RESEARCH ON PREPARATION OF NANOSCALE IRON SUPPORTED BY BENTONITE AND ITS REMEDIATION OF LEAD IONS

C. YU, J. C. SHAO, X. Q. CAI, X. N. YU*

College of Civil Engineering and Architecture, Wenzhou University, Wenzhou, 325035, China

Nano iron supported by bentonite is made by a liquid phase reduction method in this research. Through X-ray techniques (XRD), Fourier transform infrared spectroscopy (FTIR), BET, Lorentz-transmission electron microscope (TEM) and other methods, the microstructures and the chemical composition are characterized. And experiments of removing lead ions are also carried out to find a suitable mixture ratio. The results show that most made-up nano iron, with spherical particles of below 70nms, uniformly disperse in bentonite which can increase the specific area of synthetic material so as to solve the nano iron agglomeration and oxidation problems in air. By comparison, nano iron supported by bentonite has a much larger removal rate for lead ions than that of bentonite in the same environment. 30%-40% iron content of bentonite-supported nanometer iron (B-nZVI) has the highest removal rate of lead ions. In an acidic environment, the removal rate of lead ions by bentonite and B-nZVI increases with the increase of pH value. At pH 7 the removal rate of lead ions by B-nZVI is over 95%, while the removal rate of lead ions by bentonite is 81%.

1. Introduction

Lead pollution has become an important contributor to soil and groundwater pollution. Lead ions in the environment will enter the body through the biological chain and cause harm. At present, there are electrodialysis methods, adsorption methods, chemical precipitation methods, ion exchange methods and biosorption methods, etc. for the treatment of lead and other heavy metal ion wastewater [1-2]. Compared to the traditional removal method, the removal efficiency of heavy metals such as lead ions in water by nano iron is high and the time required is short. In recent years, nano iron has begun to be used in groundwater and soil pollution control, and its use in removing water and soil lead ions has rarely been reported.

Zero-valent iron particles with a particle size in the range of 1-100 nm are called nanoscale zero-valent iron. The microelectrolysis, reduction and coagulation adsorption of iron are the main removal mechanisms of heavy metals for nanowires [3-4]. Nano-zero-valent iron particles have a large specific surface area and surface energy, so the nano-iron activity and adsorption performance are high [5-6]. Study results show that nano-zero-valent iron particles have good removal effect of organic matter, inorganic salt and heavy metal pollutants [1, 7, 8]. Nanometer iron is easily oxidized, even spontaneously in air, so it must be treated before use [10-12]. Other materials to load nano iron can stabilize it air, solving the easy oxidation, easy agglomeration and other issues, improving its reactivity. Nanowires have been loaded on carriers such as starch, alumina, silica, zeolite and activated carbon to produce certain shapes of particles, maintaining the inherent properties of nanomaterials while enhancing their stability [10]. This study makes use of

─────────────────────

*Corresponding author: xnyu@wzu.edu.cn

bentonite-loaded nano iron [13].

Bentonite is a kind of montmorillonite and is the main component of clay rock, also known as montmorillonite clay rock. Bentonite's main components are silica, aluminum oxide and water. Bentonite has the characteristics of ion exchange, swelling, adsorption, electronegativity, suspension and so on. The sodium or calcium ions in the bentonite crystals can be exchanged with other cations. According to the literature reported that bentonite has enough space to load zero-valent iron particles [14]. Bentonite is dispersed evenly in water, allowing the nanometer iron to disperse. In addition, bentonite is not polluted and is cheap. The main purpose of this study is to synthesize bentonite-supported nanometer iron (B-nZVI), and to explore the abilities and mechanisms of the synthesis of metal lead ions. The effects of different iron contents, pH value of solution, initial concentration of lead ion, time, the amount of synthetic materials on the removal of lead ions, and the effect of bentonite and B-nZVI on lead removal were compared.

