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Removal of Cr(VI) from wastewater by supported nanoscale zero-valent iron on granular activated carbon

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ABSTRACT

Granular activated carbon supported nanoscale zero-valent iron (GAC–nZVI) was synthesized using liquid-phase reduction and adopted to remove Cr(VI) from wastewater. Batch experiments were used to evaluate the factors impacting Cr(VI) removal and showed that nZVI–GAC mass ratio, GAC–nZVI dosage, initial Cr(VI) concentration and pH value were all important factors. The nZVI–GAC mass ratio was optimized at 1:10 and GAC–nZVI dose was 6.0 g/L. Lower pH and initial Cr(VI) concentration could increase the Cr(VI) removal efficiency. After treatment, the residual total chromium concentration determined by flame atomic absorbance spectrometer equals to the Cr(VI) concentration determined by 1,5-diphenylcarbazide method using UV–vis spectrophotometer. This study demonstrates that the GAC–nZVI has the potential to become an effective agent for the removal of Cr(VI) from wastewater.

Keywords: Hexavalent chromium; Nanoscale zero-valent iron; Granular activated carbon; Supported

1. Introduction

Chromium is widely applied in industrial processes, such as leather tanning, electroplating, metal processing, film and mining of chrome ore. Chromium exists in mainly as Cr(VI) and Cr(III) oxidation states in the natural environment. Hexavalent chromium (Cr(VI)) is one of the most toxic and carcinogenic contaminants. In China, it is considered as one of priority controlled pollutants in water. However, Cr(III) is much less toxic and immobile and could be a nutriment for human at low concentrations. Due to toxicity, Cr(VI) must be removed from wastewaters prior to discharge into aquatic environments.

A number of treatment processes on the removal of Cr(VI) have been developed including chemical reduction [1–3], physicochemical adsorption [4,5], bioremediation [6–8], ion exchange [9,10], electrocoagulation [11], etc. Among these technologies, the use of zero-valent iron (ZVI) for chemical reduction of Cr(VI) has attracted increasing attention due to its effectiveness, rapid removal and applicability under different conditions, operational simplicity and low-cost [12–14]. It is appreciable evidence that nanoscale zero-valent iron (nZVI) particles, due to extremely high surface area, are more reactive than microscale powders and can enhance the reduction rates remarkably

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[15]. However, there are still some technical challenges in practical applications of nZVI, such as the release or escape of nanoparticles into the environment resulting in nanotoxicity [16].

Recently, technologies have been developed using porous materials as supports to immobilize the nZVI particles [17]. Activated carbon is a traditional efficient adsorbent to remove heavy metal from wastewater, which has been widely used because of its high adsorption capability, characterized by a high specific surface area. And activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies [18]. Activated carbon supported nZVI has been used to remediate arsenic [12,19], perchlorate [20], dye [21], etc., however, no studies of treating Cr(VI) by activated carbon supported nZVI have been reported. More recently, nZVI supported on chitosan [22], multi-walled carbon nanotubes [23], carbon black [24] and bentonite [25] has been reported to remove Cr(VI). However, no studies of activated carbon as support materials for nZVI to treat Cr(VI) has been reported.

In this paper, the removal of Cr(VI) from an aqueous solution was investigated using granular activated carbon-supported nanoscale zero-valent iron (GAC–nZVI) and the objectives of this paper were: (1) synthesis of GAC–nZVI by the reduction of Fe^{3+} ions with $NaBH_4$, and characterization of the produced material; (2) evaluation of its performance for Cr(VI) removal from wastewater; and (3) evaluation of the reuse possibility of GAC–nZVI.

2. Experiments and methods

2.1. Materials

All chemical reagents such as $K_2Cr_2O_7$, $FeCl_3{\cdot}6H_2O$, H_2SO_4, NaOH and ethanol were of analytical reagent grade. Distilled water (DI water) was used in all preparation. $NaBH_4$ (99.5%) was purchased from Tianjin Beilian Fine Chemicals Development Co., Ltd. GAC was provided by Kermel Chemical Reagent Co. Ltd, Tianjin, China. A stock solution containing Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ with DI water and a series of solutions used during the experiment were prepared by diluting the stock to the desired concentration.

