Activated carbon fiber-supported nano zero-valent iron on Cr(VI) removal

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Abstract. Nanoscale zero valent iron (nZVI) was adsorbed on activated carbon fiber (ACF) for efficient removal of hexavalent chromium. The composite materials were characterized by XRD, SEM, FTIR, BET and XPS. Fe²⁺ was adsorbed by ACF and then restored by NaBH₄. This sample was named ACF-nZVI-a. While Fe²⁺ was restored by NaBH₄ and nZVI was adsorbed by ACF. That sample was named ACF-nZVI-b. BET analysis indicated that ACF-nZVI-a had a high specific surface area of 1087 m²/g, while ACF-nZVI-b had a low specific surface area of 928 m²/g, which indicated that it was easier for nZVI to go into the ACF pores than ionic condition Fe²⁺. Batch experiments showed that Cr (VI) removal rate was 98.9% for ACF-nZVI-b, which was higher than that for both ACF (33.7%) and ACF-nZVI-a (50.7%). Furthermore, the removal rate of Cr (VI) by ACF-nZVI-b showed strong dependence on initial solution pH. Low pH and initial Cr (VI) concentration favored both removal efficiency and rate constants. The reaction followed a pseudo first-order model under different initial Cr (VI) concentrations. The Cr (VI) removal was attributed to both the adsorption of ACF and the reducibility of nZVI, but the main cause was the reduction of nZVI. This study demonstrated that the ACF-nZVI-b had the potential to become an effective agent for the removal of Cr (VI) from polluted water.

1. Introduction
Cr(VI) pollution has always been the focus of attention[1]. It comes from electroplating, metallurgy, mining and other industries, causing great harm to our bodies, and can even cause cancer[2-3]. Therefore, an efficient method is needed to remove Cr(VI).

nZVI is a nanomaterial with large specific surface area, high reactivity and strong reducing ability[4]. It is widely used in groundwater environmental restoration. But its shortcomings of easy oxidation and agglomeration limit its application, so researchers often modify it[5-6].

In this paper, nano zero valent iron (nZVI) was loaded on activated carbon fiber (ACF) and used to remove Cr(VI) in water. The performance of Cr(VI) removal and recyclability experiments under different influencing factors were discussed, and kinetic fitting and mechanism analysis were done.
2. Materials and methods

2.1. Chemicals
The chemicals included FeSO$_4$·7H$_2$O, NaBH$_4$, potassium dichromate. All chemicals used in the experiments were of analytical reagent grade or much better, obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of ACF-nZVI

2.2.1. Pretreatment of ACF. The ACF was cut into small pieces, then washed several times with deionized water, and then dried at 105°C for later use.

2.2.2. Preparation of ACF-nZVI. 2.0 g FeSO$_4$·7H$_2$O was dissolved in 30 mL deionized water, and 1.0 g ACF was immersed in the solution, which was shaken for 24 h at 25°C. Second, 0.55 g of NaBH$_4$ was dissolved in 20 mL of deionized water, and it was slowly added to the ACF adsorbed Fe$^{2+}$. After 30 minutes of reaction, the solid matter was recovered and washed with deionized water several times, and then stored in a sealed bottle for use. It was called ACF-nZVI-a.

During the synthesis process, under the condition that the added agent remains unchanged, the Fe$^{2+}$ was first restored to nZVI, and then was adsorbed on the ACF. It was called ACF-nZVI-b.

All the above processes were carried out under N$_2$ atmosphere.

2.3. Characterization
The bulk mineralogy of ACF-nZVI was characterized by X-ray diffraction (XRD). The corresponding surface morphologies and elemental compositions were analyzed by using a scanning electron microscope-energy dispersive spectrometer (SEM-EDS). The surface products of ACF-nZVI samples after reaction within a depth of <10 nm were analyzed by using X-ray photoelectron spectrometer (XPS). Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a Spectrum 100 (PerkinElmer, England) FT-IR spectrometer via KBr disk method. Brunauer-Emmett-Teller (BET) specific surface area of the samples by measurements of adsorption of N$_2$.

