



Removal of atrazine by nanoscale zero valent iron supported on organobentonite

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ABSTRACT

The organobentonite (CTMA-Bent) was prepared from Na⁺-saturated bentonite (Na-Bent) by intercalation with cetyltrimethylammonium bromide (CTMA), and used as a carrier of nanoscale zero valent iron (NZVI) for the removal of atrazine. The NZVI/CTMA-Bent composite was characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM), and good dispersion of nanoscale iron particles on the carrier was observed. The removal efficiency of atrazine by this composite was compared with that by commercial iron powder and NZVI itself. For both treatments by NZVI and NZVI/CTMA-Bent, the removal efficiency increased as the pH of the solution decreased, and the removal percentage of atrazine by NZVI/CTMA-Bent reached 63.5% at initial pH = 5.0 after 120 min. It is not only much higher than that (26.6%) by NZVI containing the same amount of iron, but also superior to the sum (32.1%) of reduction by NZVI plus adsorption by CTMA-Bent (5.5%). Besides, the NZVI/CTMA-Bent has a good long-term stability, and the carrier CTMA-Bent could prevent the iron ions (the byproduct of dechlorination) from leaching into the solution.

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1. Introduction

Among those chemical reductants designed for environmental remediation, zero valent iron (ZVI) is one of the most commonly used due to its inexpensiveness, good availability and stability (Doong et al., 2003; Nurmi et al., 2005). It has been suggested as a promising candidate for the reductive dechlorination of chlorinated organic compounds such as chlorinated ethane (Hocheol and Carraway, 2005), chlorinated ethene (Gotpagar et al., 1998; Venkatapathy et al., 2002), chlorophenol (Cheng et al., 2007), chlorobenzene (Shih et al., 2009) and some chlorinated pesticides (Wang et al., 2009).

As contaminants are reduced on the surface of ZVI, the iron sample with a larger specific surface area always has more reactive sites and higher efficiency on the removal of contaminants. Therefore, in comparison with commercial microscale iron, the nanoscale zero valent iron (NZVI) has a much higher activity on dechlorination (Wang and Zhang, 1997; Zhang, 2003; Liu et al., 2005). However, NZVI tends to agglomerate into large particles due to its high surface energy and intrinsic magnetic interaction, which makes it difficult to be separated and recovered after use (Phenrat et al., 2007). Besides, the surface hydrophobicity of NZVI is poor, so it is not readily accessible by hydrophobic organic contaminants, and leading to the lower removal efficiency. Using support materials to immobilize NZVI is one possible way to solve above-mentioned problems. As reported in the literatures, surfactant-modified zeolite (SMZ) (Zhang et al., 2002),

porous silica (Zheng et al., 2008), resin (Li et al., 2007), poly acrylic acid (Wang et al., 2008) and alginate bead (Kim et al., 2010) have been used for this purpose and interesting results have been obtained after NZVI being supported on those solids. However, the preparations of those composite materials were complex and the cost was high.

Bentonite, a kind of layered clay consisting mainly of montmorillonite, is often served as an adsorbent for pollution control due to its high surface area and strong adsorption capacity (Churchman et al., 2006). Besides, bentonite can be easily modified due to its exchangeable interlayer cations. The modified bentonites are more efficient adsorbents than the original one, due to the enhanced surface area and more functional groups introduced into the interlayers (Li et al., 2008, 2009; Belkhadem et al., 2008). Furthermore, these functional groups are changeable by using various modifying agents, so the modified bentonites with a high adsorption capacity can be designed according to the structure and properties of target contaminants. For example, organobentonites (Zhu et al., 1997) showed high adsorption capacity to organic contaminants (Zhu et al., 1997), and aluminum-pillared bentonite performed well on adsorbing inorganic heavy metal ions (Manohar et al., 2006). Hence, it is very interesting to investigate the potential of various modified bentonites as support materials of NZVI for removal of different kinds of contaminants. Until now, quite few studies have been reported on using such a combination for environmental remediation.

In this paper, the organobentonite was prepared from Na⁺-saturated bentonite by intercalation with cetyltrimethylammonium bromide (CTMA) and used as a carrier of NZVI. The herbicide atrazine was used as a model compound of chlorinated contaminants. The removal efficiency of atrazine by this NZVI/CTMA-Bent composite was

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tested by batch experiments, and the influence of solution pH and initial concentrations of atrazine were investigated. The performance of the NZVI/CTMA-Bent composite was compared with that by NZVI itself containing the same amount of iron.

2. Materials and methods

2.1. Materials

The original Na⁺-saturated bentonite (Na-Bent) was purchased from Inner Mongolia, China. Its cation exchange capacity (CEC) is 115 cmol/kg. Commercial iron powder (<100 mesh, Fe⁰), ferrous sulfate heptahydrate (FeSO₄·7H₂O), sodium borohydride (NaBH₄), cetyltrimethylammonium bromide (CTMA), sodium hydroxide (NaOH) and atrazine (C₈H₁₄ClN₅) were all purchased from Shanghai Chemical Co. as analytical grade.

2.2. Preparation and characterization of bentonite and iron samples

The organobentonite was prepared by a cation exchange method. Briefly, 8.38 g of CTMA was added to a 1% (w/w) Na-Bent aqueous suspension under continuous stirring for 120 min in a water bath at 70 °C. The molar amount of CTMA added was equal to the CEC of Na-Bent, and then the suspension was centrifuged, washed and dried to a constant weight. Finally, the solid was mechanically ground to less than 100 mesh and heated at 115 °C for 120 min (Li et al., 2008). The final product was denoted as CTMA-Bent.

