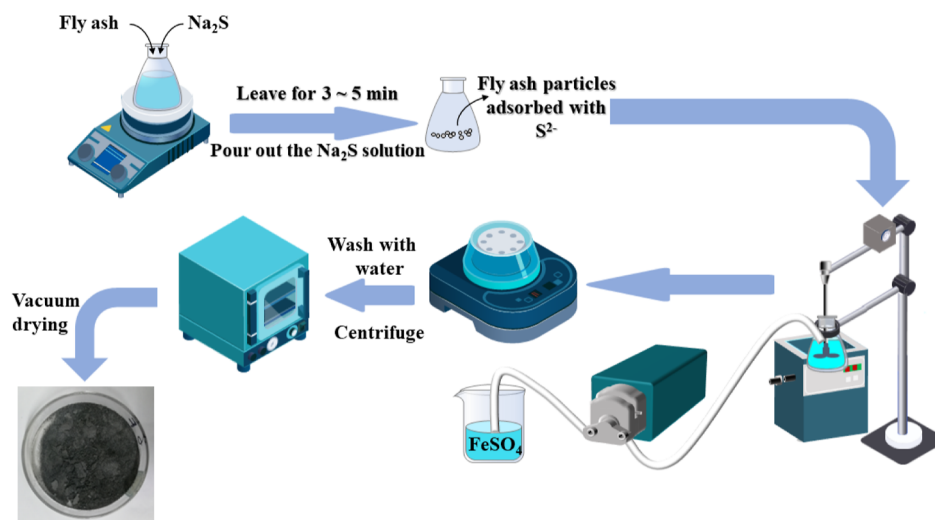


Figure 1. Flow chart of the preparation of nFeS-F.

ash has the potential to be a cheap and effective adsorbent. Wang et al.<sup>20</sup> investigated the adsorption characteristics of fly ash on Cr(VI) through intermittent experiments, and the experimental results showed that the initial concentration of Cr(VI) was 10 mg/L, and the removal rate of Cr(VI) was only 50.13%. Li et al.<sup>21</sup> treated chromium-containing wastewater with fly ash modified by polymeric aluminum chloride, and the Cr(VI) removal rate reached 80.2%. Chen<sup>22</sup> loaded iron-based nanomaterials onto the surface of fly ash by an in situ reduction method, which effectively enhanced the removal capacity of fly ash for Cr(VI).

Based on this, the author considered the use of fly ash loaded with nFeS for the treatment of acidic chromium-containing wastewater, which can solve the technical bottleneck of the small adsorption capacity of fly ash and the easy agglomeration of nFeS and ensure the adsorption of fly ash and the advantages of nFeS redox in the treatment of acidic chromium-containing wastewater to be maximized. The effects of fly ash particle size, the molarity of FeSO<sub>4</sub>, and the flow rate on the treatment of chromium-containing wastewater with nFeS-F were investigated by the response surface methodology (RSM)<sup>23</sup> to determine the optimal preparation conditions. The aim is to provide a theoretical basis for the treatment of acidic chromium-containing wastewater with fly ash-loaded FeS.

## 2. MATERIALS AND METHODS

**2.1. Experimental Materials.** Fly ash was collected from the Fuxin coal-fired power plant in Liaoning Province, China; it is new fly ash. The formation of fly ash is divided into three stages: ① pulverized coal → porous carbon particles. ② Porous carbon particles → porous vitreous body. ③ Porous vitreous body → glass beads. The main chemical composition of fly ash is shown in Table 1. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals selected for the experiments were of analytical reagent grade. Deionized water was always used to prepare the required solutions.

Acidic chromium-containing wastewater: the pH of the simulated acid mine wastewater was set to 4, and the mass concentration of Cr(VI) was 100 mg/L.

**2.2. Preparation of Composite Adsorbent nFeS-F.** 4 g of fly ash and 60 g of Na<sub>2</sub>S were placed in a conical flask, water was added, and the mixture was stirred for 8 h and set aside. The 0.45 mol/L FeSO<sub>4</sub> solution was added dropwise (0.45 mL/s) to the conical flask with a peristaltic pump, sonicated (40 kHz) for 10 min, and the suspension was poured into a centrifuge tube, centrifuged for 15 min, and washed of impurities, and the result was the new composite adsorbent material of nFeS-F. After vacuum drying, it was sealed and stored. The nFeS-F preparation process is shown in Figure 1.

