Removal of Cr(VI) by magnetic Fe/C crosslinked nanoparticle for water purification: rapid contaminant removal property and mechanism of action
Runhua Chen, Ping Wang, Meng Li, Fei Tian, Jiangjun Xiao, Xinxi Fu, Chunlian Ding and Yan Shi

ABSTRACT
In this study, a novel method based on the magnetic Fe/C crosslinked nanoparticles (MNZVI/CNTs-OH) is reported for the effective removal of Cr(VI) in aqueous solutions. Parameters that influence the effectiveness of the nanoparticles, such as pH, temperature, reaction time, and particle dosage, was analyzed. It was found that MNZVI/CNTs-OH particles exhibit significantly higher activity toward Cr(VI) removal than bare NZVI, carbon nanotubes (CNTs), and other synthetic nanomaterials. Under optimized conditions, the removal efficiency of Cr(VI) by MNZVI/CNTs-OH is up to 98% with an initial contaminant concentration of 50 mg/L, and chromium content in the residue up to 48 mg/g. Physical characterizations, including Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and TG-TD measurements, provide insights into the working mechanism of Cr(VI) purification. Our findings suggest that immobilization of MNZVI onto carbon nanotubes increase the covalent bond property, while crosslinked nanoparticles (NPs) provide the electron transfer passage from the NZVI surface and improves the dispersity of the MNZVI, thus enhancing the performance. These results demonstrate the potential of the MNZVI/CNTs-OH nanoparticles for the rapid and efficient treatment of Cr(VI)-containing wastewater.

INTRODUCTION
With the development of economy, there are more than 20,000 registered electroplating industries in China, and over 20 million tons of wastewater with extremely high concentrations of Cr(VI) is generated every day (Bin et al. 2016; Hongfei 2018). The increasing and serious Cr(VI) pollution greatly increases the risk to the eco-system and human health (Li et al. 2016). In nature, Cr(VI) is known to be highly water soluble, bioavailable, reactive, toxic, and mutagenic to human beings. It has been classified as a hazardous substance. Chronic human exposure to high levels of Cr(VI) by inhalation or oral exposure are likely to harm the liver, kidney, blood, gastrointestinal, and the immune system (Mao et al. 2017; Shi et al. 2017). Additionally, epidemiological studies have confirmed that Cr(VI) is a human carcinogen. In order to control chromium pollution, the maximum acceptable limit for total chromium in inland surface and drinking water are 0.1 mg/L and 0.05 mg/L, respectively. Cr(VI) pollution is a significant environmental concern, and an economical and feasible reduction process converting Cr(VI) to Cr(III) has received considerable attention, which is highly desired by the electroplating industries (Fu et al. 2018).

The wastewater containing Cr(VI) is generated mainly from electroplating industrial processes. Many methods such as adsorption, oxidation, catalytic hydrolysis, chemical precipitation, osmosis membrane filtration, and photocatalysis, have been developed to remove Cr(VI) from wastewater (Fang et al. 2018). Among those, catalytic reduction and adsorption technique is considered as the most promising way, due to its fast processing, environmental friendliness, and lack of secondary pollution (Lim et al. 2017). Some
traditional adsorption materials, including zeolite, chitosan, activated carbon or bio-carbon has been widely adopted to remove Cr(VI) (Al-Othman et al. 2012). However, these methods suffer from the drawback of relatively low removal capacities. This has led to researchers developing alternative nanoscale materials (Naushad et al. 2014; Kumar et al. 2016; Alqamadi et al. 2017; Naushad et al. 2017). Ren et al. synthesized nanoparticles from titanium residue by reduction method for Cr(VI) removal. It was observed that removal capacity reaches 14.49 mg/g at 298.15 K (Ren et al. 2017). ZnO-biocarbon nanoparticles reported by Yu et al. showed the maximum removal capacity of 43.48 mg/g (Yu et al. 2018).

