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Biosynthesized iron-based nanoparticles used as a heterogeneous catalyst for the removal of 2,4-dichlorophenol

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ABSTRACT

Iron-based nanoparticles (Fe NPs) synthesized by *Euphorbia cochinchensis leaves* extracts and used for degradation of 2,4-dichlorophenol (2,4-DCP) were investigated. The TEM image indicated Fe NPs were spherical and uniformly dispersed particles with a diameter of about 100 nm. The XPS results indicated Fe NPs consisted mainly of Fe(III), Fe(II), iron oxide and hydroxide. Results confirmed that the efficiency to remove 2,4-DCP was 20.6% by adsorption. The efficiency increased to 51.9% when Fe NPs were used as Fenton-like catalyst in the presence of H_2O_2. However, the removal efficiency of 2,4-DCP reached up to 64.0% when adsorption and Fenton-like oxidation were integrated. The kinetic data fitted well with the pseudo-second-order kinetic model of adsorption, while the Fenton-like process fitted the pseudo-first-order oxidation model. Furthermore, the degraded products were detected by gas chromatography mass spectrometry (GC–MS) to verify the mechanisms of degradation. It is concluded that removal of 2,4-DCP via adsorption/Fenton-like oxidation.

1. Introduction

Chlorophenols (CPs) are commonly used in pesticides, fungicides, pharmaceuticals, paper industries and as intermediates of dyes [1]. Although such applications have been strictly regulated due to mutagenic activity, potential carcinogenic dangers and resistance to biodegradation, the presence of chlorophenols continues to threaten the environment and human health even at trace level. For this reason, CPs have been listed as a priority pollutant by the US EPA and EU [2]. For the many existing chlorinated phenol contaminates, the method of removing highly toxic and long-lasting 2,4-DCP is causing growing environmental and ecological concerns worldwide [3].

The conventional processes to remove 2,4-DCP from wastewater involve biological aerobic and/or anaerobic treatment, photodegradation, oxidation and reduction [4–6]. However, these approaches are generally limited to degrading such recalcitrant organic contaminants completely. For the biodegradation of 2,4-DCP, the inherent toxicity of the intermediates are produced and reduce the ability of mineralized contaminants [2]. The biodegradation requires more energy and nutrients. Furthermore, the degraded products such as for instance 2-chlorophenol, 4-chlorophenol and phenol are also toxicity. Photocatalytic oxidation of 2,4-DCP using a photo-assisted Fenton reaction has received much attention [7]. However, the limitations of photodegradation include high cost and high energy consumption. Adsorption is a common method, but adsorption is also limited by the adsorption capacity of materials. Consequently, it is essential to develop new technology that combines adsorption and Fenton oxidation.

Fenton oxidation has recently been considered to be a potential technology for the removal of 2,4-DCP. The conventional Fenton oxidation process employs Fe^{2+}/H_2O_2 system and produces hydroxyl radicals with strong oxidative ability. Although the removal of chlorophenols with Fenton'reagent is promising, the homogeneous catalyst is usually added as ferrous salt which is rapidly consumed and the effective pH of Fenton oxidation is restricted [8]. In the contrast, the Fenton-like oxidation (H_2O_2/Fe^{2+} and Fe^{3+}) process overcomes these problems, giving rise to hydroxyl radicals and it is regarded as a more potentially effective method [9]. In addition, the removal of 2,4-DCP have integrated both adsorption and dechlorination by nZVI [10–12]. To date, the removal of 2,4-DCP using pre-adsorption/Fenton-like oxidation has been rarely reported.

Iron-based nanoparticles (Fe NPs) have a large specific surface with unique characteristics, and have been applied to remove heavy metals [13], dyes [14], arsenate and phosphate from

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wastewater [15]. The existing synthetic methods are usually derived from chemistry or physics. These methods play an essential role in the development of synthetic Fe NPs, but with the requirement of low energy consumption, low cost and being environmentally friendly, it is essential to explore an appropriate synthetic method for nanoscale iron oxide materials. Recently, Fe NPs were synthesized by leaf extract, which has emerged as an interesting technology. Fe NPs were synthesized by *green tea* extract [16–18], and palladium and iron nanoparticles were synthesized by *terminalia* extract [19]. *Euphorbia cochinchensis* can well adapt to the various environment, which are abundantly available in Fujian, China. *Euphorbia cochinchensis* extract contains various organic substances such as polyphenols, flavonoids, enzymes and proteins, these organic components reduce iron salt to Fe NPs, and cap in the surface of the Fe NPs to prevent their aggregating and improving the stability of Fe NPs.

The main objective of this study is to demonstrate an integrated technology based on the per-adsorption/Fenton-like oxidation sequential process to remove 2,4-DCP by Fe NPs as both adsorbent and catalyst. The adsorption of 2,4-DCP was conducted by biosynthesized Fe NPs, namely Fe(III) or Fe(II) iron-based oxides and hydroxides, making use of the adsorption of iron oxide and capping organic matters, then add hydrogen peroxide to constitute Fenton-like oxidation to remove 2,4-DCP.