**2.3. Single Factor Test.** The single factor method was used to investigate fly ash particle sizes (30–60, 60–90, 90–120, 120–150, and 150–180 mesh), molarities of FeSO<sub>4</sub> (0.15, 0.3, 0.45, 0.6, and 0.75 mol/L), and flow rate of FeSO<sub>4</sub> solution (0.33, 0.43, 0.53, 0.63, and 0.73 mL/s) of nFeS-F on the treatment of acidic chromium-containing wastewater. The nFeS-F was injected into the acidic chromium-containing wastewater at a solid–liquid ratio of 1:200 (g/mL), shaken at 300 rpm, and sampled at regular intervals. Each experiment was repeated three times. Based on the evaluation indexes of Cr(VI) and total chromium removal efficiencies, the optimal preparation conditions of the new nFeS-F composite adsorbent were determined.

**2.4. Response Surface Test.** Based on the single factor experiment, three levels of the three factors of molarity of FeSO<sub>4</sub>, fly ash particle size, and flow rate of FeSO<sub>4</sub> solution were selected as the response surface optimization design. The labels and level of test factors are shown in Table 2.

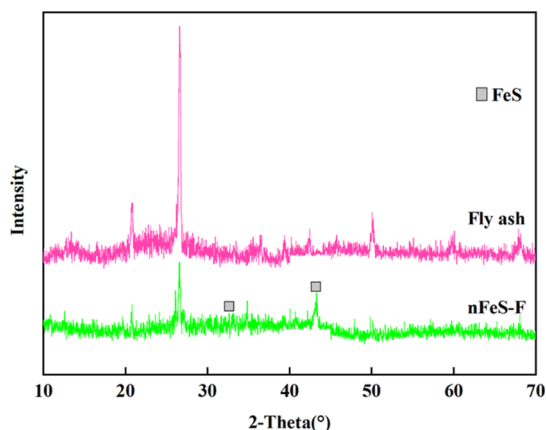
**2.5. Water Quality Testing Method.** The determination of Cr(VI) in water samples was performed by the diphenylcarbazide spectrophotometry (GB/T 7467-1987) at a wavelength of 540 nm; the total chromium was determined by potassium permanganate oxidation-diphenylcarbazide spectrophotometry (GB/T 7466-1987), measured at a wavelength of 540 nm.

**Table 2.** Level of Impact Factors and Labels

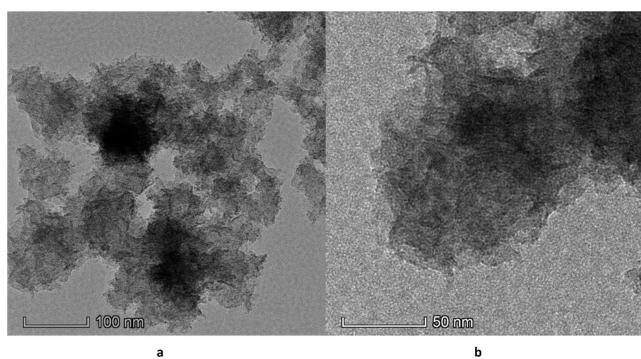
factor	labels	level		
		−1	0	1
fly ash particle size (mesh)	X <sub>1</sub>	100	130	160
molarity of FeSO <sub>4</sub> (mol/L)	X <sub>2</sub>	0.3	0.45	0.6
flow rate of FeSO <sub>4</sub> solution (mL/s)	X <sub>3</sub>	0.43	0.53	0.63

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

**3.1. XRD and TEM Analysis.** The X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterization results of nFeS-F samples and fly ash samples are shown in Figure 2.

**Figure 2.** XRD patterns of fly ash and nFeS-F.

It can be seen from Figure 2 that the loaded nFeS-F has characteristic diffraction peaks at  $2\theta = 20.85, 26.62, 50.11,$  and  $68.10^\circ$ , indicating that the loading of nano-FeS does not change the original crystal structure of fly ash. FeS diffraction peaks (PDF: # 76-0963) appeared at  $2\theta = 32.68$  and  $43.17^\circ$  of nFeS-F after loading, which indicated that FeS was successfully loaded on the surface of fly ash. As shown in Figure 3, the FeS

**Figure 3.** TEM image of nFeS-F. (a) 100 and (b) 50 nm.

crystals loaded on the surface of fly ash are sheet-like with an average length of 40–80 nm, and the morphology is similar to the nano-FeS prepared by Dai,<sup>24</sup> indicating that the ultrasonic precipitation method can load the nano-FeS on fly ash particles.