2. Experimental methods and materials

2.1 Preparation of Bentonite-Supported Nanometer Iron (B-nZVI)

Take pure water, adjust the pH to 3 with diluted hydrochloric acid, take 400ml solution in the beaker and add 3.554g FeCl2.4H2O and 9g bentonite, keep stirring for 12 hours, then add 300ml of absolute ethanol, and continue stirring for 3 hours. The ratio of high purity water to absolute ethanol was 4: 3. Take the amount of high water, add NaOH solution to adjust the pH to 11. Take 200ml solution in a beaker, add 2.036g sodium borohydride (sodium borohydride and iron input amount of the actual amount of 3: 1). Add the sodium borohydride alkaline solution slowly to the previously mixed bentonite and $FeCl_2$ solution, and stir vigorously. The whole dripping process takes about 15 minutes. After the reaction is completed, stir for 20 minutes. The supernatant was separated by centrifugation, and the remaining solid was washed three times with high purity water and washed three times with anhydrous ethanol. The sample was freeze-dried in a freeze drier. The final, finished product was packaged in a self-contained bag and stored in a refrigerator (minus 85 degrees). The iron added in this experiment accounted for 10% of the total mass. B-nZVI with different iron content was prepared by adding iron in the same way, with 20%, 30%, 40% and 50% of the total mixture. Synthesis of B-nZVI by liquid phase reduction:

$$Fe^{2+}+2BH_4^-+6H_2O \rightarrow 2Fe(s)+2B(OH)_3+7H_2\uparrow$$
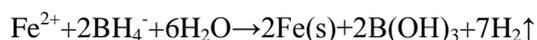
2.2 Characterization of Bentonite and B-nZVI

X-ray techniques (XRD, Bruker Company, Germany) analysis was carried out on the bio-sandstones at room temperature by a D8-Advance X diffraction meter (40kv, 40mA) with Cu (λ=1.5406Å) irradiation at the rate of 0.15s/step in the range of 5-84˚. Surface area analyzer: ASAP 2020 HD88-type surface area tester manufactured by McMurray Tikem (Shanghai) Instrument Co., Ltd. was used to determine the adsorption isotherm of N_2 at liquid nitrogen temperature and the specific surface area of the sample was calculated by the BET method. The Fourier transform infrared spectroscopy (FTIR) was used to measure the FTIR spectra of the samples, and the scanning range was 4000-400cm^{-1}. Lorentz-transmission electron microscope (TEM) images were obtained on a JEM, 2100F equipment. TEM grids were prepared using a few drops of nanoparticles followed by drying.

2.3 Removal experiments

(1) The effect of iron content in B-nZVI

0.5 g of bentonite, 0.5 g of iron content of 10%, 20%, 30%, 40%, 50% B-nZVI were added to 100ml of lead ion solution, respectively, with 500 mg/L lead ion solution, at room temperature (20°C) for 24 hours. The concentration of lead ions in the solution after 24 hours was measured by atomic absorption method, and the removal rate of lead ions in different materials was calculated. At the same time, 1000mg/L, 1500mg/L, 2000mg/L, 2500mg/L, 3000mg/L lead

solution was used to repeat the above experiments under different Pb concentration. The bentonite and different iron contents were tested under different concentration of lead ions.

(2) The effect of pH

Configure 200mg / L lead ion solution, with diluted hydrochloric acid to adjust the pH value to 3. 0.1g of bentonite, and 0.1g of B-nZVI iron having an iron content of 10%, 20%, 30%, 40% and 50%, respectively, were added to 100ml of lead ion solution, at room temperature (20°C) for 4hours. The concentration of lead ions in different reaction time solutions was measured by the atomic absorption method, and the removal rate of lead ions was calculated. At the same time, a solution with a pH of 5 and a lead concentration of 200mg/L was prepared. The above experiments were repeated under different pH conditions. B-nZVI containing different iron contents and bentonite were tested under different pH conditions.

(3) The effect of B-nZVI addition

A solution to 500mg/L of lead was prepared and 5 parts of each 100ml of the solution was mixed with 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g of 40% iron content of B-nZVI. The concentration of lead ions at different times was measured by atomic absorption spectrometry at room temperature (20°C), and the removal rate of lead ions was calculated.

