Effective removal of Cr(VI) by attapulgite-supported nanoscale zero-valent iron from aqueous solution: Enhanced adsorption and crystallization

Wenying Zhang a,b, Linbo Qian a,**, Da Ouyang a,b, Yun Chen a,b, Lu Han a, Mengfang Chen a,*

a Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
b University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS
- The introduction of AT enhanced adsorption and reduction of the Cr (VI).
- AT-nZVI (2:1) exhibited excellent efficiency for Cr (VI) removal.
- Cr (VI) removal was mainly attributed to reduction at low concentrations.
- FeCr2O4 was the dominant reduction product of Cr (VI) removal by AT-nZVI.

ABSTRACT
The attapulgite supported nanoscale zero-valent iron composite (AT-nZVI) was synthesized and used for Cr(VI) removal. X-ray diffraction (XRD) and transmission electron microscope (TEM) indicated that nZVI particles were well distributed and immobilized on the attapulgite surface. Batch experiments of Cr(VI) removal were conducted at varying mass ratios, initial Cr(VI) concentrations and kinetics. The results indicated that the removal efficiency of Cr(VI) by AT-nZVI approaches 90.6%, being greater than that by non-supported nZVI (62.9%). The removal kinetics could be more accurately explained using pseudo second order kinetics model. The composite exhibited a synergistic interaction instead of simple mixture of AT and nZVI. Reduction was the dominant mechanism at low concentrations as opposed to adsorption at high concentrations. FeCr2O4 was the main reduction product by AT-nZVI, which was attributed to the reduction of Cr(VI) by nZVI and co-precipitation of Cr–Fe oxides on the surface of AT. In the meantime, Fe(II) ion contributed to 64% for the Cr(VI) removal, which resulted from the dissolution of nZVI during the removal process. From the analysis of XRD and XPS results, the crystallization of FeCr2O4 is believed to be formed easily after the reaction of the AT-nZVI composite with Cr(VI) which is more stable and greatly reduce the risk of secondary pollution compared with nZVI. The introduction of AT enhanced adsorption of Cr(VI) and crystallization of the products. The above results suggested that AT-nZVI could be a promising remediation material for Cr(VI)-contaminated groundwater.

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1. Introduction

Cr(VI) in groundwater and surface waters has attracted much attention for its high toxicity, teratogenicity and carcinogenicity in recent decades (Xiao et al., 2018; Zhang et al., 2018a, b; Namgung et al., 2014; Zhang et al., 2017; Dong et al., 2017; Shen et al., 2016; Liu et al., 2012; Zhou et al., 2016; Diao et al., 2016; Yoshinaga et al., 2018). Cr(VI) is listed as a priority controlled pollutant by most countries in the world, and is reportedly 100 times more toxic than Cr(III) (He et al., 2018; Fu et al., 2015; Hizal and Apak, 2006; Lyu et al., 2017; Zhang et al., 2018a). The control and treatment of Cr(VI) pollution poses significant environmental challenges in many countries. Large number of technologies have been studied to treat heavy metal-polluted water, such as ion-exchange, reduction, adsorption, membrane separation, biosorbents, co-precipitation, or a combination of them (Gu et al., 2018; Li et al., 2018; Zhao et al., 2018; Zhu et al., 2018; Kadu and Chikate, 2013; Luo et al., 2013; Xu et al., 2018; Zhang et al., 2010; Yin et al., 2014; Feng et al., 2017; Beheshti et al., 2016).