2.4. Batch experiments
The batch experiment was performed in a 100 mL serum bottle under a nitrogen atmosphere. Added 50 mL of 100 mg/L Cr(VI) solution and 0.05 g of sample to each bottle. Adjusted the initial pH with HCl or NaOH solution. During the reaction, the sample was drawn with a syringe at intervals and passed through a 0.22 μm microporous membrane, and then measured by diphenyl carbamide spectrophotometry. Parallel experiments were set up in the experiment to calculate the average and standard deviation.

3. Results and discussion

3.1. Characterization of ACF, ACF-nZVI and Cr(VI)-treated ACF-nZVI

3.1.1. SEM&EDS. Figure 1 and Figure 2 show the SEM&EDS of the three materials before and after Cr(VI) solution treatment. The surface of the ACF in Figure 1a is smooth and clean. Figure 1b shows that the surface of ACF-nZVI-a is rough, and some dots can be observed adsorbed to the ACF, indicating that nZVI is well dispersed on the surface of ACF, which largely inhibited the aggregation of nZVI. In Figure 1c, the nZVI particles observed on ACF-nZVI-b are more than those observed on ACF-nZVI-a, and begin to stick together, which indicated that nZVI was more easily adsorbed on ACF than Fe$^{2+}$. This shows that ACF adsorbed Cr(VI) in Figure 1aa, after removing Cr (VI), the surface of ACF is not as smooth as before treatment. For ACF-nZVI-a (Figure 1bb), the spots on the surface become round after treatment and the surface became smooth. After ACF-nZVI-b (Figure 1cc) is processed, the network structure of the surface was destroyed, and some parts of the surface become
smooth. Moreover, Fe\textsuperscript{0} on ACF-nZVI-b almost disappeared from SEM, indicating that it was not only adsorption but also reduction reaction. EDS results also confirmed this result.

![SEM images](image1)

**Figure 1.** SEM of (a) ACF, (b) ACF-nZVI-a, (c) ACF-nZVI-b; and after treatment with Cr(VI) solution (60 mg/L) (aa) ACF, (bb) ACF-nZVI-a, and (cc) ACF-nZVI-b.

![EDS spectra](image2)

**Figure 2.** EDS of the three materials before and after Cr(VI) solution treatment.

3.1.2. **XRD.** Figure 3 shows the XRD of ACF, ACF-nZVI-a and ACF-nZVI-b. There is no diffraction peak of Fe\textsuperscript{0} in ACF. For ACF-nZVI-a and ACF-nZVI-b, the diffraction peak at 44.7° is indexed as the (110) plane of nZVI [7], which indicated that Fe\textsuperscript{2+} has been converted to Fe\textsuperscript{0}, and nZVI has been adsorbed on the ACF surface. At the same time, the nZVI peak with high-intensity ACF-nZVI-b indicated that most of Fe\textsuperscript{2+} has been reduced to nZVI and adsorbed on ACF, and nZVI was more easily adsorbed by ACF than Fe\textsuperscript{2+}.

![XRD graphs](image3)

**Figure 3.** XRD of (a) ACF, (b) ACF-nZVI-a, and (c) ACF-nZVI-b.
3.1.3. XPS. Figure 4 shows the XPS of ACF, ACF-nZVI-b and ACF-nZVI-b after treatment by Cr (VI). After Cr(VI) treatment, peaks appeared when the binding energy (BE) is 284.6, 531.2, 576.9 and 711.1 eV. These correspond to the photoelectron peaks of C1s, O1s, Cr 2p and Fe 2p, respectively, indicating that the surface of ACF-nZVI-b had absorbed Fe and Cr. The presence of C and O constituted the main body of ACF. After contact with nZVI, a new peak of about 711.1 eV appeared, which was due to the photoelectron peak of iron, indicating that iron was absorbed on the surface of ACF. The 576.9 eV peak was attributed to the Cr 2p in Figure 4, indicating that Cr was loaded on the surface of ACF-nZVI-b. The binding energy peaks of Cr 2p were observed near 578.49 and 587.0 eV, corresponding to Cr(III), indicating that the adsorbed Cr(VI) was reduced to Cr(III).

