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Montmorillonite-Supported Fe/Ni Bimetallic Nanoparticles for Removal of Cr(VI) from Wastewater

Haijiao Lu[a,b], Beiqian Tian[a,b], Jingkang Wang[a,b], Hongxun Hao*[,a,b]

[a]National Engineering Research Center of Industry Crystallization Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.
[b]Collabtive Innovation Center of Chemical Science and Engineering, Tianjin 300072, China
hongxunhao@tju.edu.cn

Cr(VI) is one of the most dangerous heavy metal contaminants and its removal is a great challenge throughout the world. With a nanometer length scale (1-100nm) and large specific surface area, higher reducing ability and activity, stronger adsorption property, better mobility than bulk or microscale iron particles, nanoscale zerovalent iron (nZVI) has shown great promise for removal of Cr(VI) from wastewater. Despite its merits, resulting from large specific surface area and intrinsic magnetic interaction, high reduction ability as well as ultrafine size, nZVI is troubled by aggregation and oxidation from the degraded system, reducing its reduction ability and limiting its application. To overcome these drawbacks, Fe/Ni bimetallic nanoparticles were synthesized by classic sodium borohydride solution reduction method to enhance the reactivity of nZVI. Furthermore, montmorillonite (Mt), which is often used as an effective protective reagent and support as well, was used to achieve well disperse of nZVI. The preparation of the composites was achieved by a simple route. This study has shown that for Mt-supported Fe/Ni bimetallic nanoparticles are promising materials for removal of Cr(VI) from wastewater.

1. Introduction

Cr (VI) is one of the most common and dangerous heavy metal contaminants. It comes from a wide variety of industries, such as paint pigments, metallurgy, tanning, and so on (Lv et al., 2012; Wang et al., 2014). It has been placed on top of the priority list of toxic pollutants by the United States Environmental Protection Agency (US-EPA) (Toth et al., 2012; Baeza et al., 2014). Cr(III) and Cr(VI) are the most common states of Cr element in nature. The toxicity of Cr(VI) is one hundred times higher than that of Cr (Shi et al., 2011).Therefore, there is great necessity to degrade Cr(VI) to Cr(III) to reduce the influence of Cr element to the environment.

With the rapid development of nanotechnology, more and more nanomaterials have been used for the removal of a wide range of contaminants (Bavasso et al., 2016), such as carbon nanotubes, nano TiO_2, nano zerovalent metals (Lu et al., 2016a). Among them, nano zerovalent iron (nZVI) has become one of the most widely used nanomaterials (Petrucci et al., 2016). Compared with normal-sized iron particles, nZVI possesses smaller size, larger surface area, stronger reduction ability and greater reactivity in the removal of contaminants (Lu et al., 2016b). It has been reported to exhibit good performance for the removal of many kinds of pollutants, including halogenated organic compounds (Liang et al., 2014), phenols (Wang et al., 2013), nitroaromatic compounds (Xiong et al., 2015), organic dyes (Hoag et al., 2009), heavy metals (Arancibia et al., 2014; Gueye et al., 2015) and so on. As a typical heavy metal, Cr has been demonstrated to be effectively removed by nZVI (Shi et al., 2011). However, nZVI is also troubled by some problems, which restrict the wide applications of nZVI. For example, resulting from large surface area and magnetic interaction by nature, nZVI tends to aggregate to form chains and be oxidized by the surroundings, which have a negative influence on the reactivity and mobility of nZVI (Luo et al., 2014). Therefore, it is of great significance to make some modifications on nZVI to further improve its properties.