3. Results and discussion

3.1 X-ray powder diffraction of the bentonite and B-nZVI

The XRD patterns of bentonite and B-nZVI are shown in Fig. 1. The diffraction peaks of B-nZVI correspond to 2θ=44.8°, which is the characteristic peak of elemental iron, indicating that the material contains elemental iron. When the iron content is 10%, there are almost no elemental iron characteristic peaks; when the iron content ranges between 20% and 40%, the elemental iron peak began to appear and became more and more obvious. When the iron content increased to 50%, the peak value of elemental iron at 2θ=44.8° was relatively low, and 2θ=35.6° also had a higher characteristic peak, corresponding to Fe_3O_4, indicating some iron is oxidized and iron content is too high, beyond the scope of the effective load of bentonite[15]. XRD results show that the diffraction peak of elemental iron in B-nZVI with iron content of 30%-40% is the most obvious, indicating that B-nZVI has the highest elemental iron content.
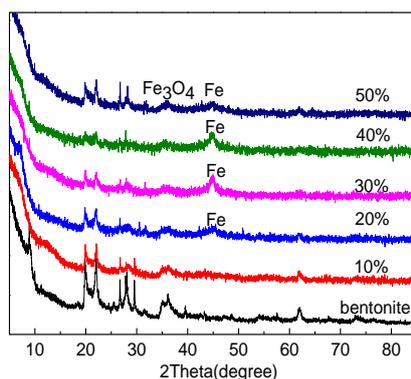

Fig. 1 XRD patterns of the bentonite and B-nZVI.

3.2 FTIR spectra of the bentonite and B-nZVI

The FTIR spectra of the samples are shown in Fig. 2. The infrared spectrum of the sample is close to 3620cm⁻¹ due to the stretching vibration of Al-OH. The absorption peaks near 3440cm⁻¹ and 1632cm⁻¹ are HOH. The strong absorption band near 1040cm⁻¹ is caused by the asymmetric stretching vibration of Si-O-Si in bentonite. The absorption spectrum appears close to 797cm⁻¹, indicates that the content of SiO2 in bentonite is relatively high. The absorption peaks in the vicinity of 520cm⁻¹ and 470cm⁻¹ are considered to be caused by the coupling of Si-OM (metal

cation) and MO in bentonite, due to the asymmetric stretching vibration of Si-O-Si in the soil [16].

By comparing the bentonite, the partial absorption peak in the infrared spectrum of B-nZVI has decreased or even disappeared, which may be due to the change of the proportion of the original bentonite caused by the addition of iron, and it is also possible that sodium borohydride destroys some of the chemical bonds in bentonite [15]. There are displaceable cations in the bentonite layer. After adding $FeCl_2 \cdot 4H_2O$, the displaceable cations are replaced by Fe^{2+}. When the sodium borohydride solution is added, Fe^{2+} is reduced to elemental Fe by sodium borohydride. Bentonite is a layered silicate, and the skeleton does not change after the synthesis of B-nZVI. Bentonite provides a loading platform for nanometer iron. The preparation of nanometer iron does not affect the main structure and chemical composition of bentonite.

Fig. 2 FTIR spectra of the bentonite and B-nZVI

3.3 Specific surface area of the bentonite and B-nZVI

Fig. 3 shows the specific surface area of bentonite and synthetic samples. The specific surface area of B-nZVI is about $46.5m^2/g$ when the iron content is 10%, and the specific surface area of B-nZVI decreases with the increase of iron content. When the iron content is 50%, the specific surface area of B-nZVI is $24.3m^2/g$. Bentonite can make the nano-iron dispersed, to avoid the nano-iron of magnetic agglomeration, effectively increasing the specific surface area of the material, which is conducive to improving the adsorption of nano-iron [6, 17].

