



Enhanced ultrasound-assisted degradation of methyl orange and metronidazole by rectorite-supported nanoscale zero-valent iron



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ABSTRACT

In this study, the rectorite-supported nanoscale zero-valent iron (nZVI/R) was synthesized through a reduction method. X-ray diffraction analysis showed the existence of the nZVI in the nZVI/R composite and X-ray photoelectron spectroscopy analysis indicated that the nZVI particles were partly oxidized into iron oxide. Scanning electron microscopy analysis revealed that the nZVI particles were highly dispersed on the surface of the rectorite. The specific surface area of the nZVI/R composite is 21.43 m²/g, which was higher than that of rectorite (4.30 m²/g) and nZVI (17.97 m²/g). In the presence of ultrasound (US), the degradation of methyl orange and metronidazole by the nZVI/R composite was over 93% and 97% within 20 min, respectively, which is much higher than that by the rectorite and the nZVI. The degradation ratio of methyl orange and metronidazole by the nZVI/R composite under US was 1.7 and 1.8 times as high as that by the nZVI/R composite without US, respectively. The mechanism of the enhanced degradation of methyl orange and metronidazole under US irradiation was studied. These results indicate that the US/nZVI/R process has great potential application value for treatment of dye wastewater and medicine wastewater.

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1. Introduction

Nanoscale zero-valent iron (nZVI), which possesses the advantages of large surface area, nanoscale dimensions and great reaction activity, has been used as a potential method in the treatment of dye wastewater and medicine wastewater [1,2]. For instance, Fan et al. [3] used nZVI particles for the degradation of methyl orange (MO) and the MO could almost be decomposed in 10 min. Chen et al. [4] synthesized nZVI particles to reduce metronidazole and the metronidazole was almost completely removed within 90 min. However, the use of the nZVI is restricted in the wastewater treatment due to its instability, easy aggregation, resulting in a crucial loss of reactivity [5,6]. To address this issue, many materials have been developed to support nZVI particles such as kaolinite [7], clinoptilolite [8], activated carbon [9], bentonite [10]. The supported nZVI composite could overcome the shortcomings of the nZVI and possesses more excellent reduction ability than the nZVI. For example, Nairat et al. [8] synthesized the natural zeolite clinoptilolite-supported nZVI composite which showed higher removal efficiency than individual nZVI for the removal of organic dyes. In addition, kaolinite-supported nZVI

[11] and resin-supported nZVI [12] all demonstrated superior reactivity to organic pollutant than nZVI.

Rectorite is an interstratified silicate mineral with a regular (1:1) stacking of mica-like layer and montmorillonite-like layer [13,14]. Moreover, the structure of rectorite exhibits more stable than that of montmorillonite [15]. Moreover, the rectorite supported nZVI composite have been hardly reported till now. From these viewpoints, the rectorite which is cost-effective and easily obtained has been chosen as supported material to synthesize the nZVI/R composite.

In addition, US has emerged as one of the effective technologies in water treatment [16] and reactive species such as hydrogen atoms, hydroxyl and superoxide radicals which are generated in US process can efficiently degrade the organic pollutants [17]. MO is a kind of azo dyes and metronidazole is an important antibiotic drug, which exist in the industrial and hospital effluents and cannot be degraded by conventional biological process effectively [18–21]. Therefore, in this research, the degradation of MO and metronidazole by the nZVI/R composite under US was investigated. Effects of operating parameters such as initial pH, the nZVI/R composite dosage and initial concentration of MO on the degradation of MO by the nZVI/R composite under US were studied. The degradation mechanism of MO and metronidazole by this system was also probed.

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2. Material and methods

2.1. Chemicals

The rectorite used in this study was from Zhongxiang, Hubei, PR China. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium borohydride (NaBH_4), ethanol ($\text{CO}(\text{NH}_2)_2$), methyl orange ($\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_3\text{SNa}$), and metronidazole were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were of analytic reagent grade and were used without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of nZVI/R composite

The nZVI/R composite was synthesized by reducing ferric ion to zero-valent iron using the borohydride reduction method [22–24]. Typically, 1 g of rectorite and 2.42 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were mixed in 300 mL of deionized water to form a mixture solution, and then the mixture solution was stirred vigorously under N_2 atmosphere for 30 min. 1.36 g of NaBH_4 was dissolved in 120 mL deionized water, and then the solution was added dropwise into the Fe^{3+} -rectorite mixture solution. When the NaBH_4 solution was added, plenty of gas was bubbled out and the mixture solution was immediately turned black. The black precipitate was centrifuged and washed for three times with absolute ethanol, and was then vacuum dried at 45 °C for 4 h.