2.2. Synthesis of GAC–nZVI

The GAC size ranged from 0.43 to 0.85 mm (20–40 mesh). Firstly, 20 g of GAC was put into 100 ml DI water. The GAC solution was heated and boiled on the stove for 10 min, then washed with DI water and dried overnight at 120℃. Secondly, 8 g of $FeCl_3{\cdot}6H_2O$ was mixed with 16 g of GAC by adding 50 ml DI water, then the mixture was agitated for 2 h. Thirdly, $NaBH_4$ solution was prepared by dissolving 3.4 g $NaBH_4$ in 50 ml DI water. Then, $NaBH_4$ solution was added slowly to the solution containing GAC–Fe^{3+} and the mixture was stirred until no significant H_2 production was observed (approximately 2 h). The ferric iron was reduced to zero-valent iron according to the following reaction [26]:

$$Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \uparrow \quad (1)$$

After the solid materials were recovered by filtering and rinsed with DI water and ethanol for several times, they were dried in *vacuum* freeze dryer and dried to constant weight under inert conditions through continuous vacuuming. Finally, the solid materials were stored in sealed bags for use.

2.3. Batch experiments

The batch experiments for the reduction of Cr(VI) were performed in 1 L flasks at room temperature. $Cr_2O_7^{2-}$ aqueous solution was added to the flask containing GAC–nZVI particles. Then the reaction solution was stirred at 150 rpm. The solutions were periodically sampled and filtered immediately through 0.45 μm membrane filters for analysis. The effects of various parameters on the Cr(VI) reduction were researched. GAC–nZVI concentrations used in this study were 2–8 g/L. The initial Cr(VI) concentrations were 15.0–50.0 mg/L. A 0.1 M H_2SO_4 or NaOH solution was used to adjust the solution pHs. During the reaction the pH was not controlled, and GAC–nZVI of different mass ratios was compared at desired concentration.

2.4. Analytical methods

Cr(VI) concentration was determined spectrophotometrically with 1,5-diphenylcarbazide at 540 nm using UV–vis spectrophotometer (UV-3101PC, Japan). And the concentration of total chromium in solution was determined using a flame atomic absorbance spectrometer (Z-2000, Hitachi, Japan). pH value was measured with PHS-25C pH meter (Shanghai). The morphology of the metal particles was observed under a scanned electron microscope (SEM S-3400 N, Hitachi Co., Japan) at an operating voltage of 15.0 kV. X-ray diffraction of GCA–nZVI before and after treating Cr(VI) was performed using X-ray power diffraction (XRD, XD-2, Purkinje General Instrument Co., Ltd., Beijing, China), which employed Cu Kα radiation. The accelerating voltage and applied current were 36 kV and 20 mA, respectively.

3. Results and discussion

3.1. Characterization of GAC–nZVI

Fig. 1 shows the SEM images of GAC–nZVI before reaction (a) and after reaction (b). As indicated in the figure, the aggregates of nZVI particles supported on GAC were observed. This type of aggregation is attributed to magnetic interactions between the primary iron particles. And the sizes of nZVI particles increase prominently after reacting with Cr(VI). This phenomenon could be attributed to the co-precipitation of Cr(III) and Fe(III) on the surface of GAC, which occurs due to a redox reaction between Cr(VI) and ZVI as the following [25],

$$Cr(VI) + Fe^0 \rightarrow Cr(III) + Fe^{3+} \tag{2}$$

The XRD patterns of GAC–nZVI before and after treating Cr(VI) wastewater were compared. The XRD of GAC–nZVI before reaction (Fig. 2(a)) showed an apparent peak of Fe^0 ($2\theta = 44.9$), which weakened significantly after the reaction (Fig. 2(b)), which is consistent with literatures [24,27].