The NZVI was prepared by a chemical reduction procedure. In brief, 250 mL of 0.108 mol/L NaBH₄ solution was dropwise added into the same volume of a 0.054 mol/L FeSO₄·7H₂O solution under continuous stirring. The mixture was stirred for another 30 min under room temperature. The metal particles formed were settled and filtered. Then the solid was washed with ethanol for several times, and finally dried under a vacuum condition. The preparation process was operated under a nitrogen atmosphere.

The supported NZVI was prepared by a similar procedure as described above, except that 8 g of CTMA-Bent was dispersed in 250 mL of a 0.054 mol/L FeSO₄·7H₂O solution under continuous stirring overnight before the addition of a NaBH₄ solution. The final mixture was labeled as NZVI/CTMA-Bent.

The Brunauer–Emmett–Teller (BET) specific surface area of above samples was obtained from nitrogen adsorption data at 77 K in an ASAP 2020 system (Micromeritics). X-ray diffraction (XRD) measurement was performed with a Rigaku D/MAX-2500 system using CuK α radiation at 0.1542 nm. The morphology of NZVI and NZVI/CTMA-Bent was observed by JEM-1010 transmission electron microscope (TEM).

2.3. Batch experiments for the removal of atrazine

Typically, each iron sample (commercial iron powder, NZVI or NZVI/CTMA-Bent) containing iron of 200 mg was added into the conical flask containing 100 mL of atrazine solution (pH = 5.0) of 28 mg/L (C₀) under stirring. The atrazine solution was deoxygenated by a N₂ stream for 10 min before the addition of iron samples, and kept sealed with a stopper during the experiment. The reduction was carried out by putting the flask in a thermostatic shaker bath at 25 ± 0.1 °C, with a rotation speed of 160 rpm. At given time intervals, a solution of 0.5 mL sample was withdrawn and filtered through a 0.22 μ m membrane. The atrazine concentrations at time *t* (C_{*t*}) were determined. The removal efficiency of atrazine was calculated by using the following equation: Removal percentage of atrazine (%) = (C₀ - C_{*t*})/C₀ × 100%.

2.4. Analytical methods

Quantitative analysis of atrazine was performed in an HP1100 (Agilent Technologies, Inc.) high performance liquid chromatography system equipped with a UV–VIS detector and a C-8 column (4.6 mm × 250 mm 5 μ m). A mobile phase of methanol–water mixture (70:30, V/V) was used at a flow rate of 0.80 mL/min. The analysis wavelength was 220 nm.

The Atomic Absorption Spectrometer (AA-6300 C, Shimadzu) was used to determine the concentration of iron. The solution pH was measured with a pH meter (PHS-2C, China). The chloride ion concentration during the reaction was measured by a chloride ion-selective electrode (pC1-1, China).

3. Results and discussion

3.1. Characterization of NZVI and NZVI/CTMA-Bent

The XRD patterns of NZVI and NZVI/CTMA-Bent confirm the formation of iron in its zero valent state with its major reflection at $2\theta = 44.8^\circ$ (Fig. 1). The BET specific surface areas were determined to be 0.35 m²/g for commercial iron powder (Fe⁰), 33.5 m²/g for NZVI, 27.7 m²/g for NZVI/CTMA-Bent and 8.82 m²/g for CTMA-Bent, respectively. The iron contents in commercial iron powder, NZVI and NZVI/CTMA-Bent samples were measured to be 91.2%, 68.7% and 24.7%, respectively.

Fig. 2 shows the surface morphology of NZVI and NZVI/CTMA-Bent. One can see from Fig. 2a that the NZVI particles exist as necklace-like aggregates. In contrast, the morphology of NZVI/CTMA-Bent in Fig. 2b indicates that the iron nanoparticles are clearly discrete and well dispersed on the surface of CTMA-Bent, without aggregation. Those particles are close to spherical with grain size ranging from 50 to 120 nm in diameter.

3.2. Comparison of atrazine removal by various samples

The removal efficiency of atrazine by various iron samples including commercial iron powder (0.2192 g), NZVI (0.2911 g) and NZVI/CTMA-Bent (0.8097 g) was investigated. The different

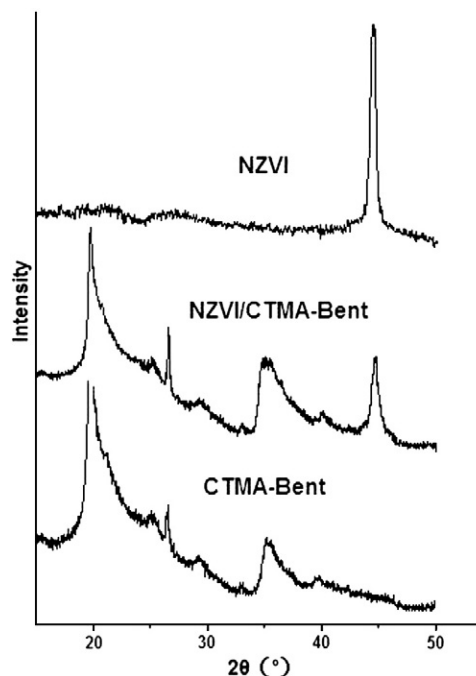


Fig. 1. XRD patterns of NZVI, NZVI/CTMA-Bent and CTMA-Bent.

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