2.3. Characterization

The structure and crystallinity of the rectorite, the nZVI and the nZVI/R composite were determined by powder X-ray diffraction (XRD) analysis on a D8 Advance diffractometer (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCALAB II XPS system with a monochromatic Mg Ka source and a charge neutralizer. SEM images of the rectorite, the nZVI and the nZVI/R composite were determined by using scanning electron microscopy (SEM, JSM-5610LV). The nitrogen adsorption–desorption isotherms were measured on an AUTOSORB-1 nitrogen adsorption apparatus (Quantachrome, USA).

2.4. Batch experiments

The degradation of MO was performed in the presence of the nZVI/R composite under US (90 W, SK2200LH). Degradation experiments were conducted in a 250 mL conical flask with US at the frequency of 59 kHz. For the degradation of MO, 0.03 g of the nZVI/R composite was added in 100 mL of 100 mg/L MO solution. The initial pH value of MO solution was adjusted to 7. At given time intervals, 5 mL of samples were drawn out and centrifuged immediately. The absorbance of MO was measured by using a UV–vis spectrophotometer (UV1750, Shimadzu Corporation, Kyoto, Japan). For the degradation of metronidazole, 0.03 g of the nZVI/R composite was added in 100 mL of 20 mg/L metronidazole solution, and remained experiments were similar to the degradation of MO.

For comparison, the degradation of MO by the rectorite and the nZVI were also conducted under the same experimental condition as described above.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the rectorite and the nZVI/R composite. It can be seen that the (002) peak at $2\theta = 6.74^\circ$ of the

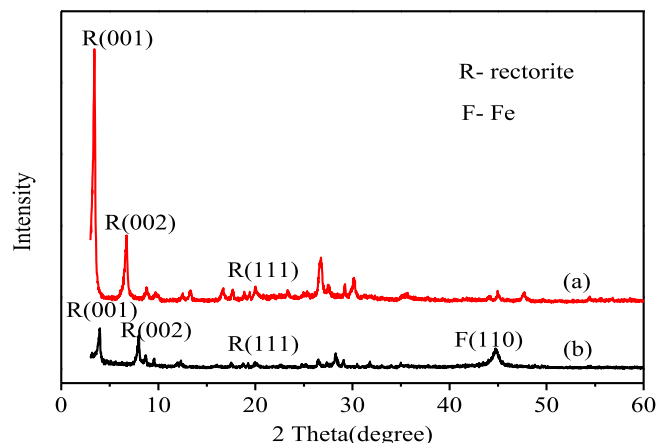


Fig. 1. XRD patterns of samples: (a) rectorite (b) nZVI/R.

rectorite shifted to $2\theta = 8.72^\circ$ after compositing with the nZVI, resulting from the delaminated phenomena and the smectite-like layers dehydration phenomena [25–27]. The diffraction peak at about $2\theta = 20.0^\circ$ in the XRD patterns of the rectorite and the nZVI/R composite can be assigned to the (111) reflection of the rectorite. The characteristic peak at $2\theta = 44.7^\circ$ [7,28] can be ascribed to the (110) reflection of the nZVI (JCPDS, File No. 87-0722), indicating the existence of the nZVI in the as-prepared composite.

3.2. XPS analysis

In order to investigate the oxidation states on the surface of the nZVI/R composite, XPS technique was employed. As shown in Fig. 2(a), the primary elements in the sample are C, O, Si, Al and Fe. The binding energies of these elements are 284.6 eV (C 1s), 532.6 eV (O 1s), 103.9 eV (Si 2p), 75.6 eV (Al 2p), and 711.7 eV (Fe 2p), respectively. As shown in Fig. 2(b), the peak at 711.7 eV corresponds to the binding energies of Fe 2p_{3/2} and the peak at 725.0 eV responds to Fe 2p_{1/2} binding energies, which suggest the existence of the oxidized iron [29,30]. Besides, the peak at 719.0 eV which corresponds to the Fe 2p_{3/2} satellite is likely from two overlapping components: the shakeup satellite for oxidized iron (2p_{3/2}) and nZVI (2p_{1/2}) [29]. The iron oxide on the surface of the nZVI might form during the vacuum drying process or in contact with aqueous solution [31,32]. No obvious peak of the nZVI (around 707 eV) was observed, which was probably because XPS is only a surface analysis technique with 2–5 nm probing depth [33,34]. However, the XRD analysis of the sample strongly demonstrates the existence of the nZVI. The reason why the iron oxides were not detected using XRD technique may be attributed to their low crystallinity.

3.3. SEM images

The SEM images of the nZVI, the rectorite and the nZVI/R are presented in Fig. 3. It can be seen that the rectorite shows schistose structure and the surface of the rectorite is smooth while the surface of the rectorite became coarser after loading with nZVI particles. The SEM image of the nZVI is presented in Fig. 3(b). The nZVI particles showed a chain-like morphology and aggregated strongly. The aggregation leads to less reaction activity. As shown in Fig. 3(c and d), the nZVI particles in the nZVI/R sample were dispersed well on the surface of rectorite without obvious aggregation. Therefore, the rectorite as supported material is available for the dispersion of the nZVI particles.

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