Magnetic carbon nanoparticles have attracted great technological interests in various aspects, due to their remarkable properties such as the characteristics of easy separation and high thermal and mechanical stability. For example, Huang et al. synthesized magnetic multi-wall carbon nanotubes, which showed high separation features and a maximum removal capacity of 16.25 mg/g at the temperature of 343 K (Huang et al. 2015). Zhou et al. produced a functionalized magnetic nanocarbon spheres for Cr(VI) removal with the max capacity of 1.57 mg/g at 315 K (Zhou et al. 2018). Fatehi et al. synthesized magnetic nanoparticles supported on activated carbon for removal Pb(II) and Cr(VI) from saline solutions (Fatehi et al. 2017). Liu et al. created a silkworm cocoon-like α-Fe₂O₃ by using a simple hydrothermal method (Liu et al. 2018). Despite promising results, the low removal capacity limit the extensive use of those magnetic nanoparticles. In order to improve the removal capacity of nanomaterials, Li et al. modified TiO₂ with hydroxyl groups for selective adsorption of Cr(VI), which greatly improved the removal capacity (Li et al. 2017). Li et al. used polyaniline to enhance the adsorptive and reduction potential of SnO₂; the photocatalytic activity of the SnO₂/PANI NC was far higher than raw SnO₂ (Li et al. 2018). Although surface modification lead to a certain degree of improvement to conventional materials in adsorptive and reduction capacity, to process needs to be further simplified and allow for faster reaction rates. Therefore, a novel nanoscales materials with both outstanding removal capacity and fast reduction kinetic towards Cr(VI) is still very much sought after (Hagemann et al. 2018).

Metal or organic components modified carbon nanomaterials have drawn great public concerns owing to its electron transfer and anti-passivation characteristics. Mohamed et al. reported an electro-spinning method to disperse titanium dioxide nanoparticles on polycrylonitrile-carbon nanotubes (PAN-CNT) for the removal of Cr(VI) ions (Mohamed et al. 2017). Recently, Abdel et al. reported a method that modified carbon nanotubes with 5,7-dinitro-8-quinolinol as potentially applicable tool for efficient removal of industrial wastewater (Abdel Salam et al. 2017). However, it is important to note that the methods are very costly. It is very important to develop a facile and cheap method for the large-scale synthesis of magnetic nanoparticles.

Therefore, to address all the challenges mentioned above, magnetic MNZVI/CNTs-OH crosslinked nanoparticles was prepared in mild conditions in this study. CNTs were first modified with ferric salts in the ethanol aqueous solution using ultrasonic vibration, followed by reduction and oxidation process to yield MNZVI/CNTs-OH. Cr(VI) removal properties on various conditions were investigated. The results of MNZVI/CNTs-OH were compared with that of commercially available unmodified carbon nanotubes, rice husks, and other synthesized nanomaterials. The results show that the performance of MNZVI/CNTs-OH is much superior than that of natural adsorbents. Finally, the surface physical and chemical properties of MNZVI/CNTs-OH before and after the contaminant removal process were characterized to understand the nature of the removal mechanism.

MATERIALS AND METHODS

Chemicals

Multiple-walled carbon nanotubes was purchased from Jichang Materials Tech Co. Ltd. Sodium borohydride, ferrous sulfate heptahydrate, hydrochloric acid, potassium bichromate, and absolute ethyl alcohol were obtained from China National Pharmaceutical Group Corporation. Distilled deionized (DI) deoxygenated water (18.2 MΩ cm) was prepared by redistillation for chemical preparation. To avoid the hydrolysis of Fe(III) solution and the oxidation of Fe(II) solution, these two solutions were freshly prepared before use. All the chemicals used in this study were of analytical grade.

Synthesis method of magnetic MNZVI/CNTs-OH

The magnetic MNZVI/CNTs-OH nanoparticles were prepared using a chemical reduction co-precipitation and the residue hot air in-situ oxidation method. In brief, 20 g of ferrous sulfate heptahydrate was dissolved in 100 g of deionized water followed by adding 20 mL of anhydrous ethanol to the solution. Then, approximately 20 mL of water-based carbon nanotube suspension was gradually added to the solution at 298 K. This solution was then continuously ultrasonic
vibration for 30 min. Thereafter, approximately 200 mL of sodium borohydride dilute solution were gradually added with a dropper under continuously stirring until a specific blackish color (indicating the formation of MNZVI/CNTs-OH) was observed. Finally, the solution was filtered, washed several times with deionized water and ethanol. The obtained solid residues were collected to a drying chamber magnetized by hot wind at 353 K for 2 h. The resulting nanocomposites were washed with anoxic DI water and separated by magnetic force. The prepared MNZVI/CNTs-OH were used for Cr(VI) removals. The flowchart of the synthesis process is shown in Figure 1.

