

Nanoscale zero-valent iron supported on mesoporous silica: Characterization and reactivity for Ni(II) removal from aqueous solution

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Abstract

NZVIs/MS composites obtained by modifying nanoscale zero-valent iron (NZVIs) with mesoporous silica nanospheres (MS) were used to remove Ni(II) from aqueous solutions. Batch experiments results revealed that Ni(II) removal efficiency by NZVIs/MS was far higher than that by MS and NZVIs, respectively. The initial pH of the solution had a great effect on the removal efficiency of Ni(II) by NZVIs/MS, as it increased from 56.8% to 79% when the initial solution pH increased from 2.0 to 10.0. The removal efficiency of Ni(II) by NZVIs/MS also increased with the increasing of the reaction temperature. Based on batch experiments and characterization results by powder X-ray diffraction (XRD), field emission scanning electron microscope (SEM) and transmission electron microscope (TEM), the possible mechanism of Ni(II) removal by NZVIs/MS was proposed and confirmed that Ni(II) was first adsorbed on the surface of the composites and then reduced to Ni(0) by NZVIs. The obtained results of this work suggested that NZVIs/MS composites can be practically and efficiently used to remove Ni(II) from contaminated water.

Keywords

Nanoscale zero-valent iron; Mesoporous silica; Nickel (II) removal; Characterization

1. INTRODUCTION

Ni(II) is an industrial contaminant in both soil and groundwater from industries such as electroplating, battery production and stainless steel processing. As a hazardous heavy metal, Ni(II) can cause great harm to the environment and human health. Thus, it should be effectively removed. Conventional remediation technologies including adsorption, electrocoagulation and ion exchange suffer from some such disadvantages as high operational costs, time consuming and the production of hazardous sludge. Additionally, these methods can be only applied to contaminants of low concentration, as high operational costs and sophisticated operation procedure hinder its further application. Therefore, it is of vital necessity to develop an effective and economical method to remove Ni(II) from contaminated water.

During the recent years, nanoscale zero-valent iron particles (NZVIs) have been widely used in the removal of a wide variety of organic and inorganic contaminants in water, such as heavy metals, nitrates, nitroamines, and halogen compounds. Due to the high specific surface area, large amount of reactive surface sites, unique redox capability and high reaction rate, NZVIs are promising in the remediation of underground and industrial water. Nevertheless, some technical challenges still exist in the application of NZVIs. For instance, the aggregation and oxidization of NZVIs decreased their mobility and reactivity, making NZVIs relatively ineffective in *in situ* remediation technology. More recently, porous materials such as bentonite, carbon nanotubes, zeolites and mesoporous carbon are used as supporting materials for NZVIs in order to inhibit the serious aggregation and increase the reactivity of iron nanoparticles to a certain degree, and a better reactivity has been obtained by these methods. There are two main reasons accounting for the improvement: on the one hand, NZVIs can be so well dispersed on the supporters that the aggregation of NZVIs is effectively prevented and their high reactivity is conserved; on the other hand, the supporters possess a strong ability to absorb the contaminants of low concentration, thus provide more opportunities for the meeting of the contaminants and NZVIs, and also lead to the improvement of the NZVIs mobility in

water.

