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# Decolorization of Methyl Orange by a new clay-supported nanoscale zero-valent iron: Synergetic effect, efficiency optimization and mechanism

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## ABSTRACT

In this study, a novel nanoscale zero-valent iron (nZVI) composite material was successfully synthesized using a low-cost natural clay, “Hangjin 2<sup>#</sup> clay” (HJ clay) as the support and tested for the decolorization of the azo dye Methyl Orange (MO) in aqueous solution by nZVI particles. According to the characterization and MO decolorization experiments, the sample with 5:1 HJ clay-supported nZVI (HJ/nZVI) mass ratio (HJ-nZVI5) showed the best dispersion and reactivity and the highest MO decolorization efficiency. With the same equivalent Fe<sup>0</sup> dosage, the HJ-nZVI1 and HJ-nZVI5 samples demonstrated a synergetic effect for the decolorization of MO: their decolorization efficiencies were much higher than that achieved by physical mixing of HJ clay and nZVIs, or the sum of HJ clay and nZVIs alone. The synergetic effect was primarily due to the improved dispersion and more effective utilization of the nZVI particles on/in the composite materials. Higher decolorization efficiency of MO was obtained at larger HJ-nZVI dosage, higher temperature and under N<sub>2</sub> atmosphere, while the MO initial concentration and pH were negatively correlated to the efficiency. HJ clay not only works as a carrier for nZVI nanoparticles, but also contributes to the decolorization through an “adsorption-enhanced reduction” mechanism. The high efficiency of HJ-nZVI for decontamination gives it great potential for use in a variety of remediation applications.

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## Introduction

Based on the intrinsic properties of nanoscale zero-valent iron (nZVI), such as small particle size, large specific surface area, high number of reactive surface sites, high reactivity and mild

reaction conditions (Liu et al., 2015; Xiao et al., 2015), nZVI particles have been extensively used as a new tool for the remediation/treatment of groundwater and wastewater contaminated with various organic and inorganic pollutants in the past 20 years (Crane and Scott, 2012; Fu et al., 2014; Guan

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et al., 2015; Tosco et al., 2014). However, there are still some technical challenges associated with its application. On the one hand, nZVI particles tend to agglomerate readily in an aqueous environment, due to inter-particle magnetic and Van der Waals interactions, and thus form big dendritic flocs and subsequent network structures, which cause a considerable decrease in their dispersibility and mobility (Li et al., 2015; Xu et al., 2014). On the other hand, nZVI nanoparticles can be oxidized easily, which diminishes their reactivity due to the formation of oxide layers blocking the serviceable active surface sites (Guan et al., 2015; Li et al., 2015; Sun et al., 2014a; Xu et al., 2014).

To overcome these drawbacks, offering a support for nZVI particles is an alternative option. In recent years, porous materials such as kaolinite (Chen et al., 2013; Jin et al., 2015), bentonite (Li et al., 2015; Lin et al., 2014; Zhou et al., 2013), resin (Fu et al., 2013), activated carbon (Xiao et al., 2015), mesoporous carbon (Ling et al., 2012), mesoporous silica (Tang et al., 2015), pumice (Liu et al., 2015), graphene (Liu et al., 2014a) and SBA-15 (Sun et al., 2014a, 2014b), have been tested as supports to inhibit the aggregation of nZVI particles and hence increase the reaction performance. Technically, an appropriate support material for nZVI particles should possess the following features: (1) stability compatible with the preparation process; (2) easily dispersed in aqueous solution; and (3) having large surface area for the payload of nZVI particles. In addition, from an engineering perspective, the support material needs to be readily available, low-cost and free of secondary pollution after its use.

“Hangjin 2<sup>#</sup> clay” (HJ clay) is a kind of natural non-metallic clay mineral which was discovered in Inner Mongolia Hangjinqi China in the 1990s. The crystal structure of HJ clay generally consists of a central octahedral Al–O sheet sandwiched between two tetrahedral Si–O sheets. Compared with other clays, such as kaolinite, montmorillonite and bentonite, HJ clay has many good characteristics, such as larger surface area, bigger pore size and more total pore volume. These favorable properties of HJ clay inspired us to consider that it may be an excellent support material for nZVI, because its unique microstructure may increase the payload efficiency of nZVI and maximize the reactivity of nZVI. Furthermore, due to the isomorphous substitution and crystallographic defects in the crystal structure, HJ clay possesses structural negative charges that are compensated by exchangeable cations that reside at or near the clay surface (Gu et al., 2010). Single-atom nZVIs may form via the reduction of Fe<sup>3+</sup>, which binds as an exchangeable cation onto the surface of HJ clay.

