



# Bisphenol A degradation enhanced by air bubbles via advanced oxidation using in situ generated ferrous ions from nano zero-valent iron/palygorskite composite materials

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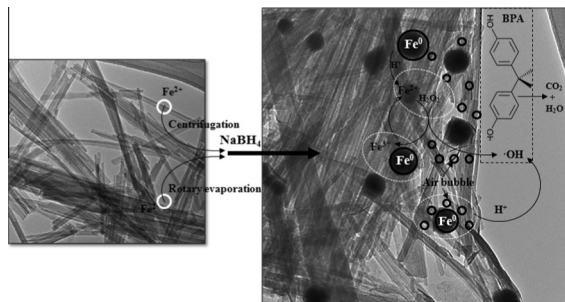
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## HIGHLIGHTS

- nZVI/palygorskite composite materials are synthesized via two routes.
- The obtained composites are characterized by XRD, SEM–EDS, TEM and XPS.
- The removal efficiencies for bisphenol A in water are studied.
- The removal efficiencies can be increased significantly with the aid of air bubbles.
- The prepared composite shows potential prospects in environmental remediation.

## GRAPHICAL ABSTRACT

Nano zero-valent iron/palygorskite composite materials were synthesized and used for bisphenol A degradation via radical reaction. Compared with pristine nano zero-valent iron and commercial iron powder, the composite materials showed superior efficiency on the contaminant removal attributed to the highly dispersed spherical nano iron particles on the surface. It was observed that the air bubbles can increase the removal percentage significantly.



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## ABSTRACT

Novel nano zero-valent iron/palygorskite composite materials prepared by evaporative and centrifuge methods are tested for the degradation of bisphenol A in an aqueous medium. A systematic study is presented which showed that nano zero-valent iron material has little effect on bisphenol A degradation. When hydrogen peroxide was added to initiate the reaction, some percentage of bisphenol A removal (~20%) was achieved; however, with the aid of air bubbles, the percentage removal can be significantly increased to ~99%. Compared with pristine nano zero-valent iron and commercial iron powder, nano zero-valent iron/palygorskite composite materials have much higher reactivity towards bisphenol A and these materials are superior as they have little impact on the solution pH. However, for pristine nano zero-valent iron, it is difficult to maintain the reaction system at a favourable low pH which is a key factor in maintaining high bisphenol A removal. All materials were characterized by X-ray diffraction, scanning electron microscopy, elemental analysis, transmission electron microscopy and X-ray photoelectron spectroscopy. The optimum conditions were obtained based on a series of batch experiments. This study has extended the application of nano zero-valent iron/palygorskite composites as effective materials for the removal of phenolic compounds from the environment.

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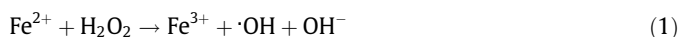
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## 1. Introduction

Bisphenol A [2,2-bis-(4-hydroxy phenyl) propane]/BPA is one of the world's most widely-manufactured chemicals, and it is prevalently used in plastic products [1,2]. However, it was found in recent years that BPA may exhibit hormone-like properties and act as an endocrine disruptor [3,4]. Some states and countries have banned the use of BPA in baby bottles [5]. However it is still used in many other products and its widespread use has resulted in its ubiquitous existence in the environment. BPA can be detected in groundwater, especially in those areas that are close to old unlined landfills [6]. Such groundwater can in turn feed into creeks or drinking water supply wells where BPA can create a significant chemical hazard. Due to its toxicity, BPA and its biodegradation products have become a major source of concern to the environment [6].

At present, there are only a few methods developed for the removal of BPA from aqueous solutions. For example, adsorption, biochemical oxidation and wet chemical oxidation and others [7–12], but all of these methods have suffered from some disadvantages such as long reaction times, high cost and low efficiency. In addition, many of the processes use high temperature/pressure or precious metal catalysts which are too expensive for practical application and widespread adoption.

Among these methods, advanced oxidation processes have been explored and found to be a promising mechanism. In particular, Fenton reaction technology follows a radical reaction and can theoretically account for the degradation of most refractory organic contaminants. It also benefits from the fact that no UV or visible light is needed to initiate the reaction; this is especially important for groundwater systems. According to Eq. (1), the ferrous ion reacts with hydrogen peroxide to form ferric ion and hydroxyl radicals, but this traditional Fenton reaction needs a continuous feed of iron salts, and after the reaction, there is a large amount of iron precipitate sludge which is a big issue in practical applications [13]. Therefore, it could be more practical if ferrous ions were generated on site [14–16]. In recent years, zero-valent iron (denoted as ZVI) has been successfully used as permeable reactive barrier for groundwater contaminants, and have been found to be most effective on chlorinated compounds [17–19]. This type of remediation exploits the reductive properties of zero-valent metal under fully anoxic conditions to improve the efficiency of reaction. Radical reaction is another inherent mechanism for contaminant degradation. With the presence of zero-valent metals, oxidants such as  $O_2$ ,  $H_2O_2$  and  $S_2O_8^{2-}$  can form radicals, which can theoretically unselectively oxidise almost all organic compounds to  $CO_2$ ,  $H_2O$  and salts [20–22]. ZVI prepared on the nano size, shows much higher reactivity and greater efficiency attributed to its small particle size and high surface area [23–25]. However, ZVI type material is not effective on phenolic compounds such as BPA.



