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Synthesis of reactive nanoscale zero valent iron using rectorite supports and its application for Orange II removal

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HIGHLIGHTS

- The nanoscale zero valent iron-rectorite composite was successfully synthesized.
- The growth of Fe crystal in the interlayer of rectorite resulted in nZVI particles at ca. 10.3 nm.
- The newly prepared nZVI-R possessed much higher efficiency for Orange II decolorization.
- The adsorption of Orange II on nZVI-R was detected at the beginning of reactions.
- nZVI-R can prevent the aggregation of nZVI and provide opportunity for contaminants treatment.

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ABSTRACT

The nanoscale zero valent iron-rectorite (nZVI-R) composite was successfully synthesized through incorporation of nano-zero valent iron (nZVI) into the natural rectorite as supports. Iron ions were imbedded in the interlayer of rectorite clay via an ion-exchange reaction, and then the exchangeable Fe(III) cations were reduced to nZVI by $NaBH_4$ in solution. The confinement of Fe crystal growth in the interlayer regions of rectorite resulted in the formation of nZVI particles at ca. 10.3 nm. The structure, morphology, Fe species, crystal phase, and elemental composition of the prepared nZVI-R composite materials were characterized using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF). Comparing with the commercially available nZVI-Junye, nZVI prepared in laboratory (nZVI-Lab) and Na-rectorite, the synthesized nZVI-R composite in this study showed superior decolorization efficiency for Orange II with 0.2 g of nZVI-R and a complete removal of Orange II achieved in less than 10 min. On the basis of FT-IR spectra, the mechanism for nZVI-R in the discoloration of Orange II was also postulated. This nZVI-R composite has potential applications in cleaning up environmental contaminants such as organic dyes or halogen compounds.

1. Introduction

The synthesis and application of reactive zero valent iron (ZVI) have been extensively studied recently for ground water remediation and hazardous waste treatment. As a strong reductant, ZVI can effectively transform a wide variety of persistent organic and inorganic contaminants, such as chlorinated organics, nitroaromatic compounds, heavy metals and organic dyes [1–5]. Major advantages of nanoscale ZVI (nZVI, 10–100 nm) include the enhanced reactivity by increasing the surface to volume ratios and providing more reactive surface sites, compared to the bulk or microscale iron particles [6,7]. In addition, nZVI is expected to offer enormous flexibility for applications in both *in situ* and *ex situ* remediation applications [8,9]. However, there are two major limiting issues associated with nZVI in its practical applications currently: (i) similar to other nanoscale materials, it has a strong tendency to agglomerate into larger particles resulting in diminishing reactivity in application condition; and (ii) the remaining nZVI in the treatment system makes the technology uneconomical and even generates secondary iron pollution. Separation and removal of the catalyst from the bulk treatment system after application is another critical step in application and the widely acceptance of this new technology.

To overcome these disadvantages, it has been proposed to stabilize the nZVI particles onto various supports including organic and inorganic materials: porous carbons [10,11], zeolite [12], resin [13,14], chitosan/silica [15], polyelectrolyte multilayers [16], clays

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[17–19], starch and carboxymethyl cellulose [20–22]. Up to now, only a few studies on the nZVI supported on clay minerals have been reported. Gu et al. [17] synthesized subnanosized ZVI using smectite clay layers as templates and reported that the subnanoscale ZVI showed superior reactivity and efficiency compared to other forms of ZVI for the reduction of nitrobenzene tested. Zhang et al. [18] prepared kaolinite supported nZVI and applied it for Pb(II) ion removal from aqueous solution. The results indicated that the synthesized nZVI is a potential environmental remediation material for the treatment of electroplating wastewater containing metal ions. Clays such as smectite and bentonite have been used as suitable catalyst supports due to their particular properties and structures as well as high abundance and low cost [23]; their high surface area and adsorption capacity for organic pollutants accumulated to be in contacts with the catalyst of the clay particles thus improve the treatment efficiency [19]. Furthermore, synthesis of nZVI on minerals that are amenable to the geochemical conditions can make the delivery of such materials into the contaminated sites to be carried out readily and functioning effectively [24].

Rectorite is an interstratified silicate mineral consisting of a regular stacking of mica-like layer and montmorillonite-like layer (1:1 ratio), and is readily available [25]. Due to the similar structure and characteristics, rectorite exhibits some excellent properties similar to montmorillonite, such as high mechanical and thermal resistance, good colloidal property in water as well as the exchangeable ion species [26,27]. On the other hand, the mica-like layer makes rectorite structurally more stable than montmorillonite. Consequently, rectorite may be more suitable for the pillared structures compared with the montmorillonite clay mineral [28]. The thickness of a monolithic rectorite layer is about 2 nm while the interlayer spacing is about 2.46 nm [29]. Similar to smectite clay, ZVI particles could be formed via reduction of Fe(III) present as exchangeable cations on rectorite [17]. Based on the so-called pillaring technique, it is possible to use rectorite as templates/supports for preparation of a new class of catalysts containing nanosized or subnanosized ZVI.