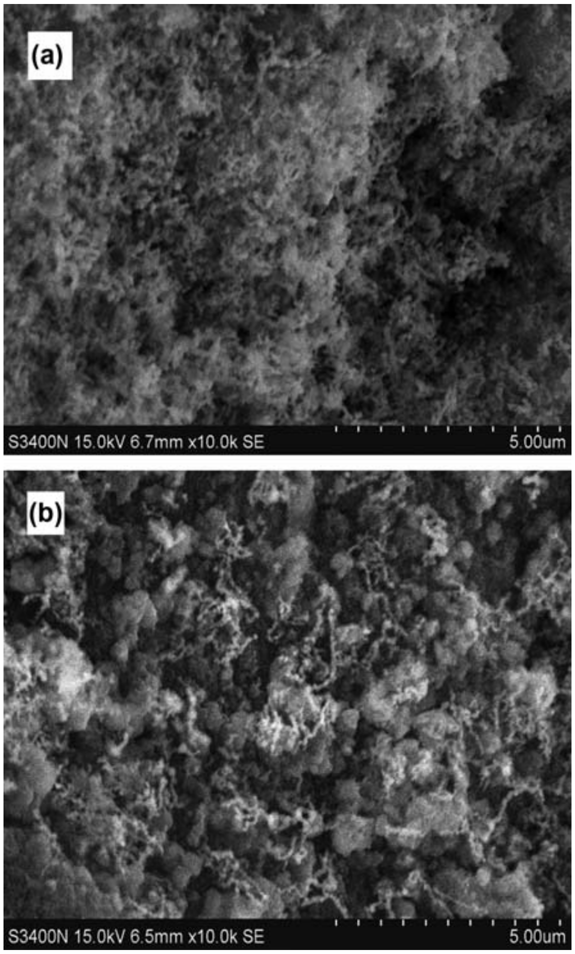

Fig. 1. SEM images of nZVI: (a) before the reaction with Cr(VI) solution (×10,000); (b) after the reaction with Cr(VI) solution (×10,000).

3.2. Conditions affecting Cr(VI) removal

Some researchers have reported that the removal of Cr(VI) by ZVI is achieved by a coupled reduction–oxidation reaction in the system in which ZVI donates the electrons to reduce the Cr(VI) to Cr(III) [28]. The Cr(VI) reduction reaction happened quickly and Cr(VI) was reduced to Cr(III) and Fe(III) was the predominant species on the surface of the GAC. The concentration of total chromium measured by flame atomic absorption spectrophotometer equalled the Cr(VI) concentration measured by the 1,5-diphenylcarbohydrazide spectrophotometer method, i.e. no dissolved Cr(III) was detected, which suggests that all the generated Cr(III) was co-precipitated with Fe(III). These observations match the results obtained by Lo, Lam, Lai and Pratt, Blowes, Ptacek [28,29]. The formation of Cr(III) precipitates is desirable for Cr(VI) remediation because the precipitated Cr(III) is insoluble

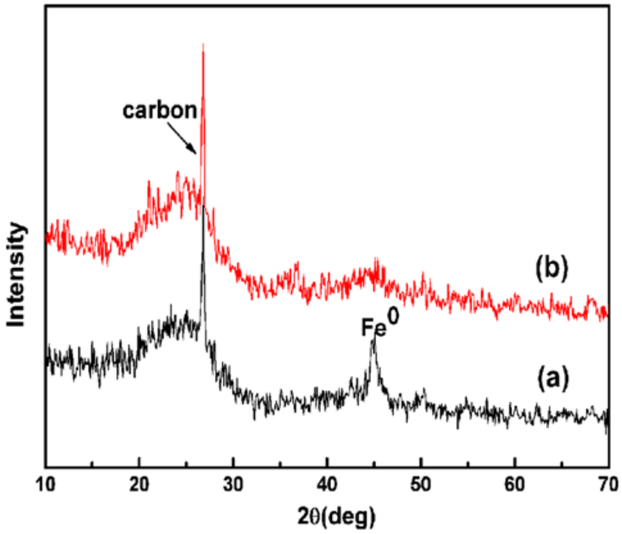

Fig. 2. XRD of GAC–nZVI, (a) before and (b) after the reaction with Cr(VI) solution.

Table 1
Batch experiments parameters and residual Cr(VI) concentration

Initial Cr(VI) concentration (mg/L)	nZVI–GAC mass ratio	GAC–nZVI loads (g/L)	pH	Residual Cr(VI) concentration (mg/L)
20.0	GAC	6.0	5.0	17.7
20.0	1:48	6.0	5.0	14.7
20.0	1:16	6.0	5.0	10.8
20.0	1:12	6.0	5.0	6.9
20.0	1:10	6.0	5.0	1.35
20.0	1:9	6.0	5.0	0.08
20.0	1:10	2.0	5.0	8.7
20.0	1:10	4.0	5.0	6.6
20.0	1:10	8.0	5.0	0.01
20.0	1:10	6.0	3.0	0
20.0	1:10	6.0	7.0	3.2
20.0	1:10	6.0	9.0	4.4
15.0	1:10	6.0	5.0	0
30.0	1:10	6.0	5.0	9.8
40.0	1:10	6.0	5.0	17.3
50.0	1:10	6.0	5.0	25.8

and the toxicity of Cr(III) is greatly reduced [30]. However, these co-precipitates may act as electric insulator and inhibit the electron transfer on the iron surface and terminate the further redox reactions. This important phenomenon suggests that nZVI supported on GAC can be exhausted after reacting with Cr(VI).