Among the modification strategies, the immobilization of nZVI on a support is one of the most frequently used. Clays (Chen et al., 2011), resins (Li et al., 2007), membranes (Bhaumik et al., 2015), graphene (Li et al., 2016) are among the best examples. As a common type of clays, montmorillonite (MMt) is characterized by its

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laminar structure, two tetrahedral layers of silica and a central octahedral layer of aluminum oxide (Zhu et al., 2011; Tepmatee and Siriphannon, 2013). MMt has a negative charge due to the isomorphous substitution process, leading to a high cation-exchange capacity of ions (Thomas et al., 2011). Besides, the high porosity of MMt is widely used in the removal of heavy metals in water (Benhammou et al., 2005). Thus, immobilizing nZVI on MMt can not only overcome the aggregation problem of nZVI, but also improve the removal of Cr(VI) by cation-exchange and adsorption. In addition, incorporating a less active metal into nZVI to form bimetallic nanoparticles has been proved to enhance the reactivity of nZVI. Among various metals, Ni has the advantages of low price and high reactivity (Lu et al., 2016a).

In this paper, montmorillonite (MMt)-supported Fe/Ni bimetallic nanoparticles were used to remove Cr(VI) from wastewater. The operating conditions were also studied. The as-prepared MMt-supported Fe/Ni bimetallic nanoparticles possessed high activity for Cr(VI) removal. The results demonstrated that they could be highly effective and efficient for removing Cr(VI) in wastewater.

2. Experimental section

2.1 Materials

Na-Montmorillonite, $FeCl_3 \cdot 6H_2O$ (ACS) and $NaBH_4$ (⩾98.0%) were purchased from Aladdin Industrial Corporation (Shanghai, China). $K_2Cr_2O_7$ (⩾99.95%) and $NiCl_2 \cdot 6H_2O$ (AR) were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Ethanol absolute (⩾99.8%) was purchased from Real & Lead Chemical Technology Co. Ltd. (Tianjin, China). 1,5-diphenylcarbazide (DPC) (AR) was purchased from Chemart Chemical Technology Co. Ltd. (Tianjin, China). Phosphoric acid (⩾85.0%) and sulfuric acid (95.0-98.0%) were purchased from Yuxiang Chemical Technology Co. Ltd. (Tianjin, China). All the compounds were used without further purification. Deionized water was used throughout in this work.

2.2 Synthesis of MMt/Fe

Montmorillonite-supported nano zerovalent iron (MMt/Fe) was synthesized under the protection of N_2 in the whole synthesis process by conventional borohydride reduction method. N_2 was purged into the system before the reaction to completely remove the air. Fe^{3+} ($FeCl_3 \cdot 6H_2O$) was reduced by $NaBH_4$ in deionized water at the presence of MMt as a supporting material (Zhang et al., 2010). According to substantial previous studies, excess $NaBH_4$ ($FeCl_3 \cdot 6H_2O$: $NaBH_4$=1:4, molar ratio) was used to ensure complete reduction of Fe(III) (Bhowmick et al., 2014). Bare nZVI without MMt was also prepared by this method for comparison. After the synthesis, Mt-nZVI and nZVI were washed by deionized water and ethanol for three times, respectively. They were dried and stored under in vacuum to prevent oxidation.

2.3 Synthesis of MMt/Fe/Ni

Montmorillonite-supported Fe/Ni bimetallic nanoparticles were prepared in a similar way to that of MMt/Fe. Based on the conclusions of many studies before, the ratio of Fe:Ni was chosen as 10:1 (Fang et al., 2011). Besides, the ratio of metals (the sum of Fe and Ni) and $NaBH_4$ remained to be 1:4 to reduce both Fe and Ni completely. Other steps were the same with section 2.2.

2.4 Characterization

X-ray diffraction (XRD) patterns of the obtained solid products were obtained using a Rigaku D/max-2500 X-ray diffraction analyzer (Rigaku, Japan) with Cu Kα (λ= 0.154 nm) radiation at 40 kV/100 mA at a scanning speed of 6 °/min. Nitrogen adsorption isotherms were measured with an ASAP 2020 adsorption analyzer at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. High resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) measurements were performed on a Tecnai G2 F20 TEM (FEI, Netherlands) at an operating voltage of 200 kV. The concentration of Cr(VI) was obtained by 1,5-diphenylcarbazide (DPC) method with a UV–vis spectrophotometer (Hitachi, U-3010, Japan) at 540 nm.