Among the in-situ groundwater remediation technologies, nZVI was regarded as a promising material for Cr(VI) removal and extensively used to treat a variety of inorganic and organic pollutants in the past two decades due to its higher reaction activity and larger specific surface area (Guan et al., 2015; Xue et al., 2018; Xie et al., 2017; Dong et al., 2016). It can reduce Cr(VI) to Cr(III) quickly, thus reducing environmental risks and hazards to human health (Costa, 2003; Petala et al., 2013). However, a significant limitation of the nZVI technology is the propensity for the iron to aggregate due to its intrinsic properties, thus resulting in reaction activity being diminished (Gu et al., 2010; Bhowmick et al., 2014; Zhang et al., 2012). The particles oxidized and aggregated easily due to the high surface energy and inherent magnetism, which impeded the contact between the nZVI and targeted contaminants (Shi et al., 2011; Zhang et al., 2010). The above reasons also limit its dispersibility and mobility in the environment, to the extent that the removal efficiency was greatly reduced. To overcome these disadvantages, many modification and/or stabilization methods for nZVI have been developed to form composite materials between nZVI and other adsorbents. Much research has been focused on supporting adsorbents, such as biochar, carbon nanotubes, clay minerals, organic and inorganic compounds, molecular sieves, and polymers (Qian et al., 2017, 2019; Zou et al., 2018; Dong et al., 2017; Fu et al., 2015; Petala et al., 2013). Among these materials, clay minerals have attracted considerable interest as potential supporting materials for nZVI due to a series of advantages such as complex porous structure, high specific surface area and ion-exchange properties, small particle size, environmental stability and low cost (Ezzatamnadi et al., 2017; Diao et al., 2016; Bhowmick et al., 2014; Zhang et al., 2010; Choi et al., 2017; Uddin, 2017).

As a natural mineral, attapulgite has abundant deposits, lower price and relatively high specific surface area compared with other clay minerals (Yin et al., 2017; Gan et al., 2009). Attapulgite was a typical kind of aluminum-magnesium silicate mineral, with parallel ribbons of 2:1 layers structure (Wang et al., 2017c; Gan et al., 2009; Yin et al., 2016). As reported in the literature, attapulgite was a potentially attractive adsorbent for some heavy metals (Yin and Zhu, 2016; Frost et al., 2010; Zhang et al., 2015; Chen et al., 2007). It possesses a large number of silanol groups on its surface, large surface area and viscosity and moderate layer charge (Chen et al., 2007; Uddin, 2017). Few studies have focused on attapulgite supported nZVI compared with other clay minerals, such as zeolite, montmorillonite, bentonite, and kaolin (Shi et al., 2011; Fu et al., 2015; Zhang et al., 2010, 2012). Frost et al. (2010), Xi et al. (2014) and Quan et al. (2014) studied the application of attapulgite supported zero-valent iron for the removal of methylene blue, bisphenol A and Cr(VI) respectively. Researchers often focused on the removal efficiency of AT-nZVI, however, the reaction mechanism of AT, nZVI and the target contaminants were ignored.

In this study, the Cr(VI) removal by AT-nZVI from aqueous solution were investigated with following objectives: (1) exploring the contribution by AT and nZVI individually among the reaction between AT-nZVI and Cr(VI); (2) evaluating the effects of loading mass ratios and initial Cr(VI) concentrations; (3) interpreting the enhanced removal efficiencies compared with nZVI.

2. Materials and methods

2.1. Materials and chemicals

The following chemical reagents were used: potassium borohydride (KBH₄, 99.9%), potassium dichromate (K₂Cr₂O₇, 99.5%) and ferrous sulfate hexahydrate (FeSO₄·7H₂O, 99.5%), absolute ethanol. Cr(VI) stock solution was prepared using potassium dichromate (K₂Cr₂O₇) of different masses. And the reagent was dried at 105 °C for 2 h in the oven before use. The pH was adjusted by either 1 mol/L HCl or NaOH. All the chemicals used in the study were of analytical grade without further purification. All the solutions were prepared with ultrapure water (resistivity of 18.25 MΩ·cm).