In the literature, there are some studies which investigated the ZVI usage via Fenton reactions as in situ ferrous ions can be generated under acidic conditions which offers an effective means of replacing continuously added ferrous ions [26]. As shown in Eqs. (2) and (3), under acidic conditions, the ferrous ions can be generated in situ from ZVI, ferric ions can be reduced to ferrous ions at the surface of  $Fe^0$ , and  $\cdot OH$  radical can be generated from Eq. (1).

To the best of our knowledge, there are only a few reports on BPA degradation using commercial ZVI [27], and no research using

nano ZVI (nZVI) especially nZVI/palygorskite composites. This work aims to assess the feasibility of nZVI/ $H_2O_2$  technology for the degradation of BPA compound. The influence of air bubbles was deliberately investigated and it was found that with the aid of air bubbles, the removal percentage can be significantly increased.

## 2. Materials and methods

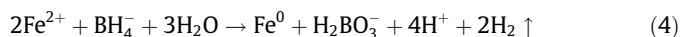
### 2.1. Chemical

$NaBH_4 \geq 98\%$  was purchased from Merck and bisphenol A  $\geq 99\%$  (Fig. 1) was purchased from Aldrich.  $H_2O_2$  (30%),  $FeCl_2 \cdot 4H_2O$  and fine iron powder  $\geq 99\%$  were supplied by Chem-Supply Pty. Ltd., Australia. All chemicals were analytical grades and used without further purification. The palygorskite used in this study was supplied by the Clay Minerals Society as source clay palygorskite PF1-1 (denoted as PF). Detailed information of this clay was reported previously [24].

### 2.2. Preparation of nZVI and nZVI/palygorskites composites

10 g of PF was processed by acid-leaching in 200 mL of 1 M or 2 M HCl solution under stirring at room temperature for 24 h. Different acid concentrations were used to study the acid leaching effects on final products' properties. The acid-leached clay was recovered by centrifugation and washed several times with deionized water to remove excess acid then dried in a 50 °C oven (dried samples were denoted as 1HPF and 2HPF, respectively).

The nZVI/palygorskite composites were prepared by the following procedures which are similar to those used in our recently published work [28]: 0.5 g of  $FeCl_2 \cdot 4H_2O$  was dissolved in a mixture of 150 mL 95% ethanol and 50 mL deoxygenated de-ionised water under stirring for about 30 min. The deoxygenated de-ionised water was prepared by purging with  $N_2$  gas for 2 h before use. Then, 5 g of 1HPF or PF was added to this solution under stirring over night, afterwards the following two different preparation procedures were applied: (A) the suspension above was concentrated through rotary evaporation at 40 °C at 40 mbar. Then, 1.5 g of  $NaBH_4$  was dissolved in 100 mL of deoxygenated de-ionised  $H_2O$ , the solution was added drop by drop to the slurry obtained above in a fume hood under stirring for 2 h. The resulting reaction can be expressed in Eq. (4).



The final solid was centrifuged, washed three times with 200 mL of 95% ethanol and dried in a 50 °C oven and stored in a desiccator; (B) similarly, the suspension was centrifuged at 3000 rpm and room temperature for 15 min in order to wipe off the excessive  $Fe^{2+}$ .

Then, 100 mL of 1 M  $NaBH_4$  was added drop by drop to the residue, sample prepared was denoted as 1HPF-Z-C.

The pristine nZVI was prepared by a similar procedure as described above, except that no PF or 1HPF was added: 3 g of  $FeCl_2 \cdot 4H_2O$  was dissolved in a mixture of 150 mL ethanol and 50 mL deoxygenated de-ionised water; then, 100 mL of 1 M  $NaBH_4$  solution was added drop by drop to the above ferrous solution in a

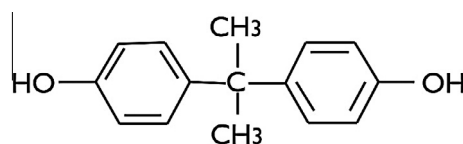


Fig. 1. Molecular structure of bisphenol A.

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