**Batch Cr(VI) removal experiments**

Batch Cr(VI) removal experiments were performed in a batch reactor containing 100 mL of Cr(VI) test solution at desired concentrations. Cr(VI) solutions of different initial concentrations were prepared by diluting the K₂Cr₂O₇ stock solution. Pre-weighted MNZVI/CNTs-OH nanoparticles were added to each reactor. The mixture was shaken in a shaker at the speed of 150 rpm. The influences of temperature (293–353 K), react duration (0–30 min), and MNZVI/CNTs-OH dosage (1–5 g/L) were evaluated. To investigate the effect of pH on Cr(VI) removal by MNZVI/CNTs-OH, the desired pH (2–10) of solution was initially adjusted with 0.1 M of HCl and 0.1 M of NaOH solution. When the reaction reached equilibrium, the composite residual were separated by filtration. Cr(VI) concentration in the supernatant was determined. All experiments were conducted in triplicate. The removal rate (η) of Cr(VI) was calculated using Equation (1).

\[
\eta = \frac{100 \times (C_0 - C)}{C_0} \times \%
\]

(1)

The removal capacity (qₑ) of Cr(VI) in solution was calculated using Equation (2):

\[
q_e = \frac{V \times (C_0 - C)}{m_0}
\]

(2)
where $C_0$ and $C$ are the initial and final Cr(VI) concentration in solution, respectively; $V$ is the solution volume (unified to 100 mL) (mL); $m_0$ is the weight of the dried mass of MNZVI/CNTs-OH (g) (Jin et al. 2018).

**Characterization methods**

The thermal stability of as-synthesized MNZVI/CNTs-OH was tested by thermo gravimetric analysis (TGA) using a SDT V3.0F (2960) instrument under oxygen gas flow at 900 °C with a heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Nicolet 6700 spectrometer (Thermo, USA) in the range of 400–4,000 cm$^{-1}$ with 4 cm$^{-1}$ resolution. All the samples were degassed at 120 °C for 5 h before analysis. The structure and crystallinity of the as-synthesized catalysts was tested by powder X-ray diffraction (XRD) analysis on an Advance Model 6000 diffractometer (Shimadzu, Japan) at the voltage of 40 kV, the current of 50 mA, and the scan speed of 2°/s from 10° to 80°. The images of surface morphologies and the energy-dispersive spectrometry (EDS) spectra were acquired by a field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, The Netherlands).

**RESULTS AND DISCUSSION**

**Characterization of the MNZVI/CNTs-OH**

The microscopic structure of both CNTs and MNZVI/CNTs-OH are shown in Figure 2(a) and 2(b), respectively. The typical unmodified CNTs with distinct filamentous overlapped smooth surface morphology are observed. The shape of MNZVI/CNTs-OH was similar to CNTs, but the size of MNZVI/CNTs-OH was bigger than that of CNTs. Furthermore, the MNZVI/CNTs-OH appeared to be a rough surface, which was intertwined like multiple ball chains cross-linked together. The SEM micrographs of modified MNZVI/CNTs-OH indicated the well-distribution of NZVI on the CNTs surface with rough porous structures, which was positive to Cr(VI) removal.
The analyses of X-ray diffraction (XRD) pattern were carried out to reveal the phase information of the as-obtained samples. In Figure 2(c), a broad peak at 26° presented the amorphous carbon feature in CNTs. This peak became weakened and shifted positively to the range of 45° in the patterns of MNZVI/CNTs-OH. The peak of MNZVI/CNTs-OH was shown to the broadening band between 42° and 46°, assigning to the facets of iron carbide. Besides, the other obvious peaks located at 42.3, 45.2, and 44.8° were assigned to FeC₈ (JCPDS-010024), Fe₃C (JCPDS-892005), and martensite (JCPDS-4412191), respectively, suggesting that the MNZVI/CNTs-OH were composed of Fe and iron carbide species.

