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Incorporation of nanoscale zero-valent iron particles in monodisperse mesoporous silica nanospheres: Characterization, reactivity, transport in porous media

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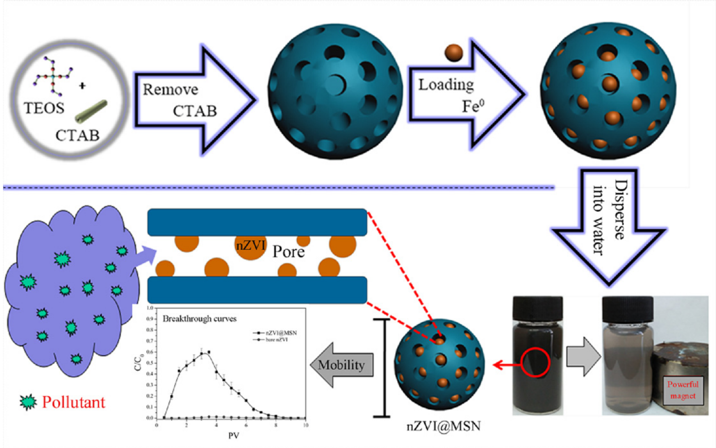
GRAPHICAL ABSTRACT

We prepared a monodisperse mesoporous silica nanospheres stabilized nZVI composites with new morphology and surface textural properties. Unlike previous reports, active nZVI particles were almost inside the channels of MSN instead of on the surface and this composites exhibit excellent reactivity and mobility compared with the bare nZVI.



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ABSTRACT

In this study, nanoscale zerovalent iron (nZVI) was incorporated inside the channels of monodisperse mesoporous silica nanospheres (MSN). The techniques of TEM, XRD, FTIR, N_2 adsorption-desorption and XPS were conducted to characterize the composition and structure of the composite materials. Results revealed that nZVI was well dispersed in the channels of MSN, and the synthesized Fe/Si composite materials (nZVI@MSN) remained monodisperse nanospheres with the size of 100 nm which was in the optimal size range for transport through porous media. The loading of Fe (wt %) in nZVI@MSN was 4.3% and the BET surface area of nZVI@MSN was 743.49 m^2/g. Batch experiment results revealed that the removal efficiency of nitrobenzene (NB) by nZVI@MSN was 42.9% higher than that of bare nZVI. Lower initial solution pH could favour the removal of NB. Most of the common ions including Na^+, K^+, Cl^-, NO_3^- and SO_4^{2-} presented no obvious effect on NB removal. While, Ca^{2+}, Mg^{2+} and HCO_3^- showed promoted inhibitory effect on NB degradation with the increased of ion concentration. After seven cycles of reduction, the removal efficiency of NB by nZVI@MSN was higher than 86%,

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indicating its high stability and durability. Transport experiments showed that nZVI@MSN performed better mobility in porous aquifer media than bare nZVI.

1. Introduction

In situ application of nanoscale zerovalent iron particles (nZVI) could help to remediate nitroaromatic compounds contamination in groundwater [1]. Nitroaromatic compounds, such as nitrobenzene (NB), which is a common toxic and stubborn compound in groundwater, could be simply reduced by nZVI. The reduction products of amido compounds are much less toxic and can be easily biodegraded [2]. As previous report shown, nZVI particles were produced with a primary size ranging from 50 to 100 nm [3]. The Tufenkji-Elimelech model assumes that the optimal size range for colloid particles to migrate through porous media is 0.1–1 μm [4,5], which indicates that these iron particles can be injected into the subsurface and used as reactive medium insitu reactive zone construction [6]. Because of its simple operation, cost-effective, and environmentally benign, in-situ reactive zone [7] in groundwater is an alternative way for reducing contaminants.

In fact, bare nZVI particles are hardly transported in the subsurface [8]. Due to the strong van der Waals and intrinsic magnetic interactions, bare nZVI tend to aggregate rapidly into micro to millimeter scale flocs [8–10]. Hydrogeochemistry of the aquifer (pH and ionic strength) can also destabilize nanoparticles, and result in aggregation [11]. These agglomerates of iron particles may plug the porous media and decrease the mobility of nZVI for transport through the subsurface, due to interception and gravitational sedimentation [12,13]. Furthermore, nZVI may be easily oxidized due to its high reactivity. The formation iron oxides layers covered on the surface can not only reduce its activity, but have a high affinity for adsorption onto surfaces of soil grains [14]. Therefore, one of the greatest challenges of nZVI technology is the successful delivery of iron nanoparticles to the contaminated zone in the subsurface.