Mesoporous silica (MS) is a material with a high specific surface area, a narrow distribution of pore diameter and a tunable pore architecture and surface property. Furthermore, its stable and interconnected frameworks could be easily modified and functionalized without any change in its mesostructure. Consequently, it has been intensively applied in catalysis and sorption, and has become the focus of environmental and energy fields. However, its application in heavy metal adsorption is limited due to the lack of abundant active sites and lower adsorption uptake. Chemical modification has been done in order to improve the adsorption ability of MS, including the introduction of atoms, the modification with organic groups and the loading of active components. It has been testified that the introduction of organic groups makes it possible to tune the surface property and pore diameter distribution of the material. Moreover, the stability of the material is improved through the modification, and thus its application value is increased in environmental field. As a result, MS is one of the most commonly used supporters for the modification of NZVIs. For instance, Tang¹ immobilized NZVIs on MS for the reductive degradation of aqueous p-nitrophenol (PNP) in aqueous solution. The PNP degradation rate by NZVIs/SBA-15 composites was higher than that by bare NZVIs, indicating that NZVIs/SBA-15 was superior to bare NZVIs in terms of antioxidation ability. Zhang² incorporated nanoscale zero-valent iron in channels of ordered mesoporous silica to enhance the reduction ability for nitrobenzene. Sun³ incorporated NZVIs inside the channels of SBA-15 rods by a “two solvents” reduction technique and used them to remove Cr(VI) from groundwater. , which The effect of the initial solution pH and humic acid was evaluated and the removal mechanism of Cr(VI) by NZVIs/SBA-15 was proposed. Batch experiments showed that the stable reducibility of NZVIs/SBA-15 was preserved within six cycles. In this paper, NZVIs/MS composites were obtained by modifying nanoscale zero-valent iron particles (NZVIs) with mesoporous silica (MS). The synthesized NZVIs/MS composites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM), and used for Ni(II) removal from aqueous solutions. Based on the results, the effect of pH and temperature on Ni(II) removal was studied, and the mechanism of Ni(II) removal by NZVIs/MS was proposed and confirmed.

2. EXPERIMENTAL SECTION

2.1 Materials and chemicals

N-Hexadecyltrimethylammonium Chloride (CTAC), tetramethoxysilane (TMOS), N-Octyltrimethoxysilane ($\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OCH}_3)_3$), methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), 3-Aminopropyltrimethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$), sodium hydroxide (NaOH), nitric acid (HNO_3) were all purchased from the Sinopharm Group Chemical Reagent, China; iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium borohydride (NaBH_4) were purchased from Aladdin Company (China). All the chemicals were of analytical pure grade and were used as received without further purification.

2.2 Preparation of functionalized mesoporous silica and NZVIs/MS composites

The functionalized mesoporous silica was prepared as describe by Li⁴. Briefly, 3.52 g CTAC, 400 mL ultrapure water, 505 mL methanol and 2.2 mL NaOH solution (1 M) were mixed and stirred at room temperature for 30 min. During the stirring, TMOS (dissolved in methanol) was added dropwise to the mixture and vigorously stirred for 1.5 h. Then, the mixture of TMOS (dissolved in 2 mL methanol) and 3-Aminopropyltrimethoxysilane (dissolved in 2 mL ultrapure water) was simultaneously added dropwise into the system and stirred for another 10 h. After stirring, the mixture was aged for 24 h, filtered and washed with deionized water and ethanol several times. Finally, the solid was dried to obtain functionalized mesoporous silica and the material was denoted as MS.

The prepared functional mesoporous silica (MS) was selected as the supporter for the preparation of

MS/NZVIs. 1 g MS was added to the ethanol solution of FeCl_3 (0.5 mL, 2 M) under stirring and was well dispersed under ultrasonic agitation. The mixture was evaporated at 50 °C for 24 h, dried at 110 °C for 2 h and cooled to room temperature. 0.5 mL NaBH_4 solution in deoxidized water (the molar ratio of $\text{B/Fe} = 4$) was added dropwise to the mixture under stirring to reduce Fe(III) to metallic Fe(0) . After the addition of NaBH_4 solution, the mixture was stirred for another 30 min. Then the mixture was centrifugated and washed with deionized water and ethanol for 3 times. The solid obtained after drying in vacuum was denoted as NZVIs/ MS.

2.3 Characterization

The θ -2 θ X-ray powder diffraction (XRD) data were collected with a D/MAX2200V diffractometer using a $\text{Cu K}\alpha$ (40 kV, 40 mA, $\lambda = 1.54178 \text{ \AA}$) source. Diffraction patterns were collected in the 2 θ range from 10° to 90° at the scanning rate of 1° min⁻¹. The morphology of the sample was investigated by field emission scanning electron microscopy (SEM, Philips XL 30). Transmission electron microscopy (TEM) was carried out using a JEOL 2010F instrument.