Additionally, to further characterize the existence of functional groups and magnetic sources on the synthesized sample, TGA analyses were carried out to provide quantitative thermo gravimetric information of the MNZVI/CNTs-OH and CNTs. The TG-TD curves were obtained under the oxygen atmosphere by heating the samples from 0 to 1,000 °C with a heating rate of 10 °C/min. As shown in Figure 2(d), the raw CNTs exhibited discernible thermal degradation at 500 °C. The weight loss of the CNTs was due to carbon removed in the form of carbon dioxide under an oxygen atmosphere at 500 °C. Thus, the MNZVI/CNTs-OH complex experienced a weight loss of 15.5% at 500 °C, which might be due to the vaporized state of hydroxyl group accounting for 10–15.5% of the total weight. In contrast to the CNTs, the MNZVI/CNTs-OH surfaces were well combined with the iron and iron oxide material, showing high crystallinity and low reactivity under the high temperature. Therefore, it indicated that the only functional group was lost in the MNZVI/CNTs-OH. These results were in agreement with the EDS and SEM patterns of the MNZVI/CNTs-OH mentioned earlier. Therefore, the magnetization and hydroxylation of CNTs during the fabrication process was convinced.

The EDS analysis for CNTs, MNZVI/CNTs-OH, and MNZVI/CNTs-OH after adsorption are shown in Table S1 (available with the online version of this paper). The EDS of MNZVI/CNTs-OH showed high content of C, O, and Fe, indicating successful synthesis of MNZVI/CNTs-OH. But the element percentage showed that the detected mass ratio of Fe/C (10.92: 73.59) was slightly higher than the theoretical ratio, which might be attributed to the formation of iron oxides wrapping on the CNTs (Dong et al. 2018). After the synthesis process, the mass ratio of oxygen dropped to 15.38%, which demonstrates that magnetic iron oxide was homogeneously distributed on the surface of MNZVI/CNTs-OH. Finally, it was seen that some magnetic iron oxides and oxide groups has been generated during the synthesis process. These functional groups such as hydroxyl and carboxyl were involved in the binding of metal ions. After adsorption of Cr(VI), the chromium was clearly observed in EDS data.

Factors effecting the Cr(VI) removal by MNZVI/CNTs

Effect of solution pH

The pH of the solution is an important parameter affecting most chemical reactions. The Cr(VI) removal were investigated at the initial pH in the range of 2–12 with 100 mg/L of Cr(VI). The results are shown in Figure 3(a). The concentrations of Cr(VI) were significant different under different pH with the similar MNZVI/CNTs-OH treatment. The removal efficiency of Cr(VI) was only 75.02% at pH 12. However, the removal rate increased to 96.94% as the pH value decrease to 2. The results indicated that the absorption efficiency increased with pH lower than 6.0. This phenomenon was due to that the hydrogen ions (H⁺) protonated the MNZVI/CNTs-OH surface and promoted CrO₄²⁻ anions transport and the stable state formation. With the increase of solution pH, some MNZVI/CNTs-OH surface was deprotonated. The negative charged surface led to strong competition between the Cr(VI) and OH⁻. Meanwhile, the Cr(VI) ions were unevenly distributed far away from the layer of MNZVI/CNTs-OH surface. Considering some economic and practical feasibility, for example, the pH value of the wastewaters is generally around 6. The pH of 6.0 as the optimized pH was selected for all subsequent experiments.

Effect of contact time

The effect of contact time on Cr(VI) removal by MNZVI/CNTs-OH was carried out at the initial concentration (100 mg/L) in neutral condition, and the results are shown in Figure 3(b). The plot of contact time was divided into three stages. At the initial stage, MNZVI/CNTs-OH removed 85% of the Cr(VI) within the first 5 min, indicating that there was a sufficient number of reaction sites at the beginning of the Cr(VI) reaction process. The accessible reaction sites are vacant, resulting in the sharp increase in the uptake of Cr(VI) on MNZVI/CNTs-OH. Meanwhile, the great concentration gradient between the solution and the surface of MNZVI/CNTs-OH accelerated the Cr(VI) diffusion process from the liquid-phase to solid-phase, which contributed to the fast increase of uptake at the initial
As the process continued (the second stage), the active sites on the MNZVI/CNTs-OH were gradually occupied and the surface diffusion was slowing down, which led to the decrease in the removal rate. The Cr(VI) removal reached equilibrium at 30 min. The removal capacity of Cr(VI) was observed to decrease from 100 mg/L to 18.5 mg/L, with the removal rate of 82.5%. Therefore, 30 min was selected as the optimum contact time for further experiment.

