



Rapid reductive degradation of aqueous p-nitrophenol using nanoscale zero-valent iron particles immobilized on mesoporous silica with enhanced antioxidation effect

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ARTICLE INFO

Article history:

Received 21 October 2014

Received in revised form 14 January 2015

Accepted 3 February 2015

Available online 10 February 2015

Keywords:

Nanoscale zero-valent iron
Mesoporous silica
p-Nitrophenol
Reduction

ABSTRACT

In this study, nanoscale zero-valent iron particles immobilized on mesoporous silica (nZVI/SBA-15) were successfully prepared for effective degradation of p-nitrophenol (PNP). The nZVI/SBA-15 composites were characterized by N₂ adsorption/desorption, transmission electron microscopy (TEM), UV–vis spectrum and X-ray photoelectron spectroscopy (XPS). Results showed that abundant ultrasmall nanoscale zero-valent iron particles were formed and well dispersed on mesoporous silica (SBA-15). Batch experiments revealed that PNP removal declined from 96.70% to 16.14% as solution pH increased from 3.0 to 9.0. Besides, degradation equilibrium was reached within 5 min, which was independent of initial PNP concentration. Furthermore, only a little PNP elimination on SBA-15 indicated that nZVI immobilized on mesoporous silica was mainly responsible for the target contaminant removal. The UV–vis spectrum and XPS measurement confirmed that the PNP removal was a reductive degradation process, which was further proved by the detected intermediates using gas chromatography–mass spectrometry (GC/MS). The excellent antioxidation ability had been discovered with more than 80% of PNP being removed by nZVI/SBA-15 treated with 30 days' exposure to air. These results demonstrated the feasible and potential application of nZVI/SBA-15 composites in organic wastewater treatment.

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1. Introduction

The concern for public health and environmental safety has been increasing over the last few decades. Chemical pollution of surface water poses a threat on the aquatic environment with hazardous effects [1]. As we know, nitroaromatic compounds (NACs) have been widely applied in industry and agriculture, which are used as pesticides, polymers, pharmaceuticals, and intermediates in synthesis of dyes [2–5]. As a species of NACs, p-nitrophenol (PNP) is a kind of dangerous substance with cumulative effects and can invade the body through the respiratory system, digestive system and skin [6]. Besides, PNP can damage DNA or inhibit the synthesis of DNA, which would cause major adverse effects on the blood, liver and central nervous system. Thus, it is necessary to develop an

efficient treatment process to decompose this refractory and toxic pollutant. Up to now, there are many techniques for the degradation of p-nitrophenol in wastewater, such as advance oxidation process (AOPs) [7], extraction [8], adsorption [9] and reduction [10,11]. As a reductive agent, nanoscale zero-valent iron (nZVI) has recently been used to treat the toxic and refractory pollutants such as metals [12], organochlorine compounds [13] and nitroaromatic compounds [14]. Due to its high surface area, abundant reactive surface sites, high reaction rate and injectability into aquifers [15], nZVI has gained extensive attention. However, the aggregation of nZVI limits its dispersibility and mobility in effluents, and the oxidation of nZVI can significantly decrease its reactivity [16,17]. Therefore, it is necessary to solve these problems for application. Recently, immobilization of nZVI on some porous materials, like multiwalled carbon nanotubes [18], zeolite [19], activated carbon [20], bentonite [21], mesoporous carbon [22] and SBA-15 [23,24], is considered as an alternative solution to solve these troubles.

In recent years, an impregnation technique named “two solvents” method has aroused researchers' interest [23–25]. Sun et al. [24] used a hydrophobic alkane solvent (cyclohexane) to prewet the

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surfaces of SBA-15 before addition of iron precursor aqueous solutions, and the synthesized nZVI dispersed well on SBA-15. Thus, this impregnation method has been confirmed to be efficient in hosting nZVI on porous materials.

In this paper, we successfully prepared nZVI/SBA-15 composites utilizing the “two solvents” technique with n-pentane, instead of cyclohexane, as hydrophobic alkane solvent. Owing to the lower boiling temperature of n-pentane, the preparation procedure of nZVI/SBA-15 obviously was cut down, which would simplify these processes. Pentane had lower interfacial tension with water, which could possibly result in the easier formation of smaller droplets of aqueous solution [26,27]. Although with lower interfacial tension, water droplets in oil would have more chances to agglomerate, they might remain dispersed to form smaller nanoparticles in the silica channels with our “two solvents” method. The prepared nZVI/SBA-15 was characterized by transmission electron microscopy (TEM) and nitrogen adsorption–desorption isotherms. For the first time, the resultant solid was applied to remove organic matters, such as PNP, from aqueous solutions. The effects of relevant parameters such as solution pH, initial concentration of PNP and contact time on the degradation efficiency of PNP by nZVI/SBA-15 were investigated. UV–vis spectrum, X-ray photoelectron spectroscopy (XPS) and gas chromatography–mass spectrometry (GC/MS) analysis of composites were applied to further analyze the mechanism of PNP degradation. In addition, the leaching of iron ions from nZVI/SBA-15 into the solution was also investigated. Finally, we compared the removal efficiency of PNP by bare nanoscale zero-valent iron particles and the composites after exposing to air to examine their antioxidation abilities. It is worth mentioning that the antioxidation activity of nZVI/SBA-15 has not been studied before.

