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Fe_3O_4@β-CD nanocomposite as heterogeneous Fenton-like catalyst for enhanced degradation of 4-chlorophenol (4-CP)

Manlin Wang[a,1], Guodong Fang[b,1], Peng Liu[a,c], Dongmei Zhou[b], Chen Ma[a], Dongju Zhang[a], Jinhua Zhan[a,*]

[a] *Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, PR China*
[b] *Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, 71 East Beijing Road, Nanjing 210008, PR China*
[c] *School of Chemistry and Chemical Engineering, Qvfu Normal University, Qvfu 273165, PR China*

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ABSTRACT

The magnetic Fe_3O_4@β-cyclodextrin (β-CD) nanocomposites were fabricated via Fe ions and β-CD in one pot and characterized as a heterogeneous Fenton-like catalyst that may be used for the degradation of 4-chlorophenol (4-CP). The catalytic capacity of Fe_3O_4@β-CD was evaluated on the basis of various parameters, including pH, H_2O_2 concentration and catalyst loading, with regards to the pseudo-first-order kinetics of 4-CP degradation. In addition, iron leaching, the effect of radical scavengers and reusability of the Fe_3O_4@β-CD nanocomposite were also studied. The results showed that Fe_3O_4@β-CD exhibited a higher catalytic ability than that Fe_3O_4 toward 4-CP degradation, the observed rate constants (k_{obs}) were 0.0373 min^{-1} for Fe_3O_4@β-CD, and 0.0162 min^{-1} for Fe_3O_4, which may be ascribed to the construction of a ternary complex (Fe^{2+}–β-CD–pollutant) that allowed the produced hydroxyl radicals (·OH) to directly attack the contaminant and simultaneously enhanced the solubility of the organic pollutant. Fe_3O_4@β-CD also exhibited an enhancement effect for chlorobenzene (CB) degradation with the k_{obs} of 0.0392 min^{-1} (k_{obs} = 0.0099 min^{-1} for Fe_3O_4), which may be due to a synergistic effect in the Fe_3O_4@β-CD composite. Furthermore, Fe_3O_4@β-CD has an excellent catalytic activity, stable mechanical strength and adequate reusability. A possible reaction pathway of 4-CP degradation dominated by ·OH was proposed according to analyses of the degradation intermediates and chloride ions. The host-guest interaction between β-CD and 4-CP were examined with density functional theory (DFT) calculations, expounding the unicity of degraded intermediate owing to the specific spatial selectivity of β-CD. The findings of this study provide a novel material used in the Fenton-like process for the degradation of contaminants.

1. Introduction

Recently, advanced oxidation processes (AOPs) have been widely applied for the remediation of contaminated soil and water due to the increasing environmental concern [2,12,14,16]. Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$) is one of the most effective AOPs, which can generate hydroxyl radicals (${}^\bullet OH$), the second strongest oxidizing agent after fluorine, and degrade pollutants efficiently [11,17,21]. The Fenton process has unique advantages, including its simple operation, mild reaction conditions, high degradation efficiency and inexpensive materials [9,30]. However, the traditional homogeneous Fenton reaction has some drawbacks; for example, (1) it is only efficient at low pH (pH 2–4) and is rather inefficient in most natural aqueous media (pH 5–9); (2) further treatments are required of the dissolved iron ions and sludge, such as neutralization of the treated solutions before discharge, which makes the Fenton process complex and uneconomical, and may even produce secondary pollution of acids or metal ions [13].

In order to overcome these problems, heterogeneous Fenton-like processes using iron-based catalysts have been recently studied extensively to decompose recalcitrant organic pollutants over a wider pH range with reduced iron loss [32]. Fenton-like oxidation mainly occurs at the solid–liquid interface, where the iron remains either in the solid phase or as an adsorbed ion [12]. Among the heterogeneous Fenton-like reactions, the inverse spinel Fe_3O_4 has been proved to be one of the most efficient catalyst, owing to its unique electric and magnetic properties [12,32]. The octahedral

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* Corresponding author.
E-mail addresses: jhzhan@sdu.edu.cn, jhzhan@ustc.edu (J. Zhan).

[1] These authors contributed equally to this work and should be considered co-first authors.

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structure of magnetite can accommodate both Fe^{2+} and Fe^{3+}, allowing the iron species to be reversibly oxidized and reduced based on the transfer of electrons between Fe^{2+} and Fe^{3+} [12,32]. It can function steadily without substantial mass loss. Therefore, Fe_3O_4 provides a promising alternative due to its large specific surface, intrinsic peroxidase-like activity and its stability, as well as its facile recycling and recovery [1,33]. However, the solubility of hydrophobic organic pollutants is a vital factor for affecting the degradation of contaminants with Fenton-like reactions, since the contribution of hydroxyl radicals in aqueous solutions for contaminants degradation was also pivotal [24]. Thus, it is necessary to use a suitable enhancing agent that increases the solubility of organic pollutants and makes them available for oxidation.

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide with seven glucose units and has been extensively employed in surface functionalization to promote the formation of host–guest inclusion complexes by providing a hydrophobic cavity, thus increasing the water solubility of organic pollutants [18,24,29]. The highly efficient absorption capacity of β-CD to some proper molecules is ascribed to its hydrophilic external surface, hydrophobic interior and specific cavity diameter (6.4 Å) via host–guest inclusion interaction [15]. The major advantages of using β-CD as an enhancing agent are (1) its much lower toxicity and higher biodegradability; (2) the lack of need for a critical micelle concentration and no formation of high viscosity emulsions, which minimizes reagent residuals; (3) the formation of a ternary pollutant–CD–iron complex, which allows direct ·OH radical attack of the contaminant, thus improving the pollutant elimination rate [34]. β-CD and its derivatives have been shown to be capable of enhancing the efficiency of Fenton oxidation [28]. Therefore, the combination of β-CD and Fe_3O_4 nanoparticles would facilitate the degradation of contaminants in the Fenton-like system.