Effect of solution temperature

The temperature of aqueous solution is one of the most important factors to characterize Cr(VI) removal property of MNZVI/CNTs-OH. The effects of temperature were investigated under different temperatures from 293 to 373 K, and the results are shown in Figure 3(c). The removal capacity of Cr(VI) increased with the increase of the temperature. It indicated that elevating temperature of solution was favorable for the Cr(VI) removal, and the removal reaction of Cr(VI) by MNZVI/CNTs-OH was an endothermic reaction. Furthermore, the Cr(VI) removal rate gradually increased from 20.37% to 86.25% with increasing temperature from 293 to 353 K. The removal capacity of Cr(VI) was observed to decrease from 150 mg/L to 18 mg/L at the temperature of 353 K. It indicated that the temperature has an obvious effect on Cr(VI) removal. To sum up, prolonging the time over 30 min would not make any sense on further improvement of Cr(VI) removal. The theoretical optimum temperature was 353 K, considering the practical reality, 313 K was appropriate for MNZVI/CNTs-OH to remove Cr(VI).

Effect of adsorbent dosage

The effect of different MNZVI/CNTs-OH dosages on Cr(VI) removal was carried out by varying the dosage from 1 to 5 g/L, and the results are presented in Figure 3(d). The dose response curve of the MNZVI/CNTs-OH showed that the dosage of materials strongly influenced the amount of
Cr(VI) removed from the solution. Increasing MNZVI/CNTs-OH from 1 to 5 g/L improved the Cr(VI) removal from 70 to 96%. It might be speculated that the increased dosage of Cr(VI) would supply more available active sites. However, any increase in material dosage more than 4 g/L did not significantly affect the removal efficiency, which was due to the resulting low Cr(VI) concentration in solution under the high materials dosage.

Comparison of Cr(VI) removal on various adsorbent

Many materials have been demonstrated to be effective adsorbents to remove hazardous heavy materials from wastewater. To evaluate the performance of MNZVI/CNTs-OH, some widely used adsorbents with their sorption capacities were investigated. The results of UV-vis absorption spectrums are shown in Figure S1 (available with the online version of this paper). The peak at 540 nm in the UV-vis absorption curve was attributed to Cr(VI). The higher Cr(VI) concentration in the solution, the stronger peak intensity was observed. It was worth noting that the MNZVI/CNTs-OH removal capacities in the current study is higher than that of the other absorbents. 70% of the Cr(VI) was removed with a much low MNZVI/CNTs-OH dose of 4 g/L in 5 min. However, comparative studies of other adsorbents showed that the efficiency of Cr(VI) removal with the similar dosage (9.6% of the rice husks, 10% of the carbon nanotubes, and 49% of the activated carbon) was much lower than that of the MNZVI/CNTs-OH. It was surprised to observe that the Cr(VI) at the initial concentration of 100 mg/L was completely removed by 4 g/L of MNZVI/CNTs-OH within 30 min (the peak at 540 nm has been flattened).

For a further comparative and comprehensive study (Liu et al. 2017), the maximum removal capacity of MNZVI/CNTs-OH with other available carbonaceous adsorbents were summarized, and the maximum removal capacity of the different materials are shown in Table 1. The maximum Cr(VI) removal capacity of MNZVI/CNTs-OH was higher than that of other adsorbents. Therefore, MNZVI/CNTs-OH is a low-cost, effective, recyclable, and promising material for the removal of Cr(VI) ions from wastewater.

Adsorption isotherms

Adsorption isotherms are critical in optimizing the use of adsorbents. Langmuir and Freundlich isotherm models were applied to describe the equilibrium adsorption data. Regression analyses of the linearized isotherms of Langmuir and Freundlich are depicted in Figure 4(a) and 4(b), respectively. The high R² values showed that Langmuir models were more suitable for describing the adsorption equilibrium of Cr(VI). Langmuir models served to estimate the complete monolayer adsorption capacity. Furthermore, it was found that the complete monolayer adsorption capacity increased from 48.0 mg/g to 83.5 mg/g with an increase in temperature from 293 K to 353 K. Therefore, the adsorption of Cr(VI) on MZVI/CNTs-OH is an endothermic process.