2.5 Removal of Cr(VI)

All experiments were carried out in 250 mL flasks containing 100 mL simulated wastewater with 50mg/L Cr(VI). Since both the erosion of nZVI was known to be less likely and the removal of Cr(VI) was of higher efficiency at lower pH (Hoag et al., 2009), pH=3 was chosen for all experiments in this study. The flasks were agitated at the speed of 400 rpm at 25 ℃. The materials prepared above were added into the solution and then the reaction was timed immediately. In the process, 2 mL of sample was withdrawn with a glass syringe at an interval of 30 min, and then filtered through a 0.22 μm membrane filter. According to the results of preexperiments, the whole reaction time was chosen to be 180 min. The concentrations of remaining Cr(VI) were detected by UV-vis spectrophotometer.

3. Results and discussion

3.1 Characterization

3.1.1 XRD

The XRD patterns of MMt, MMt/Fe, MMt/Fe/Ni are shown in Figure 1. As depicted in the XRD patterns of MMt/Fe and MMt/Fe/Ni, the peak at 2θ=44.7° demonstrated the (110) plane of Fe (JCPDS card no. 06-0696). However, seen from the XRD patterns of MMt/Fe/Ni, the X-ray diffractometer did not detect the presence of Ni in the nanoparticles, which was attributed to the low content of Ni nanoparticles. The results showed that Fe in the nanomaterials was well crystallized.

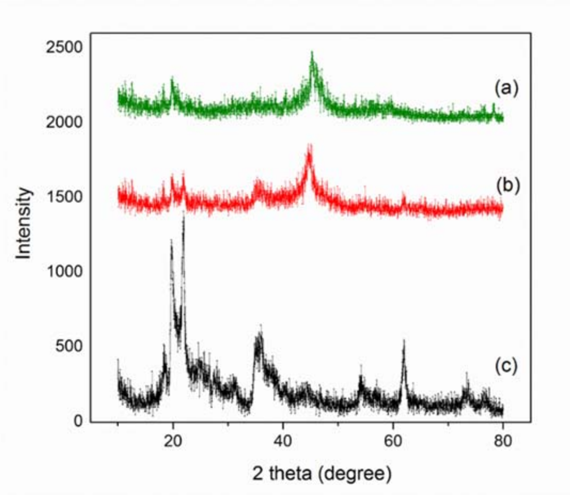

Figure 1: XRD patterns of (a) Montmorillonite (MMt), (b) MMt/Fe, (c) MMt/Fe/Ni.

3.1.2 BET

To study the surface areas of materials, nitrogen adsorption and desorption measurements were performed. The nitrogen adsorption–desorption curves of the bare Fe (nZVI), MMt/Fe and MMt/Fe/Ni are shown in Figure 2a, 2b, 2c, respectively. The N_2 isotherms exhibited type IV shape and H3 hysteresis loops. The BET surface areas of nZVI, MMt/Fe and MMt/Fe/Ni were calculated to be 39.8, 72.1 and 77.7 m^2/g, respectively. It is evident that the specific surface areas of both MMt/Fe and MMt/Fe/Ni were much larger than that of bare nZVI. As expected, MMt increased the specific surface area of nZVI significantly. And the addition of the second metal nanoparticles (Ni) slightly improved the surface area of MMt/Fe.