Nanoparticles are uniformly distributed in nFeS-F with good dispersion, which shows that fly ash as a carrier material can

effectively improve the stability of nano-FeS and inhibit the condensation and agglomeration of nano-FeS itself.

**3.2. Single Factor Test Analysis.** **3.2.1. Effect of Fly Ash Particle Size on Chromium Removal Efficiency.** The effect of fly ash particle size on the removal efficiency of Cr(VI) and total chromium is shown in Figure 4. With the decrease of fly ash particle size, the removal efficiency of Cr(VI) and total chromium by nFeS-F showed a trend of increasing and then decreasing. The removal of Cr(VI) and total chromium reached a maximum of 92.09 and 80.27% at a fly ash particle size of 120–150 mesh. This is due to the decrease in fly ash particle size and increase in specific surface area, which enhances the adsorption capacity of chromium.<sup>25</sup> At the same time, the specific surface area of fly ash increases and the adsorption sites gradually increase, making fly ash loaded with more FeS.

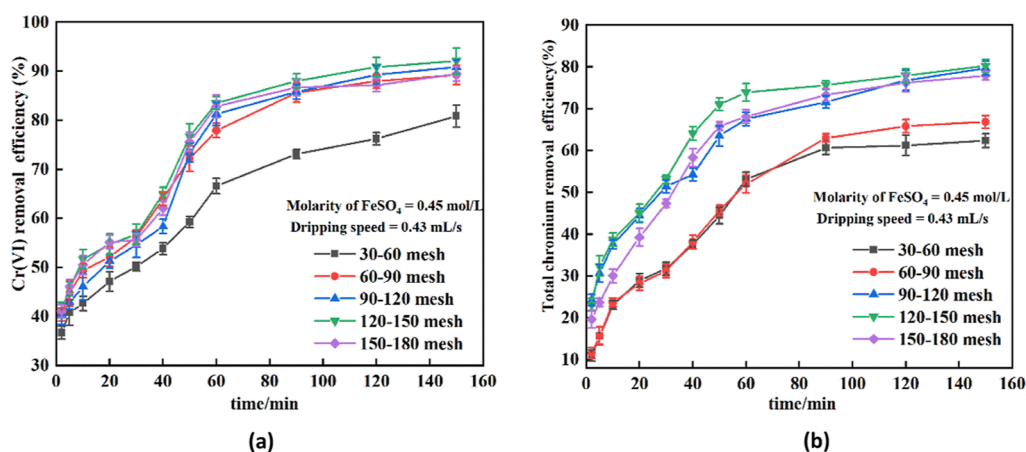
The results showed that the adsorption of Cr(VI) by nFeS-F consumes H<sup>+</sup>, and the surface of nFeS-F is positively charged, and so, the removal efficiency of Cr(VI) is improved by charge adsorption.<sup>26</sup> When the particle size of fly ash is too small, the prepared nFeS-F is easy to float on the water surface and difficult to settle in the process of treating chromium-containing wastewater, and so, the removal effect will be affected. Therefore, 120–150 mesh was selected as the fly ash particle size in the follow-up experiment.

**3.2.2. Effect of the Molarity of FeSO<sub>4</sub> on Chromium Removal Efficiency.** The effect of the molarity of FeSO<sub>4</sub> on the removal efficiency of Cr(VI) and total chromium is shown in Figure 5. When the molarity of FeSO<sub>4</sub> was 0.45 mol/L, the removal efficiency rates of Cr(VI) and total chromium reached the maximum, which were 92.58 and 82.99%, respectively. This is because the concentration of FeSO<sub>4</sub> solution has great influence on the nucleation and growth rate of crystals. When the concentration of Fe<sup>2+</sup> ions in solution increases, the number of FeS crystals increases. With the increase of FeSO<sub>4</sub> molarity, many tiny grains can provide larger collision area and more active sites, and so, the removal efficiency of Cr(VI) and total chromium increases.<sup>27</sup> The molarity of FeSO<sub>4</sub> continued to increase, but the removal efficiency of Cr(VI) and total chromium did not increase significantly, which indicated that the molarity of Fe<sup>2+</sup> in the solution had tended to be saturated. Therefore, 0.45 mol/L was selected as the molarity of FeSO<sub>4</sub> in the follow-up experiment.