Adsorption kinetics and thermodynamics

Kinetics of adsorption is an important characteristic to define the efficiency of the adsorption. In order to find a more reliable description of Cr(VI) adsorption kinetics, the experimental data of Cr(VI) adsorption were fitted with

Table 1 | Comparison of Cr(VI) removal capacities of different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Contaminants</th>
<th>Qₘₐₓ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>Cr(VI)</td>
<td>3.15</td>
<td>Gao et al. (2008)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Cr(VI)</td>
<td>3.46</td>
<td>Selvi et al. (2001)</td>
</tr>
<tr>
<td>Mesoporous magnetic γ-Fe₂O₃</td>
<td>Cr(VI)</td>
<td>16</td>
<td>Wang &amp; Lo (2009)</td>
</tr>
<tr>
<td>NZVI-Fe₃O₄ nanocomposites</td>
<td>Cr(VI)</td>
<td>20.41</td>
<td>Lv et al. (2013)</td>
</tr>
<tr>
<td>Bentonite supported nZVI</td>
<td>Cr(VI)</td>
<td>22.67</td>
<td>Belchik et al. (2011)</td>
</tr>
<tr>
<td>Chitosan-crosslinked-poly nanohydrogel</td>
<td>Cr(VI)</td>
<td>26.49</td>
<td>Sharma et al. (2017)</td>
</tr>
<tr>
<td>Pomegranate husk carbon</td>
<td>Cr(VI)</td>
<td>35.2</td>
<td>Nemr (2009)</td>
</tr>
<tr>
<td>Humus-supported nanoscale zero-valent iron</td>
<td>Cr(VI)</td>
<td>40.40</td>
<td>Fu et al. (2017)</td>
</tr>
<tr>
<td>Polyacrylamide-grafted sawdust</td>
<td>Cr(VI)</td>
<td>45</td>
<td>Raji &amp; Amirudhan (1998)</td>
</tr>
<tr>
<td>Peanut shell activated with phosphoric acid</td>
<td>Cr(VI)</td>
<td>46.73</td>
<td>ALOthman et al. (2013)</td>
</tr>
<tr>
<td>MNZVI/CNTs-OH</td>
<td>Cr(VI)</td>
<td>48</td>
<td>This study</td>
</tr>
</tbody>
</table>
pseudo-first-order model and pseudo-second-order model. The data for these two models are shown in Table 2. The calculated qe values, rate constants, and coefficient of determination (R²) values are also summarized in Table 2. These results indicated that the adsorption of Cr(VI) on MZVI/CNTs-OH followed the pseudo-second-order kinetic model, and the chemical sorption was the rate-controlling step. When the adsorption equilibrium in the studied systems was established, the Cr(VI) adsorbed on MNZVI/CNTs-OH was in equilibrium with the residual Cr(VI) in the liquid phase. Here, thermodynamic parameters such as Gibb’s free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) were estimated, the result is shown in Table S2 (available with the online version of this paper). According to the thermodynamic studies, the positive values of enthalpy change and the negative values of Gibbs free energies demonstrated that Cr(VI) onto MZVI/CNTs-OH was endothermic and spontaneous in nature.

### Possible mechanism of Cr(VI) removal

In order to elucidate the possible mechanism involved in the process of Cr(VI) removal by MNZVI/CNTs-OH. FTIR was employed to study the changes of functional groups on the MNZVI/CNTs-OH surface before and after Cr(VI) removal.

### Table 2 | Kinetic data for the adsorption of Cr(VI) on MZVI/CNTs-OH at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pseudo-first-order</th>
<th></th>
<th>Pseudo-second-order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qe (mg/g)</td>
<td>K1</td>
<td>R²</td>
<td>qe (mg/g)</td>
</tr>
<tr>
<td>293</td>
<td>6.606</td>
<td>0.044</td>
<td>0.845</td>
<td>48.18</td>
</tr>
<tr>
<td>313</td>
<td>13.18</td>
<td>0.052</td>
<td>0.832</td>
<td>52.47</td>
</tr>
<tr>
<td>333</td>
<td>25.03</td>
<td>0.056</td>
<td>0.873</td>
<td>63.62</td>
</tr>
<tr>
<td>353</td>
<td>28.67</td>
<td>0.069</td>
<td>0.851</td>
<td>82.46</td>
</tr>
</tbody>
</table>

Figure 4 | Isotherms for the adsorption of Cr(VI) on MZVI/CNTs-OH at different temperature: (a) Langmuir; (b) Freundlich.