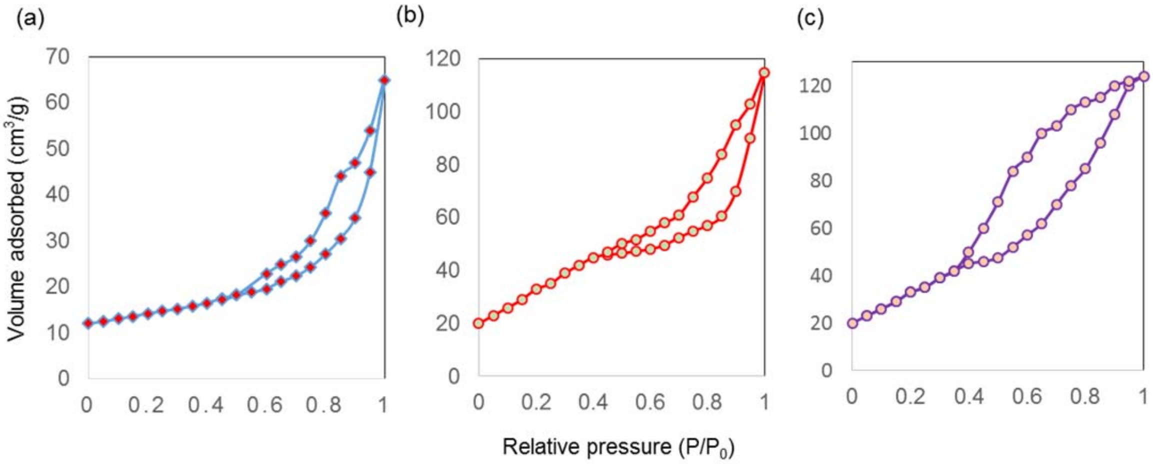

Figure 2: Nitrogen adsorption–desorption curves of (a) bare Fe (nZVI), (b) MMt/Fe, (c) MMt/Fe/Ni.

3.1.3 HRTEM-EDS

To examine the morphologies of the materials above, TEM characterization was conducted as well. The TEM image of bare nZVI is shown in Figure 3a. It can be easily seen that bare nZVI NPs suffered from the problem of aggregation and formed chains which would result in the loss of dispersity, mobility and specific surface area. As shown in Figures 3b and 3c, nanoparticles were dispersed evenly onto MMt. Since it is difficult to distinguish Fe and Ni nanoparticles just by TEM images due to their similar shape and size, elemental components analysis was also performed by energy-dispersive X-ray spectrometer (EDS) equipped in TEM. As depicted in Figure 3d, quantitative analysis revealed that the weight ratio of Fe and Ni was about 9.41:1, which was close to the theoretical value of 9.54:1 (weight ratio). Thus, the formation of both Fe and Ni nanoparticles and the uniformity of them in MMt/Fe/Ni could be verified.

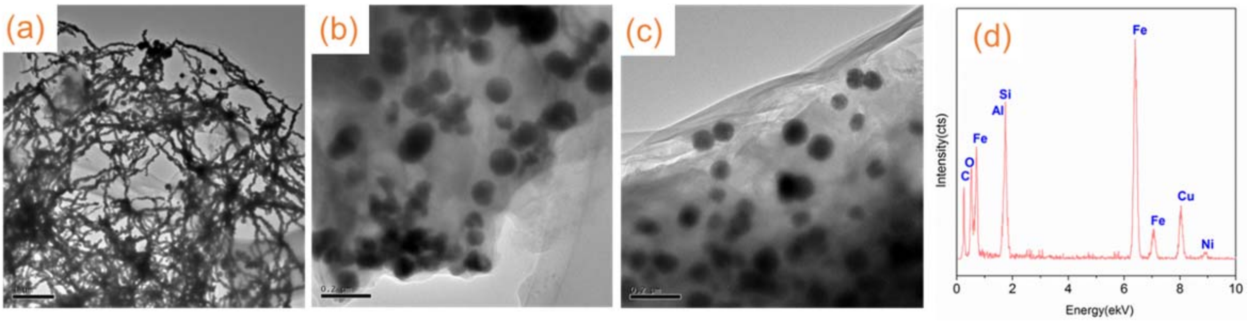

Figure 3: TEM images of (a) bare nZVI, (b) MMt/Fe, (c) MMt/Fe/Ni. (d) EDS of MMt/Fe/Ni.

