



In situ sequentially generation of acid and ferrous ions for environmental remediation



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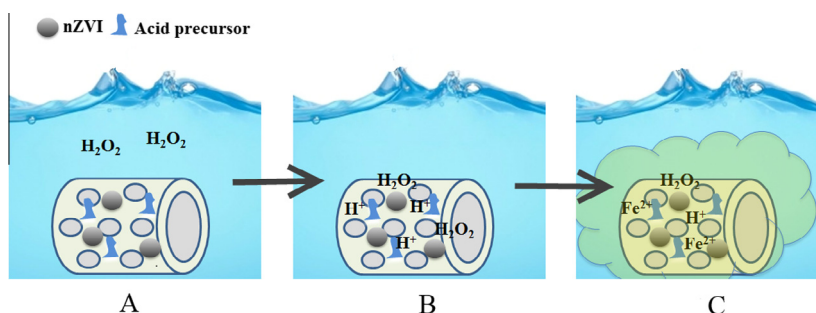
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HIGHLIGHTS

- Novel composite material that can sequentially generate acid and ferrous ions *in situ*.
- Potential solution to conventional Fenton reaction's drawbacks.
- Feasible way coupling nZVI's reductive and Fenton-like reactions for contaminants.
- New materials show very high efficiency for bisphenol A removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel heterogeneous Fenton composite materials were developed by grafting acid precursors and nano zero-valent iron particles on an acid leached diatomite, which can sequentially generate acid and ferrous ions *in situ*. The results show that the composite materials can potentially solve two of the biggest obstacles, which prevent the conventional Fenton reaction from being widely and practically adopted, namely: the continuous feed of ferrous ions and the maintenance of the optimum acidic pH condition during the reaction. In this study, samples were characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, Thermogravimetric analysis and micro organic analysis. The novel materials' degradation capacities for bisphenol A (BPA) were evaluated and optimized. This material can be easily applied to treat wastewater via Fenton-like reaction without changing pH or adding ferrous ions. The relationships between BPA removal efficiency, the amount of grafted organosilane acid precursor and doped nZVI particles on the composite materials were investigated. It is evident from the results that the novel composite materials afford highly effective removal of BPA from water at 250 mg/g. The work thus demonstrates that the novel materials could potentially be utilized for efficient remediation of recalcitrant organic compounds from the environment.

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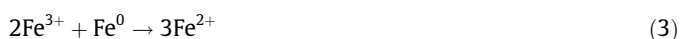
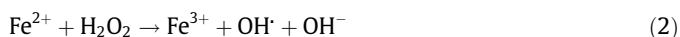
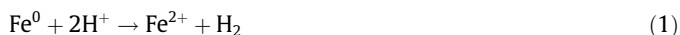
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1. Introduction

Zero-valent iron (denoted as ZVI) is effective in removing water contaminants, including chlorinated compounds, microorganisms,

disinfection by-products (DBPs) and heavy metals [1]. Nano-sized ZVI (denoted as nZVI) shows much higher reactivity and greater efficiency due to its small particle size and high surface area [2–4]. Furthermore, supporting highly dispersive nano sized zero-valent metal on an appropriate support can significantly increase the reactivity of iron particles [5–8]. In our recent work, nZVI was successfully supported on diatomite and a number of clay minerals, and the highly dispersed nano particles on the supports' surface showed significantly improved reactivity towards water contaminants [5,6,9,10]. However, nZVI alone could only remove certain contaminants via reduction and adsorption; many refractory contaminants cannot be effectively treated. For instance, nZVI alone is not effective for the removal of bisphenol A (BPA) via reduction. Introducing of another remediation material will make the process complicated. In order to achieve a broad adoption of nZVI material for water treatment, it is worth investigating the full potential of nZVI by coupling its reductive property with advanced oxidation process (AOP). AOP is also known as Fenton reaction, and has been explored and found to be one of the most effective strategies in removing contaminants. This type of process involves a radical reaction and can theoretically account for the degradation of virtually all refractory organic pollutants [11,12]. In the conventional Fenton reaction, added ferrous ions react with H_2O_2 to form ferric ions and hydroxyl radicals, which are highly efficient in degrading contaminants. However, this reaction needs a continuous addition of ferrous ions and after the reaction, there is a large amount of iron precipitate sludge (ferric hydroxide), which is a huge issue to consider in its practical applications [13]. In addition to the waste product, another inherent deficiency, which prevents the Fenton reaction from being widely adopted, is that it requires the pH of the entire contaminated water to be adjusted and maintained at a low optimum value of 2–3 [12,13]. At higher pH values, iron ions precipitate and the decomposition of H_2O_2 is accelerated without radical generation and this significantly reduces the efficiency of the system. Moreover, the required optimum lower pH condition is difficult to maintain and excessive usage of the chemicals required for this purpose can adversely affect aquatic life and microorganisms in groundwater systems [14].