2. Materials and experimental methods

2.1. Materials and chemicals

Pluronic copolymer P123 (EO20PO70EO20, EO = ethylene oxide, PO = propylene oxide) was purchased from Sigma–Aldrich (USA), and all reagents used in the experiment were of analytical reagent grade except that dichloromethane was of chromatographic reagent grade. What's more, all solutions were prepared with high-purity water (18.25 M Ω /cm) from a Milli-Q water purification system.

2.2. Preparation of nZVI/SBA-15 and nZVI

SBA-15 was synthesized as described by Zhao et al. [28]. The nZVI/SBA-15 composites were similarly prepared by a “two solvents” method at room temperature reported in Refs. [24,26]. Briefly, with the magnetic stirring, 1.0 g SBA-15 was mixed with 30 mL n-pentane followed by adding dropwise a small volume of ferrous aqueous solution which contained 1.112 g iron sulfate heptahydrate. The mixture evaporated at 60 °C for one night. Then, under the N₂ protection condition, Fe (II) or Fe (III) impregnated SBA-15 were reduced to metallic Fe⁰ in the 30 mL n-pentane solvent by adding 8 mL NaBH₄ solution (2 M) with stirring. The obtained composites were separated from the solution by a magnet, washed with methanol three times, and then dried in vacuum at 50 °C for one day.

Comparatively, nZVI was also prepared. 4.0 g FeSO₄·7H₂O dissolved in 200 mL methanol and deoxygenated water mixture (30% v/v). Soon afterwards, under the N₂ protection condition, 10 mL NaBH₄ solution (2.1 M) was added dropwise in aforementioned solution with mechanical stirring, which was kept reacting for 30 min. After filtration and then washing the separated black solid with ethanol, the nZVI was dried in vacuum at 50 °C for one day.

2.3. Characterizations

The morphological images were obtained on a FEI Tecnai G2 20 transmission electron microscope (TEM) operated at 100 kV. Nitrogen adsorption–desorption isotherms were measured on Micromeritics 2020 analyzer at 77.3 K. BET analyses were applied to determine the surface area. BJH analyses were used to derive pore size distribution and calculate the total pore volume. An X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific) was utilized to measure the surface composition and the elements' valence of nZVI/SBA-15 before and after reaction with a resolution of 0.5 eV.

2.4. Batch experiments

All batch experiments were performed in glass conical flasks undergoing shaking at 150 rpm at 25 °C, and the solution pH was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl. 0.05 g nZVI/SBA-15 or SBA-15 was added into 10 mL PNP solution for each treatment unless otherwise stated. Then, aliquots of the aqueous solutions were withdrawn by a syringe at intervals, and finally filtered by a 0.2 μ m membranes filter to separate the solid from the liquid. The antioxidation ability of nZVI/SBA-15 and nZVI were investigated by exposure to the air for 0 day, 3 days, 7 days, 14 days, 21 days and 30 days, respectively. All the experiments were carried out in duplicate, and the averages were calculated.

2.5. Analytical methods

The residual concentration of the pollutant was determined by UV–vis spectroscopy (SHIMADZU 2550) in acidic form at maximum absorbing wavelength ($\lambda = 315$ nm) [29]. The concentration of PNP was measured at pH in the range from 1 to 3 to ensure that only one form of the compound existed in the solution. What's more, the UV–vis absorption spectrum of the treated pollutant were carried out in quartz cuvettes, and the UV–vis spectrum were recorded from 190 to 800 nm using HCl solutions with the same concentration.

The concentration of total leaching iron ions of the composites in the solution was determined by a Perkin–Elmer Analyst 700 atomic absorption spectrophotometer (AAS, Perkin–Elmer, USA).

In addition, a gas chromatography–mass spectrometry (GC/MS) analytical method was set up to qualitatively determine the degradation intermediate products of PNP [30]. Before GC/MS determination, 50 mL sample was extracted using 10 mL dichloromethane for three times under acidic (pH 2.0), neutral (pH 7.0), alkaline (pH 12.0) conditions, respectively. The three extracted layers were mixed up, and then dehydrated with anhydrous sodium sulfate. Under nitrogen atmosphere, the mixture was dried at the room temperature. Subsequently, the residue was dissolved in 1.0 mL CH₂Cl₂, and 1 μ L of the liquid was injected into a QP2010-PLUS GC/MS system (SHIMADZU, Japan) equipped with a HP-5MS capillary column. The GC column was operated in a temperature program mode beginning at 40 °C for 3 min, rising by 10 °C/min to 280 °C, and holding at 280 °C for 5 min. The solvent delay was 6 min, and the total run time was 32 min. The mass range scanned was 20–500 *m/z*.

3. Results and discussion

3.1. Characterization of materials

Fig. 1 showed the transmission electron microscopy (TEM) images of SBA-15, nZVI/SBA-15 and nZVI. The TEM images in Fig. 1a–d indicated that both the two mesoporous materials had

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