3.1.4. FTIR. Figure 5 shows the FTIR in the range of 4000~400 cm$^{-1}$. The bands centered at 3440 cm$^{-1}$ and 1630 cm$^{-1}$ could be assigned to the υ (O–H) stretching vibration in the hydroxyl group related to the hydrogen bond [8]. It can be seen that some weak peaks of pure ACF at 2919 and 2856 cm$^{-1}$ are related to the C–H sp3 tensile vibration on pure ACF, but weaker on ACF-nZVI-b, explained that nZVI had an effect on C–H sp3 tensile vibration.

![Figure 4. XPS of the ACF, ACF-nZVI-b and after treatment with Cr solution(left); Cr2p of ACF-nZVI-b after treatment with Cr (VI) solution(right).](image)

![Figure 5. FTIR spectra of ACF, ACF-nZVI-b and ACF-nZVI-a(left); ACF, ACF-nZVI-b and after treatment with Cr (VI) solution(right).](image)

3.1.5. BET. Results in Table 1 imply that BET of ACF, ACF-nZVI-a and ACF-nZVI-b. The BET specific surface area of ACF, ACF-nZVI-a and ACF-nZVI-b were 1296, 1087 and 928 m$^{2}$/g, respectively. The specific surface area after adsorbed nZVI was significantly reduced, and the specific surface area of ACF-nZVI-a was higher than that of ACF-nZVI-b. At the same time, we measured the adsorption amount of iron in different materials. The iron adsorption amounts of ACF, ACF-nZVI-a and ACF-nZVI-b were 0, 15.5, and 102.5 mg/g, respectively, which also indicated the formation of iron was filled in some pores of ACF, resulting in a decrease in specific surface area. At the same time, as the iron content increases, the more the ACF was filled, the greater the specific surface area decreased.
Table 1. A table with BET of ACF, ACF-nZVI-a and ACF-nZVI-b.

| Samples        | Surface area (m²/g) | Iron adsorption capacity (mg/g) |
|----------------|---------------------|---------------------------------|
| ACF            | 1296                | 0                               |
| ACF-nZVI-a     | 1087                | 15.5                            |
| ACF-nZVI-b     | 928                 | 102.5                           |

3.2. Different material removal of Cr(VI)

Figure 6 shows the different material removal of Cr(VI). The three materials had the ability to remove Cr(VI). At 190 minutes, the percentages of ACF, ACF-nZVI-a and ACF-nZVI-b to removed Cr(VI) were 33.7%, 50.7% and 98.9%, respectively. It could be seen that ACF-nZVI-b could remove Cr(VI) most effectively, ACF-nZVI-a had a middle removal ability, and ACF has a poor removal ability. During this experiment, as a control experiment, the removal of Cr(VI) by pure ACF was studied. It was observed that the Cr(VI) removal rate of ACF was the lowest within 180 minutes, which was 33.7%. Therefore, the subsequent experiments all used the best removal effect ACF-nZVI-b to experiment.

3.3. Effects of pH on Cr(VI) removal

Figure 7 shows effects of pH on Cr(VI) removal. The results showed that Cr(VI) removal efficiency was highly correlated with pH. The removal efficiency of Cr(VI) increased significantly with pH from 9.89 to 3.11, and reached the maximum at pH 3.11. Under acidic conditions, it would accelerate the corrosion of Fe⁰, which may increase the reduction or adsorption rate of Cr(VI). When pH>4, the formation of Fe(OH)₃ and the competition between OH⁻, HCrO₄⁻ or CrO₄²⁻ may reduce the adsorption rate of Cr(VI), and the results obtained were consistent with previous studies [4]. Generally speaking, a lower pH was advantageous. When the pH value was low, the surrounding area of nZVI was positively charged. At this time, the Cr(VI) in the solution could better adhere to the surrounding area of nZVI through electrostatic reaction for redox reaction; when the pH value increased, the surface of nZVI was positively charged. Electricity was reduced, and the effect of adsorbing Cr(VI) by electrostatic action became worse. Cr(VI) in the solution was not easy to adhere to the surface of nZVI, which showed that the removal rate of Cr(VI) was reduced [9].