A practical solution, which could replace continuous addition of ferrous ions, is to generate ferrous ions *in situ* from ZVI [10,11]. In the presence of ZVI, oxidants such as O_2 , H_2O_2 and $S_2O_8^{2-}$ can form radicals, which can theoretically unselectively oxidize virtually all organic compounds to CO_2 , H_2O and salts [15–18]. At low pH condition, ferrous ions are generated from ZVI (Eq. (1)); then, the ferrous ions react with H_2O_2 to give ferric ions and hydroxyl radicals (Eq. (2)). Ferrous ions are regenerated from ferric ions at the surface of Fe^0 (Eq. (3)). Given that the weight percentage of the dispersed nano metal particles only comprises less than 10% in the composite material, it is highly feasible that this novel material can significantly minimize the production of sludge after the reaction.



However, the initial pH of the working solution still needs to be adjusted by adding acid, and it is more difficult to maintain the optimum narrow pH range during the reaction process. This inherent drawback may be overcome by introducing acid functionalities onto the supporting materials using acid precursors. Organosilanes with acid precursor functional groups, such as thiol groups, can be grafted onto the surface of certain supporting materials containing silanol groups (Si–OH) [19]. It was reported that thiol groups (acid

precursor functional groups) can react with H_2O_2 to produce sulfonic groups (acid groups) [20–23]. As H_2O_2 is also a key reactant in Fenton reaction, this will facilitate and simplify the procedure. Organosilanes can be firmly attached to the surface of the diatomite frustules by covalent bonding (–Si–O–Si–) [19] dramatically changing the surface properties of diatomite.

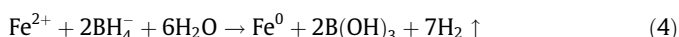
It is envisaged that a novel material, which can sequentially generate acid and ferrous ions *in situ* could solve the inherent disadvantages of conventional Fenton systems. To the best of our knowledge, this is the first time for researchers to develop and apply these novel nano composite materials for contaminated water remediation. Additionally, the efficiency and mechanism of this new reaction system have never been evaluated. In this study, the feasibility of sequentially generation of acid and ferrous ions *in situ* is the research focus. Novel composite materials were synthesized using two different organosilane grafting methods. These composite materials were tested for bisphenol A (BPA) removal from water.

2. Materials and methods

2.1. Sample preparation

Diatomite was provided by Mount Sylvania Diatomite Pty Ltd in Queensland, Australia and denoted as Da. 3-Mercaptopropyl trimethoxysilane (95%) (denoted as MPTS) and BPA ($\geq 99\%$) were purchased from Sigma–Aldrich. $NaBH_4$ ($\geq 98\%$) was purchased from Merck Australia Pty Ltd. H_2O_2 (30%) and $FeCl_2 \cdot 4H_2O$ were supplied by Chem-Supply Pty. Ltd., Australia. All chemicals are analytical grade and used without further purification. The Da was acid-leached by adding 40 g of sample into 1 L of 5 M HCl solution, then the solution mixture was stirred at 80 °C for 24 h using a hot plate with magnetic stirrer. Subsequently, the solid product was filtered and washed with deionized water and the resultant acid-leached product is denoted as Da-H.

Synthesis of nZVI/Da-H composite was undertaken by a similar procedure described previously [2,5]. In this study, 20 g of $FeCl_2 \cdot 4H_2O$ was dissolved in a mixture of 95% ethanol (300 ml) with deionized water (100 ml) and stirred for 30 min. Then 24 g of Da-H was added to this solution under stirring overnight. The resultant suspension was centrifuged at 3000 rpm for 15 min in order to remove the excess Fe^{2+} . A 0.7 M $NaBH_4$ solution was prepared by dissolving 28 g of $NaBH_4$ in 1080 ml of deoxygenated de-ionized water. (The deoxygenated de-ionized water was prepared by purging deionized water with Argon gas for 2 h.) This $NaBH_4$ solution was added dropwise to the centrifuged reddish brown solid obtained above in a fumehood under constant stirring. The reddish brown sediment was transferred to a black suspension. The resulting reaction can be expressed as:



The solid was then separated by centrifugation and washed with about 2.5 L of 95% ethanol and the sediment was dried in an oven at 50 °C overnight. The obtained solid sample is denoted as nZVI-Da-H.

Two methods were used to graft MPTS on nZVI-Da-H. Firstly, 30 mL of MPTS was directly added into 10 g of nZVI-Da-H under stirring for 24 h. To the best of our knowledge, the grafting of an organosilane on a support without a solvent was seldom reported before. The solid sample was recovered by filtration and washed with 1.5 L deoxygenated de-ionized water. Secondly, 10 g of nZVI-Da-H was suspended in 100 ml of toluene under stirring, then 30 mL of MPTS was added and the mixture was stirred at 80 °C for 24 h. The solid sample was recovered by filtration and washed several times using toluene, ethanol and 1.5 L deoxygenated de-ionized water. Finally, the two samples were dried in an oven

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