



Synthesis, characterization, and reactivity of cellulose modified nano zero-valent iron for dye discoloration



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ABSTRACT

Nano zero-valent iron (NZVI) was innovatively and successfully modified by using hydroxyethyl cellulose (HEC) and hydroxypropylmethyl cellulose (HPMC) as dispersants. The systematic characterization observations (including XRD, SEM and TEM) illustrate that, compared with bare nano zero-valent iron particles (BNZVI), the particle sizes of hydroxyethyl cellulose modified (ENZVI) and hydroxypropylmethyl cellulose modified (PNZVI) were decreased, while the dispersity and antioxidantizability of ENZVI and PNZVI particles were increased. The discoloration efficiencies of ENZVI, PNZVI, and BNZVI were compared by using dyes (including orange II, methyl orange, methyl blue, and methylene blue) as target pollutant. The results show that both the discoloration efficiency and reaction rate of ENZVI and PNZVI are higher than that of BNZVI. In addition, effects of dispersant content, dye type, pH value, initial dye concentration, iron dosage, and reaction temperature on discoloration efficiencies were studied. The results show that discoloration efficiency was decreased by increasing initial pH value and dye concentration, and it was increased with the increase the iron dosage and reaction temperature. Under optimized NZVI addition of 0.7 g L^{-1} , the discoloration efficiencies of ENZVI and PNZVI were increased to 96.33% and 98.62%, respectively. And the possible discoloration pathway and dispersant modification mechanism of NZVI were discussed. This study suggests hydroxyethyl cellulose and hydroxypropylmethyl cellulose dispersed NZVI can be utilized as a promising modified nano-material for degradation of dye wastewater.

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1. Introduction

Dyes have been widely used in many industries, like textiles, printing, leather, paper, cosmetics, and plastics. Discharging untreated dye wastewater will undoubtedly lead to severe environmental problems. The dye contaminated wastes can inhibit the sunlight from reaching the deep-water, and resulting in the negative effect on growth of aquatic organisms critically. In particular, the accumulation of dyes in water environment is hazardous to the health of human health and other creatures because of its potential toxicity, carcinogenicity, and teratogenicity. Thus, removal of dyes from wastewater is essentially necessary before they are discharged into environment. In previous literatures, plenty of methods, including adsorption [1,2], flocculation [3], membrane filtration [4], electrolysis [5,6], biological treatments [7], and oxidation [5,8] have been used for the discoloration of dyes from

wastewaters. In recent years, an emerging technology, nano zero-valent iron (NZVI) reduction technology, has aroused more and more attention on dye waste water treatment. Up to now, NZVI had been proved to be effective for degradation of a wide range of pollutants, such as chlorinated organic compounds [9], brominated organic compounds [10,11], nature organic matter (NOM) [12], organophosphate pesticides [13], estrogens [14], metronidazole [15,16], dyes [17], and heavy metals (including arsenic, chrome, mercury, and lead, etc.) [18–23] in groundwater, surface water or soil, due to its huge specific surface area, high reactivity, and relatively low price. And it was reported that NZVI is capable of discolorating and removing dyes by destroying their chromogenic group (i.e. $-\text{N}=\text{N}-$) [24].

However, one the disadvantages of NZVI technology is the aggregation of iron nanoparticles in aqua phase due to the magnetism among particles. This may cause the decrease in both adsorption sites and reactive sites of particles, resulting in the decrease in effective contact area between target pollutants and NZVI, thus degradation rate is inevitably reduced. In addition, being a strong reducing metal, NZVI is also prone to be oxidized

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under ambient environmental conditions. Hence, the modification of NZVI must be conducted for reducing its aggregation, improving its transfer performance in environmental media, and increasing its degradation ability to contaminants. Recently, some researchers immobilized NZVI on solid supports, such as PVDF membrane [15], PAN membrane [25], resin [26], silica [27,28], bentonite [29], montmorillonite [30], diatomite [31], rectorite [32], activated carbon [33,34], and multiwalled carbon nanotube [35] to restrain aggregation of NZVI. Besides, other studies for increase of NZVI dispersity and mobility in water body or soil have been focused on coating iron nanoparticles with stabilizer via steric hindrance and electrostatic repulsion. These modifiers include various polymer electrolytes and surfactants, such as chitosan [36,37], xanthan gum [38], cetyltrimethyl ammonium bromide (CTAB) [9], and carboxy methylated cellulose (CMC) [39,40], etc.