2. Material and method

2.1. Material

Euphorbia cochinchensis leaves were collected from Fujian Normal University, Fuzhou. Ferrous sulfate and anhydrous sodium sulfate were supplied by Tianjin Fuchen Chemicals Reagent Factory. Ethyl acetate, absolute ethyl alcohol and hydrogen peroxide were purchased from Guanghua Science and Technology Co., Ltd, Guangdong, China. Nitrogen was obtained from a semi-conductor factory located in Fujian, China. All the reagent solutions were prepared from chemical reagents of analytical grade. Distilled water was used in all experiments.

2.2. Biosynthesized iron-based nanoparticles

Firstly, the *euphorbia cochinchensis* leaves were dried in an oven at 60 °C. The plant extract was prepared by boiling 60 g dry *euphorbia cochinchensis* leaves in 1 L distilled water at 80 °C for 1 h. Following this the plant extracts were vacuum-filtered and stored at 4 °C for further use. Fe NPs were biosynthesized by adding the corresponding extract to 0.10 mol/L $FeSO_4$ with a volume ratio of 2:1 at room temperature and continuously stirred for 30 min. In addition, $FeSO_4$ was added to the extract drop by drop. The immediate appearance of black particles confirmed the reduction of Fe^{2+}. Then the Fe NPs were quickly rinsed with ethanol three times and collected by vacuum filtration. Fe NPs were dried under vacuum at 60 °C for 10 h. Biosynthesized iron-based nanoparticles were put into an oven to dry.

2.3. Batch experiments

To compare the removal of 2,4-DCP utilizing various methods such as adsorption, and simultaneous and sequential Fe NPs/H_2O_2 processes, batch experiments were conducted using Fe NPs. Fe NPs were added to 50 mL centrifuge glass tubes containing 20 mL aqueous solution of 50 mg/L 2,4-DCP and the initial pH of all reaction is 6.8 so that iron dosing quantity was 1 g/L in the reaction solution. In the complete adsorption process, these glass tubes were placed on a rotary shaker at 30 ± 1 °C and 250 r/min for time intervals of 0, 2, 10, 20, 40, 50, 60, 80, 100, 120 min. A similar method was employed for the simultaneous and sequential Fe NPs/H_2O_2 processes, the distinction is required for H_2O_2. Fe NPs and 10 mM H_2O_2 were added at the beginning of the simultaneous Fe NPs/H_2O_2 processes. The sequential process included that after adsorption reaching equilibrium at 50 min, adding 10 mL H_2O_2 and then the initial time for the subsequent Fenton-like oxidation at 50 min approximately. All the solutions after reaction were filtered through 0.45 μm membranes, the residual concentration of 2,4-DCP was determined by measuring absorbance at 286 nm using the UV-1929 spectrophotometer.

2.4. Characterization

Morphological characterization of Fe NPs was analyzed using Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS) served to evaluate the formation and elements valence of Fe to a depth of <10 nm using VG ESVALAB 250 spectrometer. Binding energy was calibrated using C1s hydrocarbon peak at 284.8 eV, and the analysis results were obtained in conjunction with TEM. The Fe NPs samples degassed at 110 °C prior to Brunauer–Emmett–Teller (BET) measurements. The specific surface area was determined by a multipoint BET method using the adsorption data in the relative pressure p/p_0 range of 0.05–0.3.

2,4-DCP and its degraded products were analyzed on a GC–MS analyzer (Agilent 6890-5975, USA) equipped with a DB-5 MS column, which had 30 m length, 0.25 mm i.d., and 0.25 μm film thickness. Ion source temperature was 250 °C and the injector temperatures were set at 300 °C. Helium served as the carrier gas at a constant flow of 25 mL/min (He, 99.999%). After starting under isothermal conditions at 80 °C for 6 min, the temperature was linearly raised at 10 °C/min until 250 °C and this remained the temperature for 10 min. Solvent extracted with ethyl acetate was concentrated and enriched, into which a 1.0 μL moisture-free sample of the extract was injected.

3. Results and discussion

3.1. Characterization

3.1.1. GC–MS analysis of the extract of euphorbia cochinchensis leaf

The compounds present in ethyl alcohol extract of *euphorbia cochinchensi* leaf before biosynthesis of Fe NPs were identified by GC–MS. Table 1 shows the presence of major compounds, acting as reducing agent in the synthesis process with highest concentrations, and the compound and structure. As shown in Table 1, alcohol, phenols, and ester are the major chemical constituents of the extract obtained from *euphorbia cochinchensi* leaf extracts. Many reports have indicated that aldehydes, phenols, alcohol and ester are involved in the bioreduction of metal nanoparticles [16–19].

3.1.2. TEM analysis of Fe NPs

The monophony of the Fe NPs was further characterized by TEM and HRTEM. Fig. 1a and b illustrate a TEM image of Fe NPs, and it can be clearly seen that Fe NPs were spherical in shape and uniformly dispersed, which clapped by organics, the size of Fe NPs was 100 nm. HRTEM image (Fig. 1c) further confirmed the crystal nature of Fe NPs. The lattice fringes were visible with a spacing of 0.253 nm, which was indexed to the 311 lattice plane of the inverse spinel Fe_3O_4 obtained from the JCPDS database [20]. The lattice fringe spacing was determined as 0.262 nm, which corresponded to the (109) plane of γ-Fe_2O_3 [21]. In summary, iron oxide nanoparticles were successfully biosynthesized, leading to