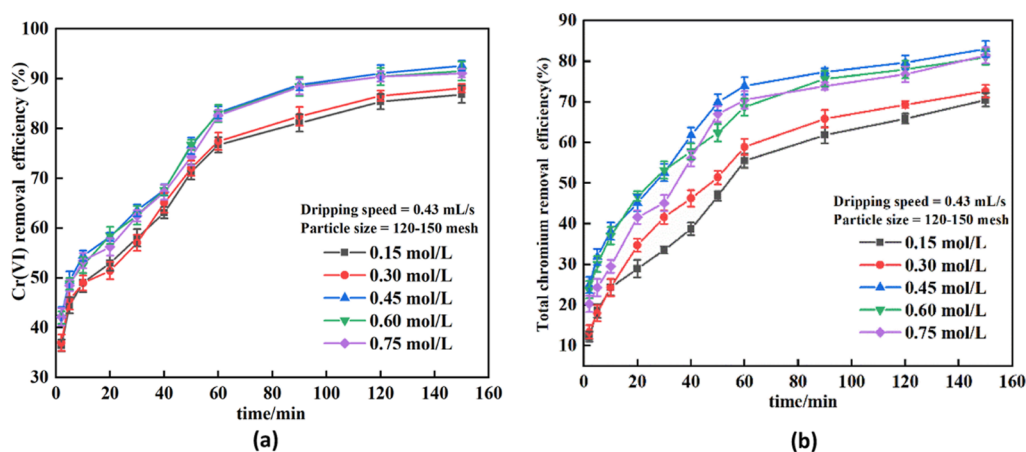
**3.2.3. Effect of the Flow Rate on Chromium Removal Efficiency.** The effect of flow rate on the Cr(VI) and total chromium removal efficiency is shown in Figure 6. It can be seen from Figure 6 that with the acceleration of the drop addition flow rate, nFeS-F showed a trend of increasing and then decreasing the removal efficiency of Cr(VI) and total chromium. When the flow rate of FeSO<sub>4</sub> solution was 0.33 mL/s, the removal efficiency rates of Cr(VI) and total chromium reached the maximum, which were 89.15 and 79.68%, respectively. It is due to the fact that the dropwise flow rate of the solution affects the crystal structure of FeS, and the supersaturated nucleation and growth rate theory of Weinman<sup>28</sup> demonstrated that the dropwise flow rate is proportional to the nucleation and growth rates of FeS crystals.

When the flow rate of FeSO<sub>4</sub> solution is small, the grain size of the nuclei is small and the surface free energy is high, which makes the removal efficiency of Cr(VI) and total chromium the highest. As the flow rate of FeSO<sub>4</sub> solution increases, the crystal size increases rapidly and the specific surface area decreases, leading to a decrease in the removal efficiency of

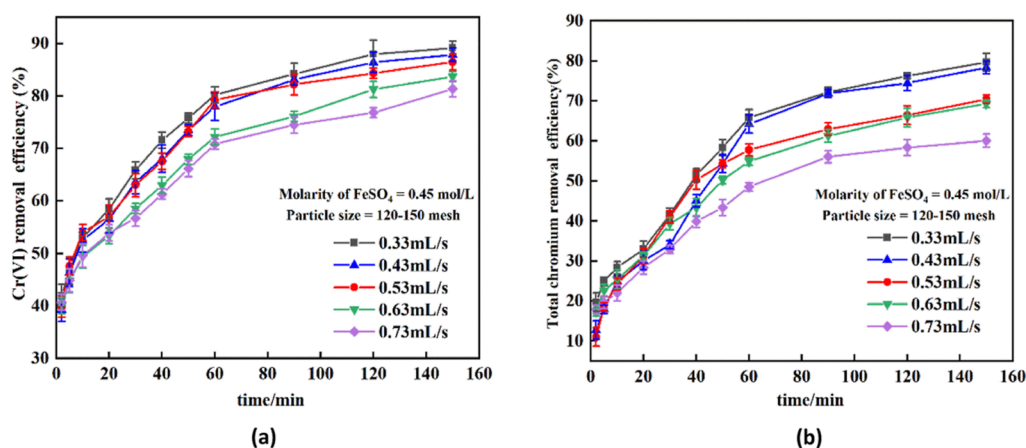




**Figure 4.** Effect of fly ash particle size on the removal efficiency of Cr(VI) and total chromium. (a) Cr(VI) removal efficiency (%). (b) Total chromium removal efficiency (%).



**Figure 5.** Effects of molarity of  $\text{FeSO}_4$  on the removal efficiency of Cr(VI) and total chromium. (a) Cr(VI) removal efficiency (%). (b) Total chromium removal efficiency (%).