2.4 Batch experiments for the reduction of Ni(II)

The reduction capacity of NZVIs/MS composites was tested using 50 mL solution of NiCl_2 in distilled water (initial concentration of Ni(II) : 10 mg/L) which was previously stirred at room temperature for 12 h in a closed vessel to ensure equilibrium. The vessel was then injected a certain amount of NZVIs/MS (2 g/L). Tests were performed at the initial pH of 7. The pH of the solutions was adjusted to the desired value by 0.01 M HCl or 0.01 M NaOH solutions. Subsequently, the vessel was sealed with a screw cap and placed in a thermostatic shaker with a speed of 200 rpm at the desired temperature. During the reaction, at certain time intervals, a volume of the suspension (6 mL) was withdrawn and centrifuged at the speed of 15000 rpm. The resulting supernatant was then diluted for 2 times and filtered by a 0.45 μm membrane filter after digestion. The concentration of Ni(II) was measured by Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Agilent 720 ES, USA).

For the sake of comparison, bare MS and NZVIs were used instead of NZVIs/MS. The amounts of MS and NZVIs equal their amounts in NZVIs/MS composites.

3. RESULTS AND DISCUSSION

3.1 Characterization

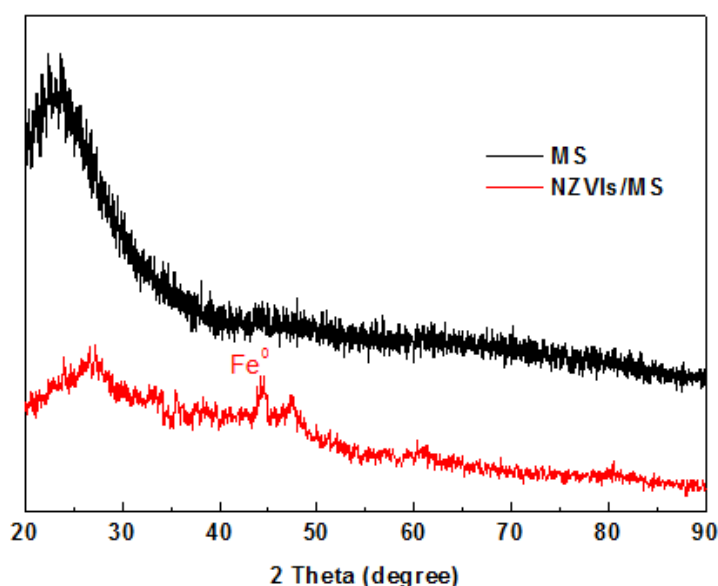


Figure 1. XRD patterns of MS and NZVIs/MS composites

Figure 1 shows the XRD patterns of MS and NZVIs/MS. As is presented in Figure 1, a diffraction peak at 44.67° corresponding to the formation of zero-valent iron (Fe(0) state (110) plane, JCPDS No. 06-0696) was observed, indicating that the formed Fe(0) nanoparticles in NZVIs/MS were loaded on MS and were non-crystalline. Meanwhile, the diffraction peak at about 25° was attributed to the non-crystalline SiO_2 (JCPDS No. 29-0085). The two diffraction peaks observed in the figure testified the combination of NZVIs and MS.