Attapulgite used in the study was collected from Xuxi County of Jiangsu Province, China. The chemical compositions of the selected attapulgite in weight percentage of oxides are SiO₂ 51.50%, Al₂O₃ 10.62%, MgO 8.77%, Fe₂O₃ 7.42%, CaO 3.45%, K₂O 1.67%, TiO₂ 1.34%, P₂O₅ 0.78%, MnO 0.32%, Na₂O 0.15%. The specific surface area was 180.46 m²/g. Attapulgite, the dominant component, comprised 67% of the sample. The other ingredients were montmorillonite of 18%, feldspar of 8%, dolomite of 4%, and quartz of 3%, respectively. Before use, the attapulgite passed through a 100 mesh sieving and was then calcined in laboratory-scale muffle furnace maintained at 100 °C for six hours. The heating procedure was 5 °C/min.

2.2. Synthesis of AT-nZVI composites

The AT-nZVI was prepared by impregnating the attapulgite with ferrous sulfate solution, followed by reduction with KBH₄ using liquid phase reduction method. The specific methods were similar to those of Shi et al. (2011) with slight modification. Firstly, 1.0 g of FeSO₄·7H₂O and desired amounts of attapulgite (25, 50, 200, 200, 400, 800, 1600 mg) depending on the mass ratios were dissolved into 50 mL of ultrapure water in a beaker. Secondly, the pH value was adjusted to 4.0 approximately in order to keep the dominant form of Fe(II) ion. After that, the suspended solution was sealed and shaken in thermostatic oscillator at 25 °C under the rotating speed of 150 rpm. After 24 h, 50 mL of absolute ethanol was added into the mixture solution which was transferred to a three-neck flask under the protection of high purity nitrogen following by stirring 30 min using mechanical agitator. After 30 min, 100 mL of freshly prepared KBH₄ (0.5 mol/L) was added dropwise and kept stirring for another 1 h.

Subsequently, the above suspended liquid was separated and washed three times with deoxygenated ultrapure water, then washed several times with deoxygenated absolute ethanol. Finally, the product was dried at 70 °C overnight under vacuum drying oven and stored in a vacuum dryer. Different loading mass ratios
(8:1, 4:1, 2:1, 1:1, 1:2, 1:4, 1:8) of AT-nZVI were prepared. nZVI was also synthesized under the same conditions without attapulgite addition.

Three samples were also prepared to explore the impact of structural iron, ferrous iron, the mixture effect of AT and nZVI. The sample of attapulgite without ferrous sulfate heptahydrate being added was obtained using the same method which is referred as AT-structural iron (AT-Fe). The sample of attapulgite saturated with ferrous sulfate heptahydrate only is referred as AT-ferrous iron (AT-Fe(II)). The physical mixture of attapulgite and nZVI is abbreviated as AT + nZVI. All synthetic processes were carried out under the protection of high purity nitrogen. All materials were stored in a vacuum dryer until further use.

2.3. Characterizations

The crystal of AT, nZVI and AT-nZVI before and after the reaction with Cr(VI) were characterized by X-ray Diffraction (XRD, RIGAKU D/MAX 2550/PC, Japan). The XRD spectra were obtained at scanning speed of 2°/min from the range of 2–70°. The scanning process used CuKα radiation and operated at 40 kV and 40 mA with a step size of 0.02°. A Philips TECNAI 12 transmission electron microscope (TEM) from Netherlands was employed to observe the morphology, microstructure and dispersion of prepared nanoparticles. An ESCALAB250Xi X-ray photoelectron spectroscopy (XPS) system was utilized for chemical valent changes among the reaction process. An Autosorb IQ3 produced from USA was applied to calculate the specific surface area (SSA) by Brunauer-Emmett-Teller method. X-ray Fluorescence (XRF-1800, Japan) was also used for elementary composition. The surface charge properties of AT and AT-nZVI were evaluated by Zeta potential measurements with a Nano-ZS90 Zetasizer (Qian and Chen, 2013; Zheng et al., 2009). AT and AT-nZVI (0.4 g/L) were suspended in 20 mL 10 mmol/L NaCl solution. The pH value of the suspensions were roughly adjusted from 3.0 to 9.0 with 1 mol/L HCl or NaOH. And then, the mixture were capped immediately and shaken on a shaker at 150 rpm and 25 °C. After equilibrating for 48 h, the Zeta potential and final pH were measured. The point of zero charge of AT and nZVI were obtained by plotting the Zeta potential against pH.