3.2.1. Effect of nZVI–GAC mass ratio

According to the report by Dou et al. [12], ZVI corrosion was enhanced by coupling with AC, and ZVI acted as a micro-anode and AC as a micro-cathode. Different mass ratio, leading to various contact area ratios of anode to cathode, would significantly affect the corrosion rate and thus the Cr(VI) removal rate. The effect of nZVI–GAC mass ratio on Cr(VI) removal is presented in Table 1 and Fig. 3, which showed that when nZVI–GAC mass ratio increased from 1:48 to 1:9, the Cr(VI) removal was significantly enhanced. After a 2-h reaction period, the residual Cr (VI) concentration of 1.35 and 0.08 mg/L was achieved at nZVI–GAC mass ratio 1:10 and 1:9, respectively. Comparably, with only GAC and without nZVI, the residual Cr(VI) concentration was as high as 17.7 mg/L after 2-h reaction. From this fact, we can conclude that nZVI plays the main role in the Cr(VI) removal. Hence, increasing nZVI–GAC mass ratio can increase the Cr(VI) removal. To explore the other conditions affecting Cr(VI) removal, an nZVI–GAC of 1:10 was selected for use in subsequent experiments.

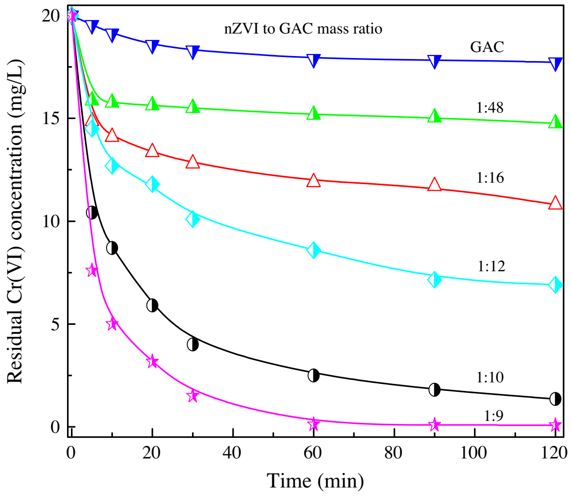

Fig. 3. Effect of nZVI–GAC mass ratio on Cr(VI) removal (initial Cr(VI) concentration, 20.0 mg/L; GAC–nZVI addition, 6 g/L; pH 5.0).

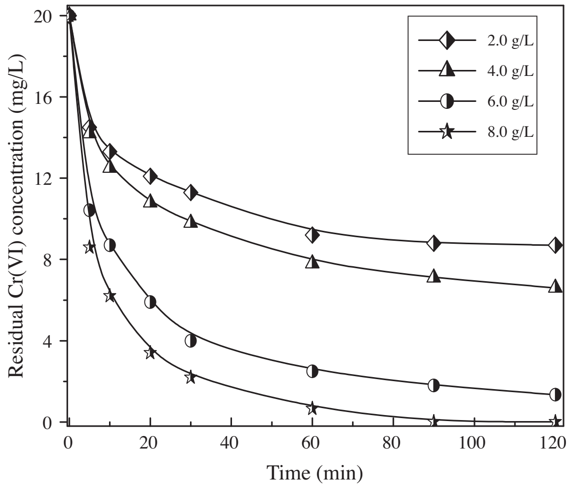

Fig. 4. Effects of GAC–nZVI loads on Cr(VI) removal (initial Cr(V) concentration, 20 mg/L; nZVI/GAC mass ratio, 1/10; pH, 5.0).

According to the literature by Hoch et al. [24], at a 10:3 Fe/Cr mole ratio, C–Fe^0 reduced a 10 mg/L Cr(VI) solution to 1 mg/L within three days. While at optimum conditions by GAC–nZVI, after treating initial Cr(VI) concentration 20.0 mg/L, the residual concentration of Cr(VI) was 1.35 mg/L within 120 min. So, we can conclude that GAC–nZVI is more efficient. And the synthesis of GAC–nZVI is simple and economical compared with the carbon black-nZVI synthesized by carbothermal method.