Fig. 3 Specific surface area of the bentonite and B-nZVI

3.4 Micro/nano-structure of the bentonite and B-nZVI

The micro/nano-structure of the bentonite and B-nZVI was observed by Lorentz-Transmission Electron Microscope (Figure 4). Figure 4a shows the micro/nano-structure of bentonite. Bentonite has a sheet-like structure with sizes in the range of 0.5-2μm. This structure can provide a carrier to the nano iron, and to a certain extent, can stabilize the nano iron, to avoid nano iron reunion. Figure 4b-f shows 10-50% iron content of B-nZVI. The nano iron particles are

evenly dispersed in the bentonite layer, and are small with no agglomeration, as shown in Figure 4b-e. The iron particles are evenly dispersed in the bentonite layer and have been formed in the aggregation state when the iron content is 50%. TEM images indicate that iron particles are mainly spherical structure in shape with sizes in the range of 20-50nm when the iron content is 10-50% (Fig4b-f).
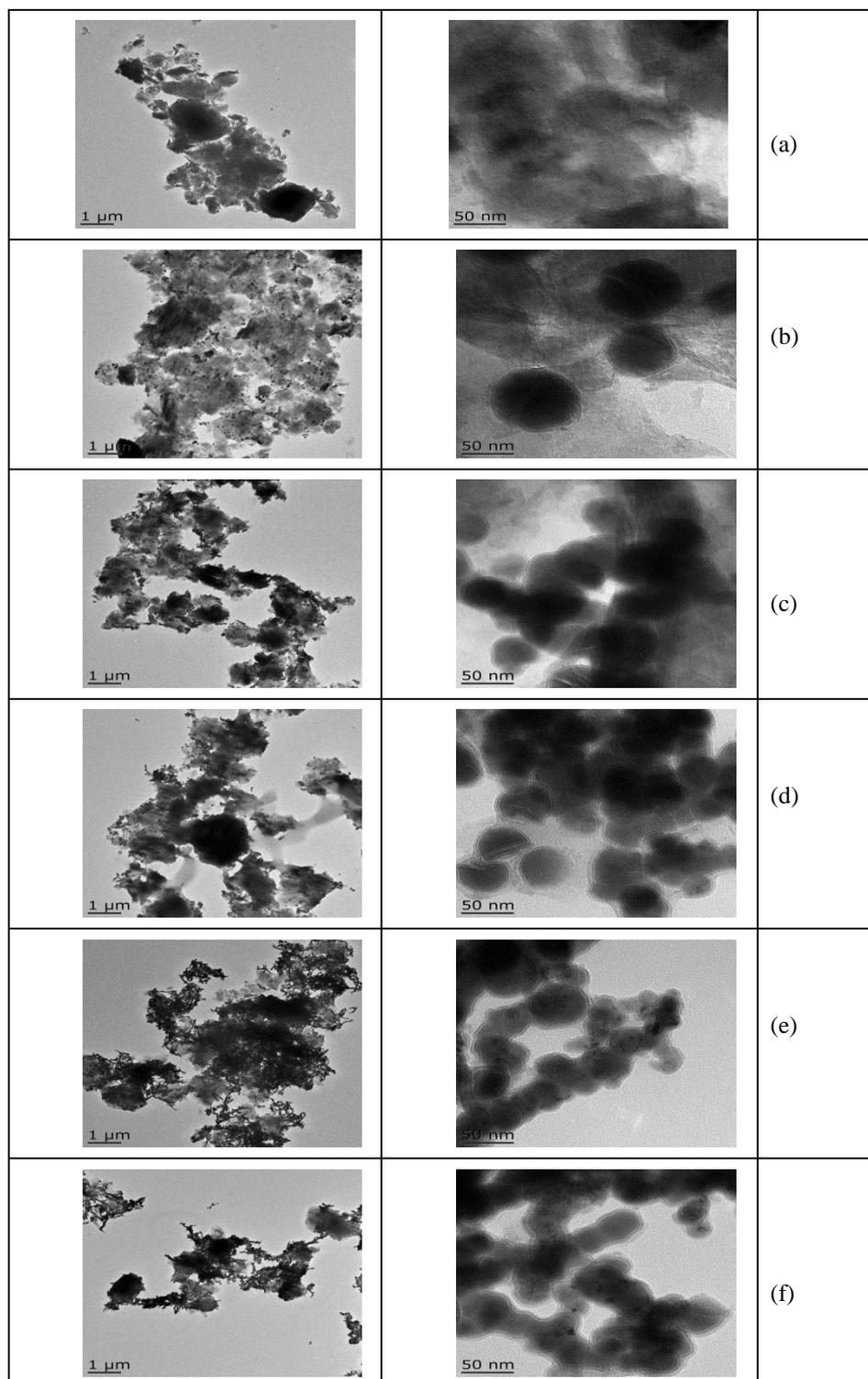