Figure 5 | FTIR spectroscopy of CNTs, MNZVI/CNTs-OH and after adsorption process.
FTIR spectrum in Figure 5(a) show the C = O and –OH stretches of MNZVI/CNTs-OH at 1,639 cm\(^{-1}\) and 3,500–4,000 cm\(^{-1}\), respectively, indicating the zeralo ions (ZVI), ferric oxide, hydroxyl, and other functional groups interacting with the CNTs surface. The band at 1,402 cm\(^{-1}\) was most likely due to the CH\(_2\) scissoring. The 1,116 cm\(^{-1}\) was assigned to the C-O stretches of COO\(^{-}\). After Cr(VI) removal Figure 5(b), the weak –OH stretches were observed on the Cr(VI) containing MNZVI/CNTs-OH, and no C = O stretches were found, suggesting Cr(VI) was bound to MNZVI/CNTs-OH by the covalent bond. It is generally believed that the movement of Cr(VI) to MNZVI/CNTs-OH surface is mainly through ligand exchange and oxidation-reduction reaction. In order to further explore the surface porosity change of the materials, Brunauer-Emmett-Teller (BET) surface areas of MNZVI/CNTs-OH before and after Cr(VI) adsorption were compared. The BET surface area of the three samples of MNZVI/CNTs-OH after individual adsorption were 63.44 m\(^2\)/g, 56.18 m\(^2\)/g, and 75.41 m\(^2\)/g, which were smaller than those (97.70 m\(^2\)/g, 87.56 m\(^2\)/g, 86.23 m\(^2\)/g) of the corresponding starting MNZVI/CNTs-OH.

As is well known, Cr(VI) exists in several main ionic forms (H\(_2\)CrO\(_4\), HCrO\(_4\), CrO\(_4^{2-}\), Cr\(_2\)O\(_7^{2-}\), and HCr\(_2\)O\(_7\)) depending on the pH. In lower pH solution, the main form of Cr(VI) is H\(_2\)CrO\(_4\) or HCrO\(_4\). As the pH increases, HCrO\(_4\) shifts to CrO\(_4^{2-}\) and Cr\(_2\)O\(_7^{2-}\). On the other hand, group characteristics of materials also change with the pH value of aqueous solutions. The maximum removal of Cr(VI) ions is observed in low pH solutions. Based on the obtained results, the possible mechanism can be deduced as surface adsorption, ion exchange, and chemical oxidation-reduction reaction.

The removal of Cr(VI) by MNZVI/CNTs-OH involved the following steps: (1) Cr(VI) adsorption and diffusion happened near the surface of MNZVI/CNTs-OH. (2) Cr(VI) was reduced on the surface of the material by the electron. (3) Electron was transferred to the electron acceptor through carbon nanotubes. Cr(VI) and deposit on the surface of the material. The pH and surface group properties were the key factors of reaction. The surface chemical reaction was the rate-limiting step in this process (Xu et al. 2017).

In acidic conditions, Cr(VI) adsorption and diffusion happened near the surface of MNZVI/CNTs-OH:

\[
\text{MNZVI/CNTs} \rightarrow \text{Ad} + \text{Fe}(\text{VI})[\text{H}_2\text{CrO}_4, \text{HCrO}_4, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-} \text{or HCr}_2\text{O}_7] \rightarrow \text{MNZVI/CNTs} - (\text{H}_2\text{CrO}_4, \text{HCrO}_4, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-} \text{or HCr}_2\text{O}_7)_m + nH^+ \tag{3}
\]

Cr(VI) was reduced on the surface of the material by the electron. There were three ways of reduction: ferrous reduction, hydroxyl reduction, and free electron reaction on the surface of materials:

\[
\text{Fe + Cr(VI)} \rightarrow \text{Fe}^{2+} + \text{Cr(III)} \tag{4}
\]
\[
\text{Fe}^{2+} + \text{Cr(VI)} \rightarrow \text{Fe}^{3+} + \text{Cr(III)} \tag{5}
\]

Fe(II)/Cr(VI) → Fe(III)/Cr(III)

\[
\text{MNZVI/CNTs(e} - \text{)}_n + \text{Cr(VI)} \rightarrow \text{MNZVI/CNTs} + \text{Cr(III)} \tag{6}
\]

Reactive group (–OH, C = C, C = O)/ organic matter + MNZVI/CNTs

\[
\rightarrow \text{MNZVI/CNTs(e} - \text{)}_n + \text{CO}_2 + \text{H}_2\text{O} \tag{7}
\]

MNZVI/CNTs(e - \text{)}_n + Fe\(^{2+}\)/Fe\(^{3+}\)

\[
\rightarrow \text{MNZVI/CNTs} + \text{MNZVI} \tag{8}
\]