In this paper, a new reactive ZVI was synthesized via an ion-exchange reaction followed by a borohydride reduction process using rectorite as the support material. The nZVI-rectorite (nZVI-R) composite obtained was characterized by a series of analytical techniques. Comparing with the Na-rectorite and other existing forms of nZVI, the newly synthetic ZVI-R nanocomposite possesses much higher reactivity and efficiency for removal of Orange II.

2. Experimental section

2.1. Materials

The rectorite used in this study was collected from Zhongxiang, Hubei, China. Its cation exchange capacity (CEC) is 48.5 meq/100 g. Orange II (>99.5%), sulfanilic acid and 1-amino-2-naphthol were obtained from Sigma–Aldrich (Milwaukee, WI). Sodium borohydride ($NaBH_4$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), absolute ethanol, acetone and hydrogen chloride (HCl) were from Nanjing Chemical Company (Nanjing, PR China). HPLC-grade acetonitrile was purchased from Tedian Company. The nZVI used was iron powder with >99.9% purity and <60 nm in sizes (Shenzhen Junye Nano Material Co., Ltd., Shenzhen, PR China). This nZVI was denoted as nZVI-Junye. All chemicals were used without any further treatment.

2.2. Preparation of ZVI-R nanocomposite and nZVI particles

The ZVI-R nanocomposite was prepared through the following steps: (i) 4 g of rectorite were dispersed in 100 ml deionized water in glass beaker and then acidified to pH 3 with 2 M HCl under vigorous stirring for about 8 h at room temperature to remove carbonate impurities. (ii) The rectorite particles with size <2 μm were obtained by the sedimentation–centrifugation procedures, and then treated with 1 M NaCl solution. Following multiple saturation treatments, the rectorite sample was washed with deionized water several times until excess Cl^- was completely eliminated (undetectable by reacting with $AgNO_3$). (iii) 200 mL of 0.2 M $FeCl_3$ solution (pH = 2) were freshly prepared and then mixed with 4 g of monovalent substituted Na-rectorite, the mixture was stirred for 12 h at 60 °C. The rectorite was then separated from the suspension through centrifugation and washed with deionized water several times to remove the excess Fe^{3+}. (iv) The Fe^{3+}-rectorite was redispersed in 100 ml of absolute ethanol and the pH was adjusted to 3. After that, 100 mL of 2 M $NaBH_4$ were added drop wise into the suspension under conditions of vigorous stirring and a N_2 atmosphere. Clay particles in the solution immediately turned black and the mixture was further stirred for 2 h. To remove excess $NaBH_4$, the modified rectorite was centrifuged and rinsed three times with absolute ethanol, and then dried in 50 °C oven under vacuum overnight.

nZVI particles were prepared through a procedure involving liquid phase reductive precipitation [30]. In brief, 30 mM of aqueous $NaBH_4$ solution was added drop wise into equal volume of 10 mM $FeCl_3$ solution under vigorous stirring and N_2 atmosphere. The resulting black suspension was further mixed for another 15 min and centrifuged to obtain the particulates. Then the nanoparticles were washed with absolute ethanol and acetone. Finally, the obtained particles were vacuum-dried. This newly laboratory made nZVI was denoted as nZVI-lab. Dried samples were stored in an anaerobic chamber filled with pure N_2 gas prior to use.

2.3. Characterization of ZVI-R nanocomposite and nZVI particles

The structure and crystallinity of ZVI-R nanocomposite were characterized using an X-ray diffractometer (XRD) with Cu Kα radiation (Switzerland ARL X'TRA, $\lambda = 1.5418$ Å). Brunauer–Emmett–Teller (BET) N_2 adsorption method with a JW-04 surface analyzer was used to measure the specific surface area of the samples. The particle morphology and microstructure were observed on a JEM-2100 (JEOL) high-resolution transmission electron microscope (HR-TEM). The bulk chemical compositions of Na-R and nZVI-R were determined by X-ray fluorescence (XRF) spectrometry (Switzerland ARL Corporation). To confirm the reduction of Fe^{3+} to Fe^0, the prepared samples were also analyzed using X-ray photoelectron spectroscopy (XPS, ULVAC PHI5000 VersaProbe). The chemical bonds on the surface of powder were detected using Fourier transform infrared (FT-IR) spectroscopy (Nexus870, Thermo Nicolet).

2.4. Determination of Orange II decolourization

The reduction efficiency of the ZVI-R nanocomposite was evaluated by testing an azo-dye Orange II as the model pollutant. The choice of the dye is due to the fact that it is widely used in the textile industry and is not biodegradable [31]. All solvents were deoxygenated and saturated with N_2 before use. In a typical experiment, 0.2 g (the best dosage in this study) of freshly synthesized nZVI-R were added into 150 mL conical flasks with glass stopples containing 100 ml of 70 mg L^{-1} Orange II solution at its natural pH. The suspension was stirred on a rotary shaker. At specific time intervals, about 1 ml of liquid sample was withdrawn from the reaction flask and filtered through a syringe filled with silanized glass wool.

Then Orange II and other reaction products (1-amino-2-naphtol and sulfanilic acid) were analyzed on a high-performance liquid chromatography (HPLC, Agilent 1200, USA) equipped with a C_{18} re-