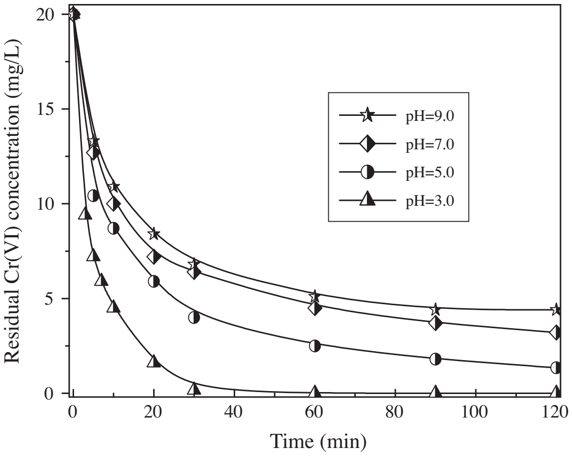

Fig. 5. Effects of pH value on Cr(VI) removal (initial Cr(V) concentration, 20 mg/L; nZVI/GAC mass ratio, 1/10; GAC–nZVI addition, 6 g/L).

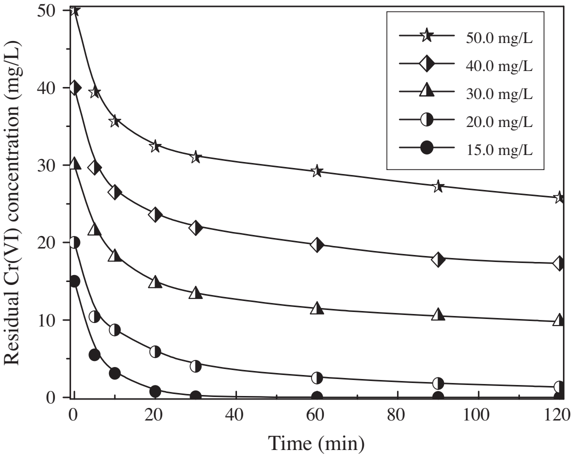

Fig. 6. Effects of initial Cr(VI) concentration on Cr(VI) removal (nZVI/GAC mass ratio, 1/10; GAC–nZVI addition, 6 g/L; pH 5.0).

3.2.2. Effect of initial GAC–nZVI loadings

Four initial GAC–nZVI concentrations were employed, and the initial loadings of GAC–nZVI in Cr(VI) solution were 2.0, 4.0, 6.0 and 8.0 g/L. The concentration of Cr(VI) decreased dramatically in the initial 20 min, then slightly declined in the later reaction. The Cr(VI) residual concentration decreased as the GAC–nZVI loading increased (Fig. 4 and Table 1). The Cr(VI) residual concentration was 1.35 mg/L at a GAC–nZVI loading of 6.0 g/L in 120 min, while only 0.01 mg/L Cr(VI) was left when the GAC–nZVI loading was 8.0 g/L. This phenomenon can be attributed to the increase in the available active sites resulting from the elevation in GAC–nZVI loading.

3.2.3. Effect of initial pH values

The initial solution pH value is important in Cr(VI) reduction using GAC–nZVI. The dependence of pH values on Cr(VI) removal was investigated by adjusting the solution pH to 3.0, 5.0, 7.0 and 9.0 with either 0.1 M HCl or NaOH. The results showed that the pH value had a distinct effect on Cr(VI) removal by GAC–nZVI. As shown in Fig. 5, a remarkable decrease in residual concentration occurred at pH 3.0, where equilibrium was achieved within 30 min and the residual Cr(VI) was below the detection limit. The Cr(VI) removal decreased significantly with increases in the initial pH, so that 4.4 mg/L Cr(VI) was obtained at pH 9.0 in 120 min while 0.16 mg/L Cr(VI) was residual in 30 min at pH 3.0.

Cr(VI) in aqueous solution was in the form of $HCrO_4^-$ between pH 1.0 and 6.0, and CrO_4^{2-} above pH 6.0 [31]. The effect of pH on Cr(VI) reduction may be influenced not only by H^+ consumption in the overall reaction but also by the relatively low solubility of Cr(III) hydroxides and iron(III) hydroxides. At lower pH, the corrosion of nZVI was accelerated and the precipitation of Cr(III) and Fe(III) hydroxides on the surface of iron was unfavourable, which led to an increase in the reaction rate [25]. The pH increased from 3.0, 5.0, 7.0 and 9.0 to 4.4, 7.2, 8.9 and 9.2, respectively. Alkaline environment is generated as expressed in Eq. (3),

$$CrO_4^{2-} + Fe^0 + 4H_2O \rightarrow Cr(OH)_3 + Fe(OH)_3 + 2OH^- \tag{3}$$

At higher pH values, Cr(III) and Fe(III) hydroxides undoubtedly developed which hindered access to the nZVI surface and inhibited further decomposition of iron surface.