Fig. 4. TEM images: (a) bentonite, (b) 10% iron content B-nZVI, (c) 20% iron content B-nZVI,

(d) 30% iron content B-nZVI, (e) 40% iron content B-nZVI, (f) 50% iron content B-nZVI.

3.5 Effect of B-nZVI iron content on removal rate of lead ions

Fig. 5 shows the removal of lead ions by B-nZVI with different iron contents. In different concentrations of lead ion solution, 40% iron content B-nZVI has the highest removal rate of lead ions, followed by 30%, 50%, 20%, 10% iron content of bentonite. When B-nZVI contained 10% iron, the removal rate of lead ions (500-1000mg/L) began to decline, which is slower than bentonite. Therefore, 10% iron content of B-nZVI for the removal rate of lead ions is better than the bentonite effect. When the iron content increased to 50%, some iron oxidized to Fe_3O_4. With the increase of lead concentration, the removal rate of each material decreased gradually. When the concentration of lead ion was between 500 and 3000mg/L, the removal rate of lead ions decreased with the increase of lead ions concentration.
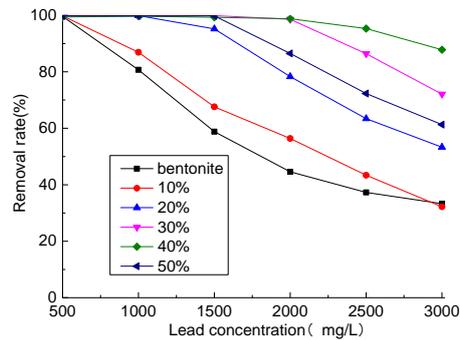
Fig. 5 Effect of different iron content on removal rate of lead ions.

3.6 Effect of pH on removal rate of lead ions

Fig. 6 shows that the higher the pH of the solution, the greater the removal rate of lead ions in the B-nZVI removal of lead ions process. At a pH of 3, the removal of lead ions from bentonite is about 11%, while that of B-nZVI is more than 35%. With the increase of pH, the bentonite and B-nZVI removal rate of lead ions is about 45%. When the pH value is 5, the removal rate of lead ions is more than 70%. When the pH is 7, B-nZVI removes more than 95% of lead ions. One of the main reasons is that the iron solution in the acidic solution reacts with H^+ ions to form a precipitate in the water [9], which affects the removal of lead ions. When the bentonite is in water, Si-O and the Al-O bonds in the lattice are broken, resulting in the breaking of the end face. When the aqueous solution is acidic, the broken bond will adsorb H^+ ions, so that the lattice is positively charged; the lead ions are also positively charged, the two are mutually exclusive, so that lead ions and bentonite-loaded nano iron experience contact reduction, reducing the reaction rate. When the solution is alkaline, the bond is adsorbed OH ions, so that the lattice is negatively charged and the negatively charged B-nZVI adsorbs more lead ions, thereby increasing the removal rate of lead ions.
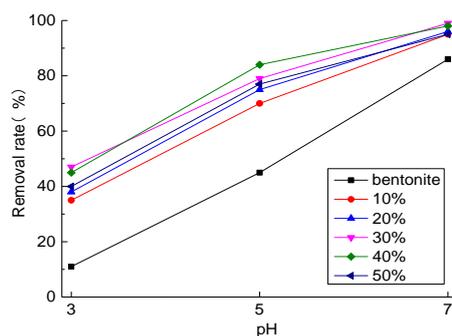
Fig. 6 Effect of pH on removal rate of lead ions.