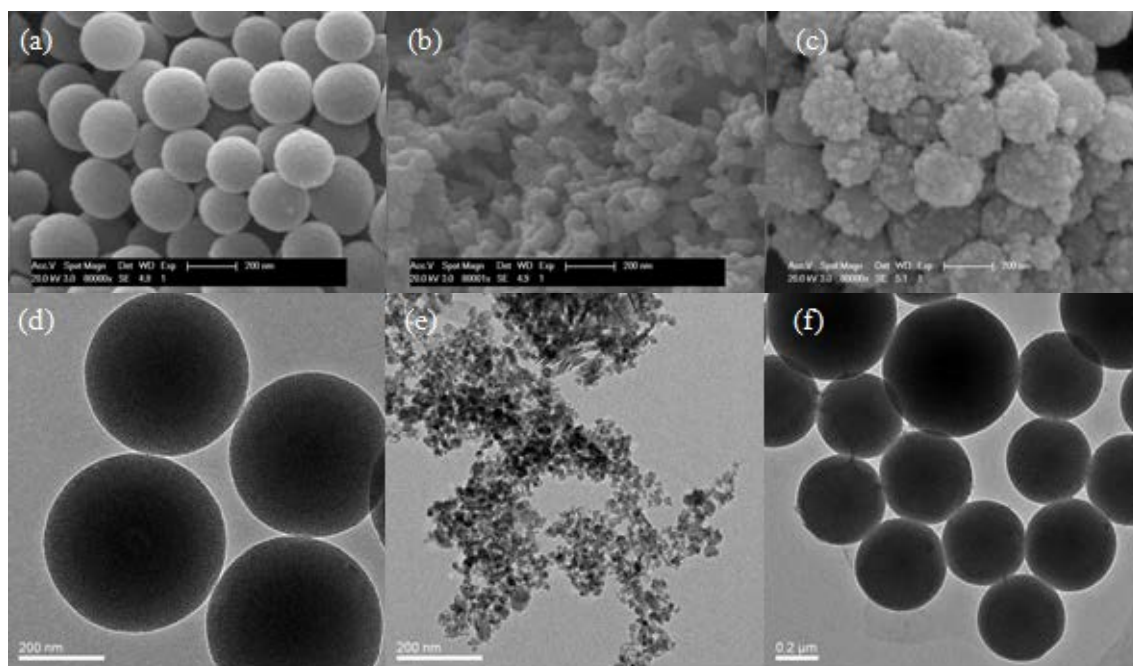


Figure 2. SEM and TEM images of MS (a,d), NZVIs (b,e) and NZVIs/MS (c,f)

Figure 2 show the SEM (a, b and c) and TEM (d, e and f) images of MS, NZVIs and NZVIs/MS, respectively. It can be told from Figure 2 (a) and (d) that MS was composed of smooth spherical particles with a diameter of 200 nm. Figure 2 (b) shows the SEM image of NZVIs reduced by NaBH_4 . The NZVIs didn't come in separate particles but in chains or bulk, as also confirmed by the TEM image (Figure 2 (e)). The agglomeration of NZVI particles could be attributed to the instability caused by the large specific area and small diameter, and the strong magnetic and Van der Waals' force. Figure 2 (c) and (f) show that NZVIs/MS composites were also composed of smooth spherical particles, with a similar diameter as MS. Additionally, NZVIs were found on the surface, and it was coincident with the XRD patterns. The results indicated NZVIs/MS was certainly the combination of MS and NZVIs. Comparing Figure 2 (b) and 2 (c), it can be found that the diameter of NZVIs was smaller in NZVIs/MS, suggesting that the existence of MS could prevent the agglomeration of NZVIs to a certain extent, and thus a higher reactivity could be obtained.

3.3 Ni(II) removal by NZVIs/MS

3.3.1 Comparison of the materials. The removal efficiency of Ni(II) by MS, NZVIs and NZVIs/MS was shown in Figure 3 (a). As is shown in the figure, the Ni(II) removal efficiency of three materials displays great difference. At a reaction time of 30 min, the removal efficiency by NZVIs/MS was nearly 70%, much higher than NZVIs (43.4%) and MS (less than 10%), and was also higher than their summation. As is known, MS has a high specific surface area and large pore volume, so the removal efficiency by MS was mainly attributed to adsorption. Meanwhile, pure NZVIs can remove Ni(II) by both adsorption and reduction. At the initial stage of the reaction, Ni(II) was adsorbed on the external surface of NZVIs. As the reaction proceeded, Ni(II) was transferred to

the internal surface and reacted with Fe(0) to form Ni(0) until an equilibrium was reached. It should be noted that the magnetic agglomeration could lead to the decrease of its specific surface area and reactivity, so the removal efficiency was low. However, when NZVIs were loaded on MS, the NZVI particles could be well dispersed, and thus the stability and reactivity were relatively high.