**Figure 6.** Flow rate of  $\text{FeSO}_4$  solution on the removal efficiency of Cr(VI) and total chromium. (a) Cr(VI) removal efficiency (%). (b) Total chromium removal efficiency (%).

Cr(VI) and total chromium. At the same time, the concentration of  $\text{Fe}^{2+}$  ions constituting FeS crystals in solution increases, the rate of grain formation is accelerated, and the number of crystals increases. After comprehensive consideration, 0.43 mL/s was selected as the flow rate of  $\text{FeSO}_4$  solution in the follow-up experiment.

**3.3. Response Surface Test Analysis.** RSM is an experimental condition finding method for solving problems related to nonlinear data processing.<sup>29</sup> Box-Behnken design is one of the common experimental design methods used in response surface optimization.<sup>30</sup> This method performs response surface analysis on the experimentally derived data results to obtain a prediction model. The prediction model is

continuous and generally curved. The advantage is that the experimental parameters can be analyzed continuously at each level during the experimental parameter optimization. The experiment considered three factors: fly ash particle size, molarity of FeSO<sub>4</sub>, and flow rate, and the degree of their effects on the removal rates of Cr(VI) and total chromium were obtained by interaction experiments. In accordance with the statistical requirements of the Box-Behnken experimental design, 17 sets of experimental regression coefficients were fitted to the equations, and the results are shown in Tables 3–5. The calculation formula is

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC$$

Table 3. Experimental Design Factors and Results<sup>a</sup>

code	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	total chromium removal efficiency (%)	Cr(VI) removal efficiency (%)
1	0.60	160.00	0.53	78.62	88.52
2	0.45	100.00	0.43	72.22	90.04
3	0.30	160.00	0.53	83.42	87.24
4	0.60	100.00	0.53	70.65	82.52
5	0.45	130.00	0.53	81.22	90.53
6	0.45	130.00	0.53	81.20	90.52
7	0.45	130.00	0.53	81.23	90.48
8	0.45	100.00	0.63	76.52	93.82
9	0.45	130.00	0.53	81.24	90.53
10	0.60	130.00	0.63	76.92	86.68
11	0.60	130.00	0.43	71.23	84.21
12	0.45	160.00	0.43	79.32	92.42
13	0.45	160.00	0.63	87.62	94.32
14	0.30	130.00	0.63	80.96	90.12
15	0.45	130.00	0.53	81.22	90.54
16	0.30	100.00	0.53	76.62	87.32
17	0.30	130.00	0.43	78.02	87.52

<sup>a</sup>Notes: X<sub>1</sub> is the molarity of FeSO<sub>4</sub>, mol/L; X<sub>2</sub> is the size of fly ash, mesh; and X<sub>3</sub> is the flow rate of FeSO<sub>4</sub> solution, mL/s.

where  $y$  is the predicted corresponding value,  $A$ ,  $B$ , and  $C$  are the coded values of the independent variables, and  $\beta$  is the constant term.

According to the experimental results of response surface design in Table 3, a quadratic polynomial model between fly ash particle size, FeSO<sub>4</sub> molarity, flow rate of FeSO<sub>4</sub> solution, and Cr(VI) and total chromium removal efficiencies was established. The regression equation of Cr(VI) removal efficiency is as follows:  $Y = 90.52 - 1.28A + 1.10B + 1.34C + 1.52AB - 0.032AC - 0.47BC - 4.82A^2 + 0.70B^2 + 1.43C^2$ ; the regression equation of total chromium removal efficiency is as follows:  $Y = 81.22 - 2.70A + 4.12B + 2.65C + 0.29AB + 0.69AC + 1.00BC - 3.02A^2 - 0.88B^2 - 1.42C^2$ , where  $A$  represents the molarity of FeSO<sub>4</sub>, mol/L;  $B$  represents the size of fly ash, mesh; and  $C$  represents the flow rate of FeSO<sub>4</sub> solution, mL/s. It can be seen from Tables 4 and 5 that the  $p$  values of the regression model of Cr(VI) and total chromium removal efficiencies are both <0.0001, indicating that the model is extremely significant;  $p$  values of misfit terms are all >0.05, and it shows that the model fits well with the experiment, and the regression equation can be used to analyze the experimental results instead of the real points. The correction determination