2.4. Batch experiments

2.4.1. The effect of different ratios

The Cr(VI) removal experiments were carried out by adding the different mass ratios of AT-nZVI (8:1, 4:1, 2:1, 1:1, 1:2, 1:4, 1:8) into 20 mL of 40 mg/L Cr(VI) solutions in a 22 mL vial (with 10 mmol/L NaCl as background electrolyte). Total iron concentrations for all samples were kept the same. The initial pH of the solution was adjusted to 3.0. The mixtures were shaken on a thermostatic oscillator keeping at 150 rpm/min with constant temperature at 25 °C after the samples being added into the Cr(VI) solutions. After equilibrating, the mixtures were filtered through a 0.45-μm membrane filter. Finally, the Cr(VI) concentrations remaining in the solution were measured by the ultraviolet–visible (UV) spectrophotometer method at fixed characteristic wavelength of 540 nm (UV-2700, SHIMADZU Co Ltd, Japan) with the detection limit of 0.004 mg/L. The final pH of the supernatant was also measured by STAR A214 (Thermo Scientific Co Ltd, USA). The total Cr was determined by flame atomic absorption spectrophotometry (Spectra AA 220FS, Agilent Technologies Co Ltd, Japan). The other elements were determined by ICP-OES. All sacrificial experiments were conducted in triplicate for the purpose of quality assurance.

2.4.2. Kinetic removal experiments

Kinetic experiments using AT, nZVI and AT-nZVI were carried out as described herein. The initial Cr(VI) concentration was 40 mg/L with 10 mmol/L NaCl and the initial pH was adjusted to 3.0. Then Cr(VI) solution was added into the glass vials, which were placed on thermostatic oscillator keeping at 25 °C and 150 rpm/min with samples taken at selected time intervals from 0 h to 24 h.

2.4.3. The effect of initial concentrations

The effect of initial Cr(VI) concentrations were carried out with the sample-to-water ratios of 2:5. The initial Cr(VI) concentrations were 5, 20, 40, 60, 80, 100 mg/L, respectively, with 10 mmol/L NaCl as background solution. The initial pH was adjusted to 3.0. Then, the vials were shaken on thermostatic oscillator for 12 h and kept at 150 rpm and 25 °C. The Cr(VI) concentrations remained in the supernatant and final pH were measured after being filtered through a 0.45-μm membrane filter.

2.4.4. The comparison of Cr(VI) removal behavior by different iron species

The comparison of Cr(VI) removal behavior by AT + nZVI and AT-nZVI were conducted under the initial Cr(VI) concentration of 40 mg/L and initial pH of 3.0 with other reaction conditions being consistent with those mentioned above (in Section 2.4.3).

The roles of structural and non-structural iron on Cr(VI) removal efficiency were investigated by adding 8.0 mg of AT-Fe, AT-Fe(II) and AT-nZVI into 20 mL of Cr(VI) solution in 22 mL vials, respectively at an initial Cr(VI) concentration of 40 mg/L. The Cr(VI) concentrations were measured after the solutions were shaken on a thermostatic oscillator for 12 h and filtered through a 0.45-μm membrane filter.

The contribution of Fe(II) iron which was generated from the reaction process was examined by adding a quencher of Fe(II), namely, 1,10-phenanthroline to the vials (Zhang et al., 2018a). The Cr(VI) solution with an initial concentration of 40 mg/L and 1,10-phenanthroline with the dosage of 0.90 g/L were added into the 22 mL vial simultaneously. Then, 8.0 mg of AT-nZVI was added into the vial. The Cr(VI) concentrations were measured after the solutions in the vial were shaken on a thermostatic oscillator for 12 h and filtered through a 0.45-μm membrane filter.