3.3.2 Effect of temperature on Ni(II) removal. It has been confirmed by many works that temperature has a great effect on the reaction rate, especially for displacement reactions. The effect of temperature on the Ni(II) removal efficiency by NZVIs/MS was evaluated at the initial Ni(II) concentration of 10 mg/L and the initial pH of 7. As is shown in Figure 3 (b), for a reaction duration of 1 h, the removal rate of Ni(II) by NZVIs/MS increased with the rise of temperature. The result could be explained that a higher temperature led to the increase of the vibration rate of Ni(II), and thus gave rise to the contacting frequency for Ni(II) and NZVIs/MS. Additionally, a higher temperature resulted in the decrease of viscosity of the solution, which favoured the transfer of electrons reducing Ni(II) to Ni(0).

3.3.3 Effect of pH on Ni(II) removal. Aqueous solution pH has a strong impact on the adsorption process, as it affects the surface charge of the adsorbent and the degree of ionization and speciation of the metal contaminants, so the removal efficiency of metal ions by NZVIs can be greatly affected by the pH of the solution. In order to evaluate the effect of pH on the removal efficiency by NZVIs/MS, Ni(II) removal efficiency at different pH values were tested at a reaction time of 30 min. As is displayed in Figure 3 (c), Ni(II) removal by NZVIs/MS was highly pH-dependent. At the pH range of 2-10, the removal efficiency increased with the increasing pH value. The trend of pH dependence of Ni(II) removal is in accordance of the works of Zhang⁵ and Unuabonah⁶. In the acidic medium, the Ni(II) removal was mainly attributed to the strong reducing ability of Fe(0). The abundant existence of H⁺ accelerated the erosion of iron, and thus contributed to the reduction of Ni(II), and slowed the inactivation of iron to provide more active sites. However, the high concentration of H⁺ was unfavorable for the adsorption of Ni(II). When the pH value was above 7, Ni(II) could combine with OH⁻ and was easily adsorbed by NZVIs as the surface was negatively charged. Besides, a higher pH is advantageous to the hydrolysis of Ni(II), and the hydrolysis product has a stronger affinity. Therefore, an alkaline solution is more favorable for the Ni(II) removal by NZVIs/MS.

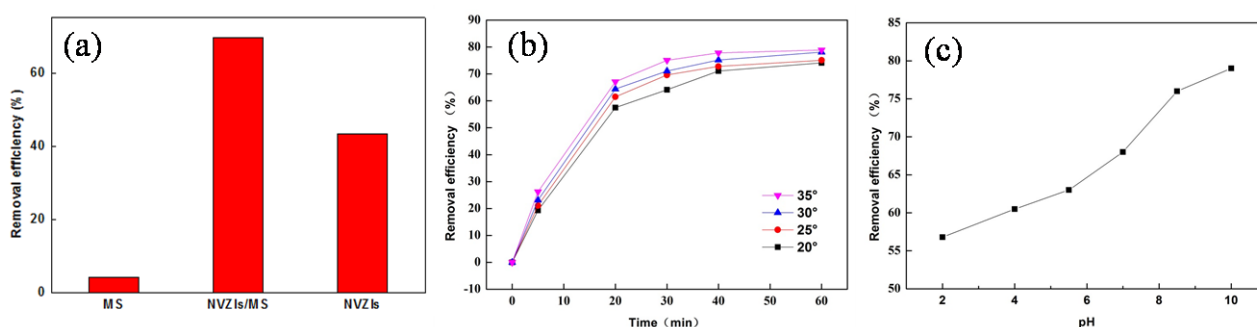


Figure 3. The Ni(II) removal efficiency (a) and effect of reaction temperature (b) and initial pH (c)

3.3.4 Mechanism of Ni(II) removal by NZVIs/MS composites. To better understand the mechanism of Ni(II) removal by NZVIs/MS composites, the composites were collected, freeze dried and characterized by SEM and TEM before and after reaction with Ni(II).

Figure 4 shows the SEM images of fresh NZVIs/MS (a) and NZVIs/MS after reaction (b), indicating that there existed little change in the structure of the composites before and after reaction. The NZVIs on the surface remained small spheres with a core-shell structure but the spheres were wrapped with a thin passivation layer after reaction with Ni(II). It can be seen from the TEM images that the diameter of NZVI particles was 30-50 nm and the shell had a thickness of ca. 3 nm.