Among all reported stabilizers, water-soluble polysaccharides have been proved to be the best stabilizer due to their low cost and environmental compatibility. This kind of stabilizer can not only control the particle size during the Fe⁰ formation process, but also prevent agglomeration of the NZVI in liquid phase. Thus, the size and reactivity of NZVI are able to be significantly improved. Cellulose is one of the most abundant renewable natural polymeric materials, which is employed in extensive utilizations, like cosmetic and pharmaceutical. And it is reported that one of cellulose chemical derivatives, CMC was successful used for stabilizing NZVI and other nanoparticles [41,42] to decontaminate several pollutants in soil and groundwater [43]. Both hydroxyethyl cellulose (HEC) and hydroxypropylmethyl cellulose (HPMC) are important chemical derivatives of cellulose and they have a large amount of relatively easily accessible hydroxyl units that can be bonded with a number of functional groups. To the best of our knowledge, there are no literatures available for investigation on modification of NZVI by using HEC and HPMC and their degradation efficiency of organic dyes. The main purpose of this study is to provide a novel method of NZVI modification for improving the dispersion of NZVI by coating HEC and HPMC as modifiers. Several typical organic dyes (including orange II, methyl orange, methyl blue, and methylene blue) were used as target pollutants for discoloration reaction by using the as prepared HEC modified NZVI (ENZVI) and HPMC modified NZVI (PNZVI), respectively. The further objectives of this study are as follows: (1) revealing the influence of HEC and HPMC on both discoloration reactivity and the stability of NZVI, (2) evaluating the effect of the modifier coatings on discoloration efficiency and kinetics under different reaction conditions, and (3) further elucidating the mechanism of coating layers for NZVI-dye discoloration system.

2. Materials and methods

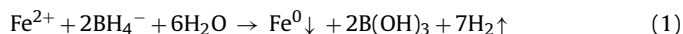
2.1. Materials

Orange II, methyl orange, methyl blue, methylene blue, and potassium borohydride (KBH₄, AR) were from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Ferrous sulfate heptahydrate (FeSO₄·7H₂O, AR) was from Fuchen Chemical Regents Factory (Tianjin, China). Ethanol (AR) was obtained from Shandian (Yunnan, China). Acetone (AR) was obtained from Chuandong (Chongqing, China). Hydroxyethyl cellulose (HEC, USP) and hydroxypropylmethyl cellulose (HPMC, USP, 2% viscosity: 6 mPa·s) were purchased from Aladdin (Shanghai, China). All chemicals were reagent pure grade or above and used without further purification.

2.2. Synthesis of modified NZVI

The modified NZVI was synthesized in an anaerobic glovebox under the protection of purified N₂. Firstly, 20 g FeSO₄·7H₂O was

dissolved in 100 mL deionized water. Then, a certain volume stabilizer (HEC or HPMC, 10 g L⁻¹) solution was added into the FeSO₄ solution with electromagnetic stirring for 15 min. After intensive mixing, KBH₄ solution, which was prepared by dissolving 15 g KBH₄ in 100 mL deionized water, was dropwised into the mixture solution. When delivering all of the KBH₄ solution, there appeared to be plenty of black solid precipitation, which are ENZVI or PNZVI. Subsequently, the solid precipitation was filtered by 0.2 μm membrane filter under vacuum. The modified NZVI was obtained by washing the solid precipitation with deionized water, absolute ethanol, and acetone sequentially for 3 times. These particles were dried in a vacuum drying oven under room temperature and restored in vials for further characterization and discoloration reaction. The reduction mechanism according to formula as following:



For comparison, the unmodified pristine NZVI was prepared according to the aforementioned method without stabilizer added. The as-prepared bare NZVI was denoted as BNZVI.

2.3. Characterizations

The particle crystal structure was characterized by X-ray diffraction (XRD, D/max2200 X-ray diffractometer with Ni-filtered Cu Ka radiation operating at an accelerating voltage of 45 kV). The microscope features of the BNZVI, ENZVI and PNZVI were observed with a high-resolution transmission electron microscope (TEM, JEOL Ltd., Japan) at an accelerating voltage of 100 kV. The surface morphologic features of prepared BNZVI, ENZVI, and PNZVI were examined by a high-resolution field emission scanning electron microscope (FE-SEM, JEOL Ltd., Japan) with an accelerating voltage of 5 kV. BET (Brunauer–Emmett–Teller) specific surface areas of BNZVI, ENZVI, and PNZVI were measured from N₂ physisorption method with a TriStar II 3020 V1.03 analyzer (Micromeritics Instrument Corporation). The surface chemical structure and composition of dispersant modified iron particles were investigated using spectrum one Fourier transform infrared spectroscopy (FT-IR) (Perkin–Elmer Instrument Co. Ltd., USA). The surface chemical states were characterized by using Thermo ESCALAB 250 XPS instrument.

2.4. Batch experiments

Four typical organic dyes, orange II, methyl orange, methyl blue, and methylene blue were chosen as target pollutants, and their chemical structures are shown in Fig. 1. Batch discoloration experiments were carried out in 250 mL reaction bottles and each bottle was filled with 100 mL dye solution. A certain amount of NZVI was added into each reaction bottle and shaken back and forth at 170 rpm. All experiments were conducted under aerobic condition in triple. The effect of dispersants content, dye types, initial solution concentrations, pH values, NZVI dosage, and reaction temperatures were investigated to optimize the reaction conditions. The UV–vis spectra of dyes were recorded from 190 nm to 750 nm using a UV-2450 visible spectrophotometer (Shimadzu, Japan). The maximum absorbance wavelengths for orange II, methyl orange, methyl blue, and methylene blue were found at 483 nm, 463 nm, 596 nm, and 664 nm, respectively. The extraction of reaction samples was filtered by 0.45 μm membrane filter and dilution constant volume with deionized water. Concentrations of above-mentioned solution were measured with UV-vis spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., China).

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