3. Results and discussions

3.1. Structural characterization

The morphology of AT, nZVI and AT-nZVI was explored by TEM. As displayed in Fig. 1, the attapulgite was existed as individual rods with an average length of 400 nm and a diameter of 10 nm approximately or elongated bundles of many rods in order or interwoven network structure. There were lamellar impurities exhibited around the rods. It can be seen clearly from Fig. 1b that nZVI particles were distributed in chains, aggregating into larger ones gradually due to intrinsic magnetic properties and high surface energy. However, the nZVI particles were evenly dispersed and immobilized on the AT surface in the AT-nZVI composite. The specific surface area of AT-nZVI was significantly decreased to 122.70 m²/g compared with AT. The introduction of nZVI to the AT-nZVI composite improved the dispersion and stability of nZVI particles leading to increased active sites for the reaction between Cr(VI) and AT-nZVI.

The AT, nZVI and AT-nZVI composites were also analyzed by XRD. As illustrated in Fig. 2, the diffraction peaks for attapulgite with 2θ of 8.42°, 13.62° and 19.78° were recorded, corresponding to characteristic attapulgite diffractions of (110), (200) and (040), respectively (Zhang et al., 2015). The 2θ of 44.6° was observed in
the spectrum of nZVI, which confirmed the presence of $\alpha$-Fe$^0$ (Fu et al., 2015; Qian et al., 2017). When nZVI was supported with AT, both typical diffraction peaks of AT and nZVI were emerged in the XRD spectrum of AT-nZVI. Moreover, the crystallinity of the $\alpha$-Fe$^0$ was increased for the AT-nZVI. According to the previous studies (Su et al., 2016; Pensini et al., 2013; Anderson and Benjamin, 1985), the iron could be absorbed onto some aluminum-silicate sites and the incorporation of SiO$_2$ increased the crystallinity of ZVI. It can be deduced that the aluminum-silicate particles within AT structure served as effective carriers for the nZVI. These results confirmed that the nZVI was successfully loaded onto the AT.

3.2. Cr(VI) removal behaviors

3.2.1. The Cr(VI) removal by AT, nZVI and AT-nZVI

The Cr(VI) removal by AT, nZVI and AT-nZVI with mass ratio of 2:1 were investigated simultaneously. As illustrated in Fig. 3a, the Cr(VI) residual concentrations in solution with the initial concentration of 40 mg/L were 39.65, 14.85, 3.83 mg/L for AT, nZVI, AT-nZVI after 12 h, respectively. The Cr(VI) removal by AT was considered insignificant, mainly due to the electrostatic repulsion between AT and Cr(VI). However, the Cr(VI) removal efficiencies of 90.6% and 62.9% were achieved by AT-nZVI and nZVI respectively. The introduction of AT in the AT-nZVI composite enhanced the removal efficiency for Cr(VI) compared with the non-supported nZVI, suggestive of AT played the important role in Cr(VI) removal.

3.2.2. The kinetic of Cr(VI) removal

To better understand the removal processes and transformation mechanism of Cr(VI), the Cr(VI) removal kinetics by AT, nZVI and AT-nZVI with mass ratio of 2:1 were investigated. As illustrated in Fig. 3a, equilibrium for the reaction was reached within approximately 12 h. In case of AT, the residual concentrations for Cr(VI) in solution remained nearly unchanged from 0 to 24 h. But the Cr(VI) concentrations in the solution sharply decreased within 1 h, corresponding to removal efficiencies of 67.2% and 41.82% in case of AT-nZVI and nZVI respectively. The removal efficiencies of Cr(VI) were in reducing order of AT-nZVI $>$ nZVI $>$ AT. Based on the kinetics curves, three stages of the removal processes of Cr(VI) by AT-nZVI observed and attributed to the following: (1) rapid reaction stage between 0 and 1 h; (2) slow removal stage between 1 and 12 h and (3) equilibrium stage between 12 and 24 h.