In this study, a novel nZVI composite material, HJ clay-supported nZVI (HJ-nZVI), was synthesized and tested as a decontamination material for the first time. The optimal mass ratio of HJ/nZVI in the preparation was obtained in terms of the decolorization efficiency of Methyl Orange (MO). The performance of HJ-nZVI materials for MO decolorization was also compared with that obtained by physically mixing nZVI with HJ clay (HJ + nZVI). The morphology, properties and reactivity of the as-prepared HJ-nZVI were further analyzed to reveal the reason for the superior performance of HJ-nZVI. Finally, we investigated the variables influencing the MO decolorization efficiency (e.g., dosage, N<sub>2</sub>, initial pH, initial

concentration and temperature), and an “adsorption-enhanced reduction” mechanism for MO decolorization by HJ-nZVI was proposed. We hope that the study here not only provides a novel nZVI composite for decontamination, but also provides a method to ascertain the optimum load conditions for a support material to maximize the efficiency of nZVI.

## 1. Materials and methods

### 1.1. Materials and chemicals

The natural HJ clay used in this study was obtained from the region of Hangjinqi of the Ordos area in Inner Mongolia. The properties and composition of HJ clay are as follows (suspension with 1:4 soil/water ratio): pH 8.8–9.1; cation exchange capacity (CEC) 32.2 cmol/kg; SiO<sub>2</sub> 50.9 wt.%; Al<sub>2</sub>O<sub>3</sub> 15.2 wt.%; CaO 6.4 wt.%; Fe<sub>2</sub>O<sub>3</sub> 5.9 wt.%; MgO 3.6 wt.%; K<sub>2</sub>O 3.6 wt.%; Na<sub>2</sub>O 0.9 wt.%; TiO<sub>2</sub> 0.6 wt.%; and loss of ignition 12.9%. After drying overnight at 80°C, the HJ clay was ground and sieved through a 200 mesh screen prior to use.

Sodium borohydride (NaBH<sub>4</sub>), iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), MO, hydrochloric acid (HCl), sodium hydroxide (NaOH), absolute ethanol (99%), MO (99%), and sulfanilic acid (>99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). All the chemicals were analytical reagent grade and used without further purification. MO solution with various concentrations was prepared by diluting a stock solution to the target concentration using deionized water. Deionized water from a Millipore Milli-Q system (18 MΩ/cm) was used for all experiments.

### 1.2. Preparation of HJ clay-supported nZVI particles

HJ-nZVI samples with different mass ratios of HJ/nZVI were prepared under N<sub>2</sub> atmosphere using a conventional liquid-phase reduction of ferric iron (Shi et al., 2011; Zhang et al., 2010). Taking the HJ-nZVI sample with 1:1 HJ/nZVI as an example, first, 2.0 g HJ was placed into a three-necked open flask, and a ferric solution prepared by dissolving ferric chloride hexahydrate (9.66 g) in an ethanol/water solution (50 mL, 4:1 v/v) was added and stirred for 20 min. Subsequently, a freshly prepared solution (3.54 g of NaBH<sub>4</sub> in 100 mL) was added at the speed of 1–2 drops per second into the mixture, which was vigorously stirred under a N<sub>2</sub> atmosphere. Black particles were gradually produced as the color of mixture turned from red brown to light yellow and eventually to black. Afterwards, the mixture was further stirred for 1 hr. To remove the excess NaBH<sub>4</sub>, the formed suspension was filtered by vacuum filtration and the black nanoscale precipitates were washed three times with absolute ethanol. Finally, the precipitate was dried in a 50°C oven under vacuum overnight and kept in a nitrogen atmosphere prior to use. The obtained HJ-nZVI samples were denoted as HJ-nZVI1 (1:1 HJ/nZVI), HJ-nZVI5 (5:1 HJ/nZVI) and HJ-nZVI10 (10:1 HJ/nZVI) for the sake of discussion. The actual nZVI loading amounts onto the HJ clay were measured to be 80.9, 84.3 and 92.4 mol% of the added ferric salts, for HJ-nZVI1, HJ-nZVI5 and HJ-nZVI10, respectively. As such, the mass percents of nZVI in the composites were 40.5%, 13.9% and

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