The deposition of trivalent chromium on the surface of the MNZVI/CNTs-OH:

\[
\text{MNZVI/CNTs} - (\text{OH})_3n + n\text{Cr(III)}
\]

\[
\rightarrow \text{MNZVI/CNTs(O}_3 - \text{)}_n + 3n\text{H}^+ \tag{9}
\]

MNZVI/CNTs – Fe – (OH)\(_3\)\(_n\) + nCr(III)

\[
\rightarrow \text{MNZVI/CNTs - Fe - (O}_3 - \text{Cr)}_n + 3n\text{H}^+ \tag{10}
\]

Regeneration studies

The reusability of adsorbents is of great importance as a cost-effective process in water treatment. In order to investigate efficiency of Cr(VI) removal and MNZVI/CNTs-OH regeneration, the wastewater with different initial concentrations of 9.5 mg/L, 5.4 mg/L, and 2.3 mg/L was selected as the initial solution. 0.05 M of HCl was selected as the regeneration solvent. Six cycles of adsorption–desorption studies were accordingly carried out. As shown in Figure 6, the removal rate was more than 70% at the first three cycles.
After three cycles, the adsorption capacity of Cr(VI) was reduced, which was due to the loss of iron and organic groups during the process of activation recovery. After three consecutive adsorption–desorption cycles, over 75% recovery ratio was obtained, indicating the high regeneration capacity of MNZVI/CNTs-OH. In addition, Cr(VI), Cr(III), and Fe(III) entered the activation fluid and formed the surface of MNZVI/CNTs-OH during the activation process, which provided an effective way to recall chromium resources, without any secondary pollution.

CONCLUSIONS

In summary, a magnetic Fe/C crosslinked nanoparticle has been successfully synthesized by sequential chemical reduction, co-precipitation, and oxidation under mild conditions, resulting in nanosized ZVI particles homogenously distributed on the CNTs framework. The MNZVI/CNTs-OH exhibited outstanding Cr(VI) removal performance from contaminated water based on the combination of surface reduction and covalent coordination. The improved performance was attributed to the high surface area and the effect of the electronic conductivity between ZVI and CNTs, which is significant in reducing the corrosion of the iron surface. More significantly, the MNZVI/CNTs-OH also demonstrated desirable environmental stability, fast Cr(VI) removal under different environmental conditions, and ease of separation. At the same initial Cr(VI) concentration (100 mg/L), among the CNTs, husk and active carbon, and synthetic adsorbents, MNZVI/CNTs-OH stands out for having the highest Cr(VI) removal efficiency and the shortest contact time. Collectively, our results suggest a strong potential for the MNZVI/CNTs-OH nanoparticles in rapid removal of Cr(VI) from wastewater.

ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China (51804353), Hunan Provincial Natural Science Foundation of China (Science Foundation for Youths grant no. 2018JJ3885), Hunan Provincial Natural Science Foundation of China (Joint Funds of Provincial and Zhuzhou Municipal grant no. 2018JJ4010), and Key R&D Program of Hunan Province (2018SK2044).

REFERENCES


Alqadami, A. A., Naushad, M., Alothman, Z. A. & Ghfar, A. A. 2017 Novel metal-organic framework (MOF) based composite material for the sequestration of U(VI) and Th(IV) metal ions from aqueous environment. ACS Applied Materials and Interfaces 9 (41), 36026–36037.


Fang, W., Jiang, X. X., Luo, H. J. & Geng, J. J. 2018 Synthesis of graphene/SiO2/polypyrrole nanocomposites and their...


Kumar, A., Sharma, G., Guo, C., Mu, N., Pathania, D., Dhiman, P. & Kalia, S. 2016 Magnetically recoverable ZrO₂/Fe₃O₄ chitosan nanomaterials for enhanced sunlight driven photoreduction of carcinogenic Cr(VI) and dechlorination & mineralization of 4-chlorophenol from simulated waste water. *RSC Advances* 6 (16), 13251–13263.


Liu, J., Mwamulima, T., Wang, Y., Fang, Y., Song, S. & Peng, C. 2017 Removal of Pb(II) and Cr(VI) from aqueous solutions using the fly ash-based adsorbent material-supported zero-valent iron. *Journal of Molecular Liquids* 243, 205–211.


First received 21 August 2018; accepted in revised form 26 November 2018. Available online 7 December 2018