The kinetic data were simulated with first order, second order, pseudo first order and pseudo second order reactions, respectively. The $R^2$ of the fitting curves indicated that Cr(VI) removal by AT-nZVI and nZVI could be more accurately explained using the pseudo second order kinetics model, as depicted in Fig. 3b. The result suggested that chemisorption, rather than diffusion/ion exchange, was the rate-limiting step to adsorption (Yin et al., 2017; Gan et al., 2009).

Based on the above discussions, both the reaction rate and removal capacity of AT-nZVI (2:1) were significantly improved in comparison with that of non-supported nZVI for Cr(VI) removal.
important role in the Cr(VI) removal.

3.3.2. The effects of initial Cr(VI) concentrations

The effect of initial concentrations on the Cr(VI) removal capacity by AT, nZVI and AT-nZVI were undertaken for initial concentrations ranging from 5 to 100 mg/L. As presented in Fig. 4c, removal capacities for the Cr(VI) under different initial concentrations were in reducing order of AT-nZVI > nZVI > AT. Similar to the performance under the initial Cr(VI) concentration of 40 mg/L explained above, the effect of AT on the Cr(VI) removal were insignificant by other initial concentrations. The Cr(VI) removal capacity by nZVI were expected to be less than or equal to that of AT-nZVI. And similar varying tendency observed between nZVI and AT-nZVI on Cr(VI) removal. The removal capacities by AT-nZVI were increased at about 37.56, 153.55 and 266.65 mg/g under the initial Cr(VI) concentrations of 5, 20 and 40 mg/L, respectively. The Cr(VI) removal capacities are dramatically increased and reached the maximum at the initial concentration of 40 mg/L, however, these started to decrease gradually under the initial concentration above 40 mg/L. Compared with the Cr(VI) removal capacity under the initial concentration of 40 mg/L, the reduction of the Cr(VI) removal capacities at 12.28%, 21.50% and 50.20% was noted under the initial Cr(VI) concentration of 60, 80 and 100 mg/L respectively. In case of the non-supported nZVI or AT-nZVI, the decrease of the Cr(VI) removal capacities with the high initial concentrations of above 40 mg/L resulted from the fast formation of Cr–Fe inactivating layer (Dong et al., 2017; Huang et al., 2018). The inactivating layer greatly inhibits the continuing reactions with Cr(VI) under high initial concentrations. This was mainly because AT-nZVI with positive charge produce electrostatic adsorption with Cr(VI) anion. At high Cr(VI) concentrations, a large number of Cr(VI) anions were distributed around the composite and formed Fe–Cr layer instantaneously, thus enclosing the nZVI and blocking the electron transfer. The higher initial Cr(VI) concentration led to faster formation of inactivating layer, hence the lower removal efficiency. Due to the increase of insoluble Fe–Cr deposition on AT-nZVI surface, the electron transfer from AT-nZVI to the solid-liquid interface was blocked and further reaction between AT-nZVI and Cr(VI) was impeded. Fig. 4d depicted the change of final pH with different initial concentrations and illustrated that the pH increase in case of AT-nZVI was greater than that of nZVI and AT, suggesting enhanced reaction with Cr(VI). The changes of final pH were more pronounced with initial concentrations below 40 mg/L, with no differences being observed under the high initial concentrations above 40 mg/L. The reduction process of Cr(VI) was accompanied with a mass of H+ depletion, resulting in the sharp increase of pH. Therefore, Cr(VI) removal was dominated by the reduction and adsorption respectively under the initial concentration below and above 40 mg/L. Those results were similar to those undertaken by Huang et al. (2018).