To improve nZVI mobility through the subsurface, it is necessary to prevent particle aggregation and improve the antioxidation abilities of nZVI. In recent years, surface modification of nZVI with various materials have been investigated, such as surfactants [15,16], emulsified vegetable oil [17], starch [18] and carboxymethyl cellulose [9,19] as modifiers to enhance steric or electrostatic repulsions of particles to prevent their corrosion and aggregation.

The past decade, several investigations focused on various porous silica materials serving as the alternative carriers for the loading of nZVI have been carried out. Unlike the above listed modification agents, silica is the major natural component of the subsurface, nontoxic and high stability in aqueous media [20]. There is no need to aware of the potential harm that introducing other agents into subsurface could bring new pollution. Furthermore, due to the larger surface area of porous silica matrices, the activity of loading nZVI may additionally be promoted. For example, Zhang et al. [21] has found that, by stabilizing nZVI on SBA-15, the aggregation of nZVI was effectively inhibited and the degradation efficiency for aqueous NB was higher than that of bare nZVI. Sun et al. [22,23] developed a new “two solvents” reduction technique to incorporate nZVI particles inside the channels of SBA-15. The resulting nZVIs/SBA-15 composites could rapidly remove both Cr(VI) and NB from aqueous solution with higher degradation efficiency than bare nZVI. However, due to the larger particles size of platelet or fiber porous silica matrices, these kinds of supported materials are only suitable for treating contaminants in water, but hardly deliverable into contaminant plume.

To improve nZVI for effective in-situ remediation of groundwater contamination, in the present work, we report on the synthesis and incorporated nZVI particles into the channels of 100 nm monodisperse mesoporous silica nanospheres (MSN) using “two solvents” reduction method. Nanoscale MSN could be used as the vehicle for delivering nZVI in groundwater and targeting the contaminant. More interesting, unlike the previous reports [4,24], active nZVI particles were almost inside the channels of MSN instead of on the surface. The shell of MSN could protect the internal nZVI against deactivation, and weaken the affect of natural geochemical conditions. In addition, the negative surface potential of MSN shell also could enhance the mobility of iron particles, due to the electrostatic repulsion between MSN shell and quartz sand. The final materials were tested for their applicability in the remediation of aqueous NB and transport in porous media. The objectives of this work were: (a) to synthesize and characterize the nZVI@MSN composites, (b) to investigate the reactivity of nZVI@MSN for aqueous NB, (c) to clarify the transport behaviors of nZVI@MSN in porous aquifer media.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS) was supported by Macklin (Shanghai, China), Cetyltrimethylammonium bromide (CTAB), ammonium hydroxide (25–28 wt% NH_3 in water), nitrobenzene (NB), acetonitrile and methanol purchased from Beijing Chemical Regent Co., Ltd., All other chemicals obtained from Tianjin Guangfu Fine Chemical Research Institute. All the chemicals were used without further purification. Deionized water with a resistivity of 18 MΩ cm was used in all experiments.

2.2. Synthesis of MSN

The synthesis of MSN was achieved as described by Teng et al. [25]. Typically, CTAB (0.64 g) was dissolved in a mixed solution of ethanol (96 mL), water (228 mL), and concentrated ammonia aqueous solution (4.0 mL, 25 wt%). After this solution was stirred at room temperature for 15 min, 4 mL TEOS was rapidly added under vigorous stirring. After 3 h of stirring, the product was separated off by centrifuge and dried at 85 °C in vacuum oven. The final white solids were washed at 65 °C with acidic (HCl) ethanol (approximately 0.12 w/w) for three times to ensure the removal of structure directing agent and then recovered by centrifugation.

2.3. Preparation of nZVI@MSN and bare nZVI

NZVI@MSN was synthesized according to the reported method [22] and the formation process was shown in Fig. 1. Typically, the

Fig. 1. The formation process of nZVI@MSN.