3.7 Effect of B-nZVI addition on removal rate of lead ions

With the increase of the amount of materials, the removal rate of lead ions is effectively improved, which is due to the increase of the amount of reactants, increasing the surface area, adsorption sites and activity of nano iron. Figure 7 shows that the removal rate of lead ions had reached 94% at 4 hours with the addition 0.5g of reactants, and only 50% at 4 hours with 0.1g.
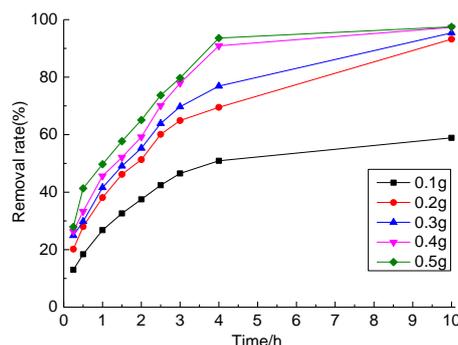

Fig. 7 Effect of B-nZVI content on removal rate of lead ions.

4. Conclusions

(1) The B-nZVI was synthesized by liquid phase reduction method. The B-nZVI was analyzed by BET, FT-IR, XRD, TEM and other methods. The bentonite could provide the loading platform for nanometer iron and increase the surface area, to solve the problems of easy oxidization in air and easy reuniting, among others, of nano iron.

(2) B-nZVI can be used to remove lead ions. By comparison, B-nZVI had better effect than that of bentonite alone, and the removal efficiency of lead was 30%-40%.

(3) Under the acidic condition, the removal rate of lead ions with the increase of pH for bentonite and B-nZVI. When the pH was 5, the removal rate of lead ions was about 70%. The removal rate of lead ions was 81% when the pH of the solution was 7. However, B-nZVI had more than 95% removal of lead ions.

Acknowledgements

References

[1] X. Zhang. Chemical research **21**, 97 (2010).

[2] H.X. Hu. China Resources Comprehensive Utilization **2**, 22 (2008).

[3] J.T. Nurmi, G.T. Paul, S. Vaishnavi, et al. Environmental Science & Technology **39**, 1221(2005).

[4] C.C. Yan, W.F. Cheng, L. Pan, et al. Journal of water resources and water engineering **24**, 20 (2013).

[5] K. Yu, C. Gu, A. Stephen, C. Liu, et al. Environmental Science & Technology **46**, 8969 (2012).

[6] A.B. Cundy, L. Hopkinson, L.D. Whitby. Science of the Total Environment **400**, 42 (2008).

[7] Y. F. Gao, N.Y. Gao. Water & Wastewater Engineering **37**, 108 (2011).

[8] M. P. Sherman, D. Johng, M. Thomase. Environmental Science & Technology **34**, 2564 (2000).

[9] L. N. Shi, X. Zhang, Z.L. Chen. Water Research **45**, 886 (2011).

[10] Y. Y. Gao, Q.X. Zhou. Journal of Agricultural Environmental Science **32**, 418 (2013).

[11] H. Su, Z. Fang, P.E. Tsang, et al. Environmental Pollution **214**, 94 (2016).

[12] N. Ezzatahmadi, G.A. Ayoko, G.J. Millar, et al. Chemical Engineering Journal **312**, 336 (2017).

[13] A. Soliemanzadeh, M. Fekri. Chinese Journal of Chemical Engineering **25**, 924 (2016).

[14] Y. Liu, Y.M. Li, L.H. Wen, et al. Spectroscopy and Spectral Analysis **26**, 1939 (2007).

[15] X.L. Weng, S. Lin, Z.X. Chen, et al. China Science: Chemistry **42**, 17 (2012).

[16] J,J, Nie, L.J. Wang, H. Zhou. Rock and Mineral Analysis **28**, 67 (2009).

[17] Z.H. Diao, X.R. Xu, H. Chen, et al. Journal of Hazardous Materials **316**, 186 (2016).