Table 4. Variance Analysis Table of Second-Order Model of Cr(VI) Removal Efficiency

variance source	sum of squares	degree of freedom	mean square	F-value	p-value
model	152.16	9	16.90	47.18	<0.0001
A-molarity of FeSO <sub>4</sub>	13.18	1	13.18	36.79	0.0005
B-the size of fly ash	9.68	1	9.68	27.01	0.0013
C-the flow rate of FeSO <sub>4</sub> solution	14.44	1	14.44	40.31	0.0004
AB	9.24	1	9.24	25.79	0.0014
AC	0.01	1	0.01	0.011	0.9166
BC	0.88	1	0.88	2.46	0.1603
A <sup>2</sup>	97.76	1	97.76	272.87	<0.0001
B <sup>2</sup>	2.05	1	2.05	5.73	0.0478
C <sup>2</sup>	8.62	1	8.62	24.07	0.0017
residual error	2.50	7	0.35		
degree of misfit	2.50	3	0.83	151.86	0.0658
pure error	0.0022	4	0.00055		
total deviation	154.67	16			

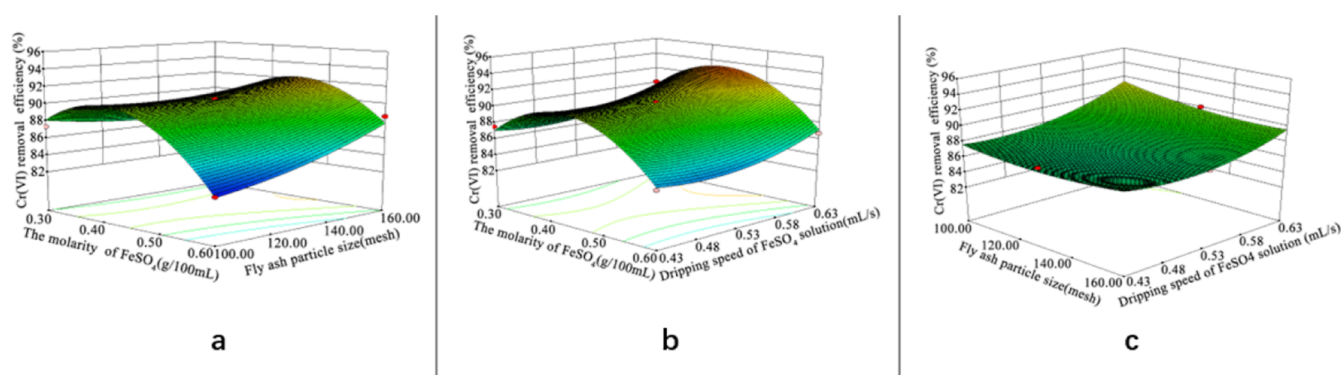
coefficients  $R_{adj}^2$  of the two models were 0.9629 and 0.9750, respectively, indicating that 3.71 and 2.5% of the variance, respectively, could not be explained by the model.<sup>31</sup> The coefficients of variation were 0.67 and 0.89, respectively, which further indicated that the model was accurate and suitable for preliminary analysis and prediction of Cr(VI) and total chromium removal efficiency.

**3.3.1. Cr(VI) Removal Efficiency.** It can be seen from Figure 7a that there is a significant interaction between FeSO<sub>4</sub> molarity and fly ash particle size on the Cr(VI) removal efficiency ( $P = 0.0014 < 0.01$ ). The significant order is as follows: FeSO<sub>4</sub> molarity > particle size of fly ash. In the selected experimental range, the removal efficiency of Cr(VI) first increased and then decreased with the increase of FeSO<sub>4</sub> molarity and gradually decreased with the increase of fly ash particle size. It can be seen from Figure 7b that the interaction between FeSO<sub>4</sub> molarity and flow rate of FeSO<sub>4</sub> solution has no significant effect on the Cr(VI) removal efficiency ( $P = 0.9166 > 0.05$ ), and the significant order is as follows: flow rate > FeSO<sub>4</sub> molarity. In the selected experimental range, the removal efficiency of Cr(VI) increased first and then decreased with the increase of FeSO<sub>4</sub> molarity and gradually increased with the increase of flow rate of FeSO<sub>4</sub> solution. It can be seen from Figure 7c that the interaction between fly ash particle size and flow rate of FeSO<sub>4</sub> solution has no significant effect on the Cr(VI) removal efficiency ( $P = 0.1603 > 0.05$ ), and the significant order is as follows: flow rate > fly ash particle size. In the selected experimental range, the removal efficiency of Cr(VI) decreased with the increase of particle size and increased with the increase of flow rate of FeSO<sub>4</sub> solution.