3.2.4. Effects of initial Cr(VI) concentrations

The effect of initial Cr(VI) concentration on Cr(VI) removal was investigated in the range of 15.0–50.0 mg/L. Fig. 6 shows the residual Cr(VI) under different Cr(VI) initial concentrations. The Cr(VI) residual concentration was 0.09 mg/L at 30 min with initial Cr(VI) concentration of 15.0 mg/L, but 25.8 mg/L at 120 min with Cr(VI) initial concentration of 50.0 mg/L. The lower removal efficiencies of Cr(VI) were found at higher concentrations of Cr(VI), which is attributed to non-availability of sufficient number of nZVI. When the initial Cr(VI) concentration increased, the nZVI is not increased correspondingly. And it is clear that the residual concentration of Cr(VI) increased with the increase of initial Cr(VI) concentration, and the absolute

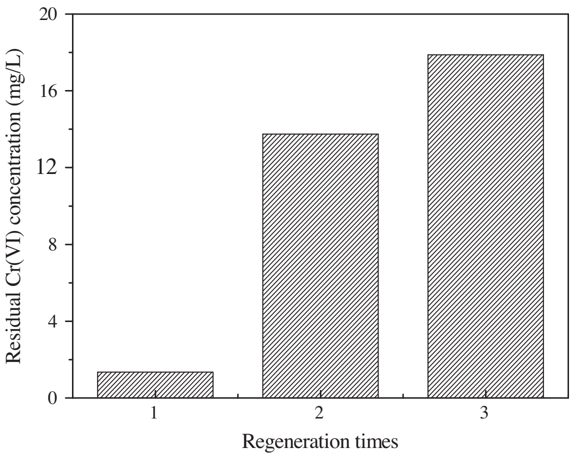

Fig. 7. The variation of Cr(VI) removal by GAC–nZVI after reusing three times (Cr(VI) initial concentration, 20.0 mg/L).

removal amount increased with increasing initial Cr(VI) concentration.

3.2.5. *GAC–nZVI reuse*

The efficiency of GAC–nZVI was tested by recycling it for the removal of Cr(VI) with respect to the optimized conditions. After each run, fresh Cr(VI) solution is replaced in the reactor using the recycled GAC–nZVI after washing with DI water. It was shown that the removal of Cr(VI) was dramatically reduced after being used only once (Fig. 7). From second to third run, the residual Cr(VI) concentration was 13.7 and 17.9 mg/L, respectively. The rapid deterioration of GAC–nZVI was ascribed to the active nZVI exhausted and the inability of the redox reaction between Cr(VI) and nZVI to proceed further since Cr(VI) reduction was a chemical controlled and irreversible process. The results also confirmed that the active ingredient of GAC–nZVI was nZVI which acted as a reductant, while GAC only played a role as a dispersant and stabilizer. And further research must be carried out to slow and control the degree of nZVI oxidation and as a consequence, a more effective regeneration method may emerge.

4. Conclusions

GAC–nZVI was synthesized, characterized and investigated to remove Cr(VI) from wastewater. Batch experiments indicated that the Cr(VI) removal increased with nZVI–GAC mass ratio and GAC–nZVI loading increasing, and fell with the initial Cr(VI) concentration and pH increasing. After treating Cr(VI), no dissolved Cr(III) ions were detected, suggesting that all the generated Cr(III) was co-precipitated with Fe(III). This phenomenon is desirable for Cr(VI) treatment because the precipitated Cr(III) is insoluble and the toxicity of Cr(III) is greatly reduced. At optimum conditions, after treating initial Cr(VI) concentration 20.0 mg/L, the residual concentration of Cr(VI) was 1.35 mg/L. Based on the above results, it was considered that GAC–nZVI was effective and could be used to remove Cr(VI) from wastewater. However, further research must be carried out to slow and control the degree of nZVI oxidation in the atmosphere and as a consequence, a more effective regeneration method may emerge.

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