Therefore, it is inferred that the initial concentrations of Cr(VI) have significant impact on Cr(VI) removal efficiency by AT-nZVI. The removal of Cr(VI) was mainly predominated by the reduction at low concentrations, whereas the electrostatic adsorption becomes significant at high concentrations between Cr(VI) anion and positively charged AT-nZVI. The Cr(VI) was not only an oxidant but also inactivator for AT-nZVI.

3.4. The contribution of non-structured iron

Previous researches (Gu et al., 2010; Hofstetter et al., 2003; Neumann et al., 2008) showed that Fe(II) is present in both surface-bound and structural iron species after the reduction reaction. As these iron were active in the reductive transformation process for some pollutants and the role of the iron species such as the
supporting nZVI (AT-nZVI), the surface-bound iron (AT-Fe(II)) and the structured iron (AT-Fe) was investigated in this study. As illustrated in Fig. 5a, the AT-nZVI has the highest Cr(VI) removal efficiency of 90.6% at the equilibrium time compared with 2.8% for AT-Fe(II). The control experiment with AT-Fe(II) showed negligible reducing action of Cr(VI) indicating the minimal contribution of exchangeable iron for the removal of Cr(VI) by the AT-nZVI. Furthermore, there was no detectable reduction of Cr(VI) with AT-Fe, suggesting that the structural iron existed in aluminosilicate state within the selected attapulgite clay did not participate in the
Cr(VI) removal. Therefore, the non-structural Fe from AT-nZVI was responsible for the reduction action instead of AT-Fe(II).

3.5. The synergistic interaction of AT and nZVI

The comparison of the Cr(VI) removal by AT + nZVI and AT-nZVI (2:1) was made and the results are illustrated in Fig. 5b. The Cr(VI) residual concentrations in solution under the scenario of 40 mg/L initial Cr(VI) concentration were 10.86 and 3.83 mg/L for AT + nZVI and AT-nZVI respectively. The introduction of AT enhanced the Cr(VI) removal activity by acting as a dispersant for nZVI within AT + nZVI or AT-nZVI. The Cr(VI) removal efficiency of the AT-nZVI composite was higher than that of the AT + nZVI mixture. It indicated that the composite of AT-nZVI was not a simple mixture of AT and nZVI, but synergistic interactions taking place between them during the synthesis processes that formed more stabilized structure of AT-nZVI. Therefore, more binding sites were provided to benefit the effective removal of Cr(VI).

3.6. Proposed reaction mechanism

To give a better understanding of the mechanism of Cr(VI) removal by AT-nZVI, XPS spectra of AT-nZVI and nZVI before and after the reaction with Cr(VI) were compared and analyzed (Fig. 6). It is exhibited that the peaks of Cr were appeared after the reaction with Cr(VI), indicating that Cr was incorporated into the composite and participated in the removal processes. In addition, two valence states of chromium (Cr(VI) and Cr(III)) were coexisted in the spectra of Cr 2p after the reaction (Fig. 6b). The peaks of Cr 2p 1/2 at 588.4 eV and Cr 2p 3/2 at 579.4 eV were the characteristics of Cr(VI) species, respectively, and those at 586.8 eV and 576.7 eV belonged to corresponding peaks of Cr(III) species. The above results indicated that both the adsorption and reduction of Cr(VI) were operative within the reaction system.

As shown in Fig. S1, the adsorption of anions was favored when the pH was less than the point of zero charge of 6.8 with the predominant species of Cr(VI) being HCrO₄⁻. HCrO₄⁻ has lower adsorption free energy compared with other forms of Cr(VI) (Xu et al., 2018). Therefore the adsorption occurs due to the dissimilar charge of AT-nZVI and Cr(VI) during the reaction. The results were consistent with those reported in the literature (Wang et al., 2017a, 2017b, 2018).

Fig. 5c presented the time-concentration curves of Cr(VI), Cr(III) and total Cr during the reaction. The slope of Cr(III) curve rapidly increased within the first 0.5 h indicating the fast increase of Cr(III) attributed to the reduction of Cr(VI).