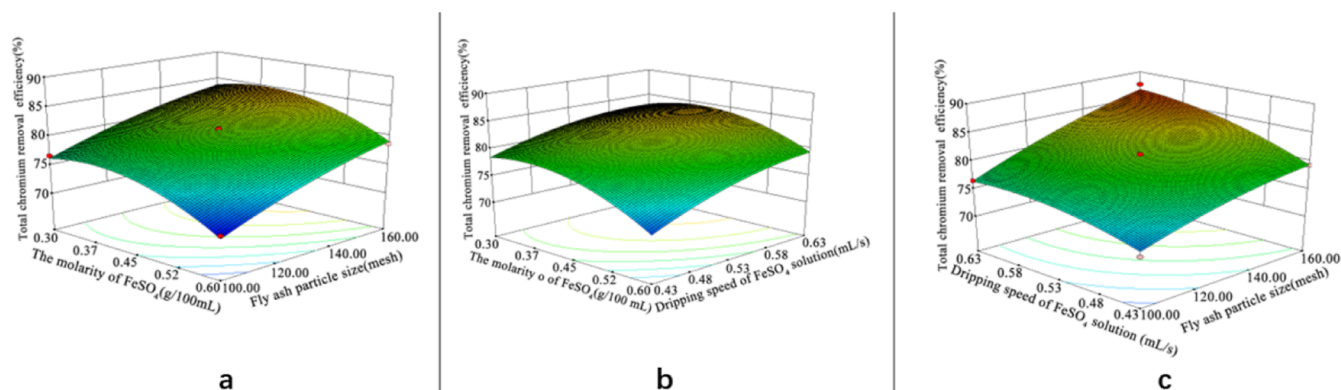
**3.3.2. Total Chromium Removal Efficiency.** It can be seen from Figure 8a that the interaction between molarity of FeSO<sub>4</sub> and fly ash particle size has no significant effect on the total chromium removal efficiency ( $P = 0.4317 > 0.05$ ), and the fly ash particle size is dominant among the two factors. In the selected experimental range, the removal efficiency of total chromium first increased and then decreased with the increase of FeSO<sub>4</sub> molarity and gradually decreased with the increase of

Table 5. Variance Analysis Table of Second-Order Model of Total Chromium Removal Efficiency

variance source	sum of squares	degree of freedom	Mean square	F-value	p-value
model	311.01	9	34.55	70.27	<0.0001
A-molarity of FeSO <sub>4</sub>	58.32	1	58.32	118.60	<0.0001
B-the size of fly ash	135.87	1	135.87	276.33	<0.0001
C-the flow rate of FeSO <sub>4</sub> solution	56.33	1	56.33	114.57	<0.0001
AB	0.34	1	0.34	0.69	0.4317
AC	1.89	1	1.89	3.84	0.0907
BC	4.00	1	4.00	8.13	0.0246
A <sup>2</sup>	38	1	38.30	77.88	<0.0001
B <sup>2</sup>	3.25	1	3.25	6.61	0.0370
C <sup>2</sup>	8.53	1	8.53	17.35	0.0042
residual error	3.44	7	0.49		
degree of misfit	3.44	3	1.15	52.13	0.0710
pure error	0.00088	4	0.00022		
total deviation	314.44	16			



**Figure 7.** Response surface plot of Cr(VI) removal efficiency under the interaction of various factors. (a) Cr(VI) removal efficiency under the interaction of molarity of FeSO<sub>4</sub> and fly ash particle size. (b) Cr(VI) removal efficiency under the interaction of molarity of FeSO<sub>4</sub> and flow rate of FeSO<sub>4</sub> solution. (c) Cr(VI) removal efficiency under the interaction of flow rate of FeSO<sub>4</sub> solution and fly ash particle size.