3.4. Effects of initial Cr(VI) concentrations on Cr(VI) removal

Figure 8 shows effects of initial Cr(VI) concentrations on Cr(VI) removal. The removal efficiency of Cr(VI) decreased with the increase of the initial Cr(VI) concentration. The Cr(VI) removal rate was close to 100% within 40 minutes at a Cr(VI) concentration of 20 mg/L, and the removal rate at 40, 80, and 100 mg/L Cr(VI) concentrations at the same time was 97%, 95%, 70%. The Cr(VI) removal rate reached 100% at 160 minutes at a Cr(VI) concentration of 100 mg/L, and the reaction time was significantly prolonged.
3.5. Cyclic reaction

Figure 9 shows cyclic reaction for ACF-nZVI-b. The experiment was carried out in a 100 mL serum bottle with 50 mL of 100 mg/L Cr(VI) solution and 0.05 g ACF-nZVI-b, and adjusted the initial pH with HCl or NaOH solution. After 3 hours of reaction, the sample supernatant was drawn with a syringe and passed through a 0.22 μm microporous membrane, and then placed in a centrifuge tube for determination. After the Cr (VI) removal experiment, the material was separated into solid and liquid, and the solid was washed with deionized water, and then the second experiment was carried out with 8 cycles. At the same time, nZVI was used as a reference for comparison, and the results showed that as the number of cycles increases, the removal rate gradually decreased, but it is obvious that the decline rate of ACF-nZVI-b is slower than that of nZVI. After eight cycles, the removal rate of ACF-nZVI-b still remained at about 70%, while nZVI is only about 40%.

3.6. kinetics analysis

Figure 10 shows kinetics for Cr (VI) removal on ACF-nZVI-b in different initial Cr(VI) solution. Results in Table 2 imply that A table with kinetic parameters. As the initial concentration increases, the rate constant decreases. Obviously, the removal of Cr(VI) by ACF-nZVI-b showed a strong dependence on the initial concentration. The removal rate of Cr(VI) decreased as the initial concentration increases. The activity of ACF-nZVI-b at different initial concentrations of the solution could be considered as the main factor for removing Cr (VI) to obtain a higher Cr (VI) removal rate.

![Figure 8](image1.png)

**Figure 8.** Effects of initial Cr(VI) concentrations on Cr(VI) removal.

![Figure 9](image2.png)

**Figure 9.** Cyclic reaction for ACF-nZVI-b and nZVI.

![Figure 10](image3.png)

**Figure 10.** Kinetics for Cr (VI) removal on ACF-nZVI-b in different initial Cr(VI) solution.

| Initial Cr(VI) concentrations (mg/L) | 20   | 40   | 80   | 100  |
|-------------------------------------|------|------|------|------|
| Kobs (min⁻¹)                       | 0.0977 | 0.0850 | 0.0575 | 0.0306 |
| R²                                 | 0.994 | 0.986 | 0.997 | 0.993 |

*Table 2. A table with kinetic parameters.*
4. Conclusions
In this experiment, ACF-nZVI was synthesized, characterized and used to remove Cr(VI) from water. The results showed that during the synthesis process, first restoring Fe^{2+} to nZVI and then adsorbed on ACF could make more nZVI particles be adsorbed on the surface of ACF. At the same time, ACF as a carrier material could disperse nZVI well and prevent nZVI from agglomerating. Batch experiments showed that compared with ACF-nZVI-a and pure ACF, ACF-nZVI-b was more efficient in removing Cr(VI). The percentages of ACF-nZVI-b to removed Cr(VI) was 98.9%. With the increase of the number of cycles, the removal rate gradually decreased, but it was obvious that the decline rate of ACF-nZVI-b was slower than that of nZVI. After eight cycles, the removal rate of ACF-nZVI-b remained at about 70%, while nZVI was only 40%. The reaction mechanism was mainly based on the reduction of Cr^{6+} by nZVI on the ACF, with adsorption as a supplement.

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