Fe(0) at 706.6 eV was only observed before the reaction with Cr(VI) and disappeared after the reaction (Fig. 6c), suggestive of the Fe(0) being involved during the reaction, then converted to other valence states. The peaks of nZVI and AT-nZVI were shifted differently after the reaction with Cr(VI), indicating different reactions taking place leading to the formation of various precipitates. The above analysis signified that the electron donor was Fe(0)
Cr(III)/Cr(VI) was in reducing order of nZVI processes provided a mass of electrons to reduce Cr(VI) to Cr(III). These indirect multi-electron transfer of Fe(II)-dominated process. These acidic conditions to release a large quantity of Fe(II) ions. It was the solution. On the other hand, Fe(0) was rapidly corroded under the nZVI to the adsorbed Cr(VI) with no electron released into the solution. On one hand, this absorbed Cr(VI) anions occurred redox reactions with Fe(0) or Fe(II) solution after the reaction with Cr(VI).

Fe(0) was rapidly corroded under acidic conditions to release Fe(II) ions quickly into the solution. In order to examine the reaction processes and mechanism in detail, the roles of Fe(II) were investigated by quenching experiments. Fig. 5d illustrated that the presence of 1,10-phenanthroline inhibited the reduction of Cr(VI) by 64% compared with the scenario in which 1,10-phenanthroline was not added. These suggest that Fe(II) formed from the dissolved nZVI accounted for 64% of the Cr(VI) removal rate during the reaction and the remaining attributed to the direct multi-electron transfer from the conduction band of nZVI to the adsorbed Cr(VI).

Therefore, based on the above analyses, the detailed reaction pathways and mechanism were proposed. Firstly, Cr(VI) anions of HCrO₄⁻ were absorbed onto the surface of the composite due to the similar charge between AT-nZVI and HCrO₄⁻. Secondly, the absorbed Cr(VI) anions occurred redox reactions with Fe(0) or Fe(II) ions dissolved from Fe(0) under acidic conditions. On one hand, this was the direct multi-electron transfer from the conduction band of nZVI to the adsorbed Cr(VI) with no electron released into the solution. On the other hand, Fe(0) was rapidly corroded under the acidic conditions to release a large quantity of Fe(II) ions. It was the indirect multi-electron transfer of Fe(II)-dominated process. These processes provided a mass of electrons to reduce Cr(VI) to Cr(III). Finally, FeCr₂O₄ was the main degradation product by AT-nZVI, mainly due to the reduction of Cr(VI) by nZVI and co-precipitation of Cr—Fe oxides on the surface of AT. The introduction of AT enhanced the adsorption of Cr(VI) and the crystallization of FeCr₂O₄ by AT-nZVI compared with nZVI and Fe(II) solution after the reaction with Cr(VI).

4. Conclusions

In this study, attapulgite supported nanoscale zero-valent iron composite was synthesized successfully. The results revealed that AT-nZVI can rapidly reduce Cr(VI) in aqueous solution. The adsorption, reduction and co-precipitation were predominant reactions during the Cr(VI) removal. The loading mass ratio of 2:1 between AT and nZVI was optimized with the initial Cr(VI) concentration of 40 mg/L. FeCr₂O₄ was the main degradation product by AT-nZVI, mainly due to the reduction of Cr(VI) by nZVI and co-precipitation of Cr—Fe oxides on the surface of AT. Two primary electron transfers of the reaction were identified: direct and indirect electron transfers from nZVI- and Fe(II)- predominated processes. The FeCr₂O₄ is observed to be formed easily after the reaction of the AT-nZVI composite with Cr(VI) which is more stable and greatly reduce the risk of secondary pollution. The introduction of AT enhanced the adsorption of Cr(VI) and the crystallization of FeCr₂O₄. It is concluded that the composite of AT-nZVI can potentially be applied to treat Cr(VI) contaminated groundwater due to high-efficiency, environmentally friendliness and low-cost.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.01.070.

References