**Figure 8.** Response surface plot of total chromium removal efficiency under the interaction of various factors (a). Total chromium removal efficiency under the interaction of molarity of FeSO<sub>4</sub> and fly ash particle size. (b) Total chromium removal efficiency under the interaction of molarity of FeSO<sub>4</sub> and flow rate of FeSO<sub>4</sub> solution. (c) Total chromium removal efficiency under the interaction of flow rate of FeSO<sub>4</sub> solution and fly ash particle size.

fly ash particle size. It can be seen from Figure 8b that the interaction between molarity of FeSO<sub>4</sub> and flow rate of FeSO<sub>4</sub> solution has no significant effect on the total chromium removal efficiency ( $P = 0.0907 > 0.05$ ), and the fly ash particle size is dominant among the two factors. In the selected experimental range, the removal efficiency of total chromium increased first and then decreased with the increase of FeSO<sub>4</sub> molarity and gradually increased with the increase of flow rate of FeSO<sub>4</sub> solution. It can be seen from Figure 8c that the interaction between fly ash particle size and flow rate of FeSO<sub>4</sub>

solution has a significant impact on the total chromium removal efficiency ( $P = 0.0246 < 0.05$ ), and the fly ash particle size is dominant among the two factors. In the selected experimental range, the removal efficiency of total chromium gradually decreased with the increase of particle size and gradually increased with the increase of dripping flow rate.

According to the experimental results of response surface, the optimum preparation conditions of nFeS-F were optimized by Design-Expert. The optimum preparation conditions of nFeS-F were as follows: the molarity of FeSO<sub>4</sub> is 0.45 mol/L,

the fly ash particle size is 120–150 mesh, and the flow rate of FeSO<sub>4</sub> solution is 0.43/100 mL.

Based on the experimental results of the response surface, the experimental conditions were optimized using Design-Expert, and the predicted optimal preparation conditions of nFeS-F were obtained as FeSO<sub>4</sub> concentration of 0.45 mol/L, fly ash particle size of 120–150 mesh, and flow rate of 0.43/100 mL. To confirm the accuracy of the predicted values, validation experiments were conducted under this preparation condition, and the results showed that the removal rates of Cr(VI) and total chromium were 92.87 and 83.53%, respectively. The difference between the model predicted values and the actual experimental values was within 10%,<sup>32</sup> which shows that the model can accurately simulate the influence of different factors on the removal efficiency of Cr(VI) and total chromium and has practical value.

#### 4. CONCLUSIONS

In this study, a quadratic multiple regression equation (model) between fly ash particle size, FeSO<sub>4</sub> concentration, flow rate, and Cr(VI) and total chromium removal was developed based on the Box-Behnken experimental design method. Through 17 sets of fitting experiments, it was shown that the model fitted well with the experiments and the optimal preparation conditions of nFeS-F were obtained. nFeS-F, as an adsorbent material, can be used as a filler material for adsorption columns or permeable reaction walls and thus has some application value for the treatment of chromium in wastewater and contaminated water bodies. Detailed conclusions are as follows.

- (1) Fly ash-loaded nano-FeS material was successfully prepared by the ultrasonic precipitation method, which realized the superposition of fly ash and nano-FeS on chromium removal ability, and gave full play to the efficient reduction ability of nano-FeS on Cr(VI) and effectively removed Cr(VI).
- (2) The response surface method was used to establish the prediction models for the removal of Cr(VI) and total chromium, and the correlation coefficients of the models were 0.9629 and 0.9750, respectively, with good fit and small experimental errors, which could predict the effect of Cr(VI) and total chromium removal by nFeS-F prepared under different fly ash particle sizes, FeSO<sub>4</sub> material concentrations, and flow rates, respectively.
- (3) The response surface model predicts that the optimal preparation conditions for nFeS-F are molarity of FeSO<sub>4</sub> of 0.45 mol/L, fly ash particle size of 120–150 mesh, and flow rate of 0.43 mL/s.
- (4) The optimum preparation conditions resulted in 92.87 and 83.53% removal of Cr(VI) and total chromium, respectively. The differences between the model predicted values and the actual experimental values were within 10%, indicating that the model was accurate and reliable.

#### AUTHOR INFORMATION

##### Corresponding Author

Xuying Guo – College of Mining and College of Science, Liaoning Technical University, Fuxin, Liaoning 123000, China; [orcid.org/0000-0002-2005-5418](https://orcid.org/0000-0002-2005-5418); Email: guoxuying@lntu.edu.cn

#### Authors

Zhiyong Hu – College of Mining, Liaoning Technical University, Fuxin, Liaoning 123000, China  
Xinle Gao – College of Mining, Liaoning Technical University, Fuxin, Liaoning 123000, China  
Yanrong Dong – College of Civil Engineering, Liaoning Technical University, Fuxin, Liaoning 123000, China  
Saiou Fu – College of Civil Engineering, Liaoning Technical University, Fuxin, Liaoning 123000, China

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.2c03699>

#### Notes

The authors declare no competing financial interest.

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