In this paper, a β-CD-coated Fe_3O_4 catalyst was prepared in one pot and used to promote the Fenton oxidation of contaminant. 4-chlorophenol (4-CP) and chlorobenzene (CB) were selected as model pollutants, since they are widely used in the production of some herbicides, fungicides, insecticides and preservatives, and have been recorded as priority pollutants by the US Environmental Protection Agency (EPA) and European Decision 2455/2001/EC [20,22,27]. The physical and chemical properties of Fe_3O_4@β-CD composites were characterized and the catalytic performances were assessed according to the effects of key variables, such as pH, H_2O_2 concentration and catalyst dosage. The reaction kinetics, material stability and degradation mechanism were also evaluated.

2. Experimental

2.1. Chemicals

The chemicals used in this study are described in the Supporting information (SI, Text S1).

2.2. Preparation and characterization of Fe_3O_4@β-CD

The magnetic particles were prepared according to a previously reported simple one-pot method [3]. Briefly, $FeSO_4{\cdot}7H_2O$ (2.78 g) and $Fe_2(SO_4)_3$ (4 g) were dissolved in 25 mL H_2SO_4 aqueous solution (0.5 mol/L) with vigorous stirring under N_2. After 30 min stirring, 250 mL 4 mol/L NaOH solution (including 12.8 g β-CD) was added drop-wise. The reaction was conducted for 1.5 h with constant and vigorous stirring under N_2 at 80 °C. The obtained β-CD-modified Fe_3O_4 particles were washed several times with ethanol and deionized water, and dried in a vacuum at 60 °C for 6 h. Characterization of Fe_3O_4@β-CD is presented in SI Text S2.

2.3. Degradation experiments

Batch experiments were conducted in a conical flask (25 mL) placed on a rotary shaker at 100 rpm. The reaction solution was prepared by adding a required amount of catalyst to a solution containing the probe compound (4-CP) that was pH-adjusted in the range of 2.0–8.0 by addition of H_2SO_4 or NaOH. A known dosage of H_2O_2 was added to the suspension to initiate the reaction. The final concentration of H_2O_2 and catalyst loading were 10–50 mM and 0.5–2.0 g/L, respectively. Samples were taken at regular intervals and filtered through a 0.22 μm filter film and quenched with excess ethanol. The solid catalyst separated from the solution was rinsed with 2.5 mL methanol four times. The rinse liquid was collected and mixed for analysis. The amount of residual 4-CP was calculated from the sum of that in the aqueous and solid phases. The CB degradation experiments were conducted under the same reaction conditions as 4-CP degradation. The stability of the catalyst was evaluated by isolating it with a magnet, washing, drying under vacuum and reusing it for the next reaction under similar conditions.

2.4. Electron paramagnetic resonance (EPR) studies

5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as spin-trapping agent. The mixture for the standard EPR spin trapping experiment contained 1.0 g/L magnetic nanoparticles (MNPs) and 0.1 M DMPO. After completely mixing, the solution was analyzed by EPR. EPR spectra were also obtained with DMPO or MNPs alone. The spin trapping signals were recorded after 1 min. EPR spectra were also obtained for MNPs solutions in the presence of 10 mM ethanol, as well as MNPs solutions at different pH values after 1 min. Details of instrument are described in SI Text S3.

2.5. Analysis

Details about the analysis could be found in SI Text S4. 4-CP and CB degradation was described with pseudo-first-order equations: $\ln(C_0/C_t) = k_{obs}t$, where t is the reaction time (min), k_{obs} is the apparent rate constant (min^{-1}), and C_0 and C_t are 4-CP concentrations at times of $t = 0$ and $t = t$, respectively [23].

2.6. Computational details

Computational details are described in SI Text S5.

3. Results and discussion

3.1. Characterization of Fe_3O_4@β-CD

TEM images are shown in Fig. 1 and depict the morphology and particle size of Fe_3O_4, Fe_3O_4@β-CD and reused Fe_3O_4@β-CD. It can be observed that Fe_3O_4 and Fe_3O_4@β-CD are quasi-spherical and almost uniform, with diameters of 10–20 nm. The image of Fe_3O_4@β-CD composites reused three times (Fig. 1C) showed no obvious change after the oxidation reaction, which is in accordance with the results of XRD.

Fig. 1A displays the XRD patterns of Fe_3O_4 (top), Fe_3O_4@β-CD (middle) and reused Fe_3O_4@β-CD nanocomposites (bottom). Fe_3O_4 exhibited a spinel structure with five characteristic peaks, marked (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0). The intensity of the XRD peaks decreased when Fe_3O_4 particles were modifed with β-CD. However, Fe_3O_4 and Fe_3O_4@β-CD had similar diffraction peaks, indicating that β-CD did not affect the crystal structure of Fe_3O_4.

The FT-IR spectra of Fe_3O_4 (top), Fe_3O_4@β-CD (middle) and reused Fe_3O_4@β-CD nanocomposites (bottom) are given in Fig. 1B for comparison. The strong band at 570 cm^{-1} in the top trace is