3.2 The effect of materials

As shown in Figure 4, MMt, bare nZVI, MMt/Fe and MMt/Fe/Ni of the same weight (0.8g/L) were used for the removal of 50 mg/L Cr(VI) in water, respectively. According to the results, the order of removal capacity for Cr(VI) turned out to be MMt/Fe/Ni> MMt/Fe> nZVI>MMt. Compared with bare nZVI, the enhancement of the reactivity of MMt/Fe was resulted from the immobilization on MMt, which inhibited the aggregation of nZVI and thus improved the surface area of nZVI. The formation of Fe/Ni bimetallic nanoparticles on MMt further enhanced the reactivity of MMt/Fe. As mentioned above, since MMt can adsorb Cr(VI) due to high porosity and cation exchange, the combination of MMt, nZVI and Ni nanoparticles can synergistically improve the removal efficiency of nZVI.

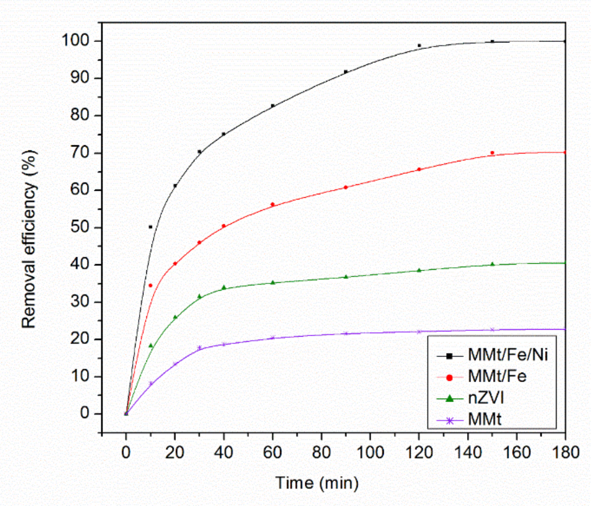

Figure 4: The removal of 50 mg/L Cr(VI) (pH=3, T=25℃) by different materials.

3.3 The amount of MMt/Fe/Ni

To figure out the optimum amount of MMt/Fe/Ni, further experiments were conducted. The results were shown in Figure 5. It is obvious that with the amount of MMt/Fe/Ni increased from 0.4 to 0.8 g/L, both the removal rates and efficiency of Cr(VI) were significantly increased. Further increasing the amount of MMt/Fe/Ni from 0.8 to 1.0 g/L did not show significant enhancement on the removal rates and efficiency. Therefore, 0.8 g/L MMt/Fe/Ni was determined for high-efficient removal of Cr(VI).

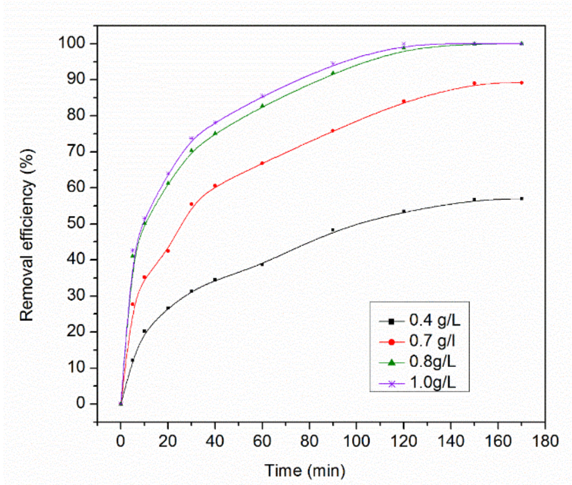

Figure 5: The removal of 50 mg/L Cr(VI) (pH=3, T=25 ℃) by different amounts of MMt/Fe/Ni.

4. Conclusions

In this study, montmorillonite-supported Fe/Ni bimetallic nanoparticles were successfully synthesized by a facile method. Montmorillonite provided an efficient support for nZVI and enriched Cr(VI) nearby, enhancing the removal efficiency of nZVI. In addition, Ni nanoparticles improved the reducing activity of nZVI for removing Cr(VI) significantly. The synergistic effect between montmorillonite, Fe and Ni nanoparticles turned out to effectively enhance the reactivity and efficiency of nZVI for the high-efficient removal of Cr(VI) in wastewater. Therefore, the as-synthesized montmorillonite-supported Fe/Ni bimetallic nanoparticles hold great potential for the removal of heavy metals in wastewater treatment.

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