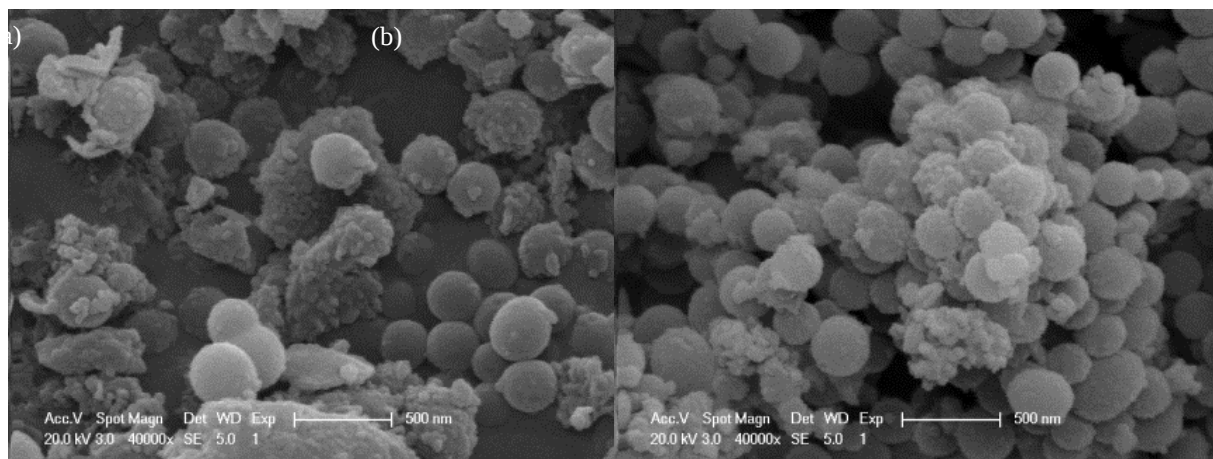
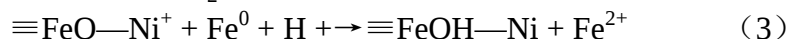
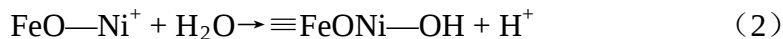
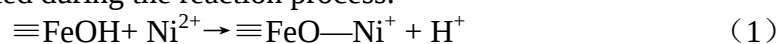


Figure 4. SEM images of fresh NZVIs/MS (a) and NZVIs/MS after reaction with 10 mg/L Ni(II) for 1h (b)

As is known, the oxidation-reduction potential of Ni^{2+}/Ni is -0.24V and it is slightly higher than Fe^{2+}/Fe , so Ni(II) can be easily reduced to Ni(0). After the reaction, NZVIs were oxidized to a thin layer of flocculent substances, which was inferred to be the mixture of the hydroxide of Fe and Ni. The result was in accordance with the previous work of Li and Zhang⁷, who demonstrated by experiments that the removal of Ni(II) by NZVIs was due to the synergistic effect of adsorption and reduction. Based on the characterization and experiment results, the following mechanism is suggested during the reaction process:



4. CONCLUSIONS

In this study, nanoscale zero-valent iron particles were loaded on mesoporous silica. By this method, the problem of aggregation of NZVIs was effectively solved. The NZVI particles were well dispersed on the silica. By this method, the specific surface area of NZVIs was greatly enlarged and the reaction rate had increased accordingly.

The removal efficiency of Ni(II) by NZVIs/MS was up to 70% at a reaction time of 30 min, whereas the removal efficiency by NZVIs with the same iron content was only 43.4% under the same reaction condition. The Ni(II) removal efficiency of NZVIs/MS was far higher than that of MS and NZVIs, and was also higher than their summation, indicating the synergistic effect of the adsorption efficiency of MS and the reduction efficiency of NZVIs. Ni(II) was first adsorbed on the surface of the composites and then reduced to Ni(0) by NZVIs. In summary, the obtained results of this work suggest that NZVIs/MS composites can be practically and efficiently used to remove Ni(II) from contaminated water.

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