



Heterogeneous Fenton catalytic degradation of phenol based on controlled release of magnetic nanoparticles



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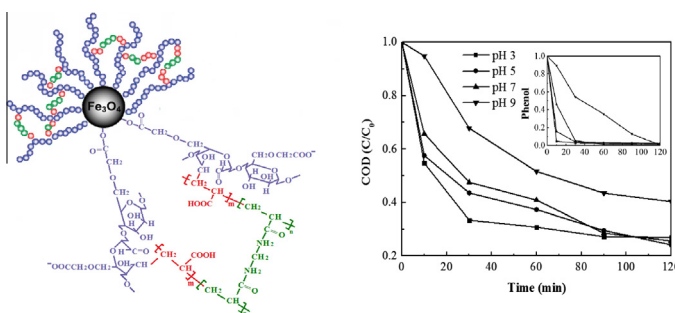
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HIGHLIGHTS

- Fe_3O_4 MCNs were synthesized by co-precipitation and graft copolymerization method.
- A pH-responsive release of Fe_3O_4 active surface has been achieved.
- Fe_3O_4 MCNs performed high catalytic activity within a wide pH range from 3 to 9.
- Fe_3O_4 MCNs remained good stability and activity even after several recycles.

GRAPHICAL ABSTRACT

The fabrication strategy and catalytic property of Fe_3O_4 MCNs.



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ABSTRACT

This study reports a new strategy for stabilizing nanocatalyst with the pH-responsive hydrogel as a stabilizer. The hydrogel coated Fe_3O_4 magnetic composite nanospheres (MCNs) with an average size of 70 nm were synthesized by the co-precipitation method followed by an in-situ graft copolymerization. This novel composite catalyst was used for the catalytic degradation of phenol and the catalytic capacities of Fe_3O_4 MCNs in Fenton systems with different pH conditions, temperatures, H_2O_2 concentrations and catalyst doses were investigated. Under the optimized condition, the removal efficiency of phenol and chemical oxygen demand (COD) reached 98% and 76%, respectively. The catalytic activity of this nanocatalyst remained high (COD removal efficiency were around 75%) within a wide pH range from 3 to 7. Phenol could be almost completely eliminated from solution in 120 min even at pH 9. The outstanding catalytic performance of Fe_3O_4 MCNs could be related to the pH-responsive swelling of polymer hydrogel. The swollen polymeric network prevented the aggregation of Fe_3O_4 , thus providing larger surface area of nanocatalyst. Meanwhile, the hydrophilic hydrogel facilitated contact between the solution and the catalyst, which could improve the diffusion of reactants. Furthermore, the Fe_3O_4 MCNs exhibited superior catalytic recyclability. A COD removal efficiency of more than 60% was still obtained after eight catalytic cycles.

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1. Introduction

Phenol is an important chemical raw material, widely used in industrial and medical agents and so on. High concentrations of phenol can cause protein denaturation or precipitation, so has a

direct role in the damage for a variety of cells. Phenol-containing wastewater discharged into water, not only impede the growth and reproduction of aquatic life, endangering agriculture, but also threaten to human health [1–3]. It is therefore essential to develop effective treatment techniques for the removal of phenol in wastewater.

The Fenton technique ($\text{Fe}^{2+}/\text{Fe}^{3+} + \text{H}_2\text{O}_2$) proved to be one of the most effective methods for degrading organic pollutants in

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wastewater [4–6]. However, the traditional homogeneous Fenton process has many critical drawbacks, such as requirement of further treatments for the dissolved iron ions and generated iron-containing sludge, and neutralization of treated solutions before discharge because of the essential condition of acidification (pH 2–4), which makes this method complicated, uneconomical, and even generates secondary pollution of acid or metal ions [7,8].

To overcome these disadvantages of the homogeneous Fenton process, the heterogeneous Fenton-like systems, where soluble Fe^{2+} is replaced by Fe-containing solids (e.g., Fe^0 , Fe_2O_3 , FeOOH , and so on) have been recently developed [9–15]. Especially since Gao et al. found that the magnetite (Fe_3O_4) nanoparticles had peroxidase-like activity towards phenolic or aniline compounds [16], this novel catalyst has received a great deal of attention due to its several important features for a Fenton reaction, e.g. (i) it contains Fe^{2+} which might play an important role as an electron donor to initiate the Fenton reaction according to the classical Haber-Weiss mechanism, (ii) the octahedral site in the magnetite structure can easily accommodate both Fe^{2+} and Fe^{3+} , which means that Fe^{2+} can be reversibly oxidized and reduced back in the same structure, and (iii) the combination of oxidation states +2 and +3 in magnetite aids to enhance decomposition of hydrogen peroxide [17,18]. The catalytic activity combined with other features, such as easy preparation, biocompatibility and convenient separation from solution by external magnetic field, endow Fe_3O_4 many remarkable advantages in wastewater treatment.

However, the Fe_3O_4 magnetic nanoparticles (MNPs) have a strong tendency of aggregation because of their high surface energies and intrinsic magnetic interactions. The aggregation of MNPs would reduce their surface/volume ratio and dispersion stability in aqueous solution, thus reducing the catalytic activity [19,20]. In order to improve the rate of catalytic degradation reaction, many attempts have been made to increase the stability and activity of MNPs, such as the use of surfactants and chelating agents [21,22], immobilization of Fe_3O_4 in or on supports [23–26], introduction of ultraviolet light and ultrasonic irradiation [27–30]. Although effective particle stabilization was achieved through strong inter-particle electrostatic and/or steric repulsions, stabilizers brought a surface diffusion barrier, which inhibited interactions between the highly reactive surface of nanoparticles and the target contaminants. The ultrasonic irradiation can be used to decrease mass transfer limitation and provide additional cavitation effect in heterogeneous catalytic system, but external energy input is required. Therefore, it is still challenging to develop a convenient and highly efficient heterogeneous catalytic system based on MNPs.

In previous studies, little attention was paid to the response of the stabilizer on the reaction condition. Considering that pH play a central role in Fenton reaction, an ideal stabilizer should respond rapidly to the pH change and release the catalyst in the optimum pH range. The advantage and difference of the current study as compared to the existing references were the designed stabilizer (polymer coating) was maintained in a stretched state under a wide pH range of 3–9, which could provide steric stabilization to prevent aggregation. This loose coating did not obviously obstruct the contact of target substance with the active site of the inner catalyst. Instead, the hydrophilic property of polymer favored the interfacial reaction between the reactants and Fe_3O_4 .

The “live” stabilizer designed in this study is hydrogel. Hydrogel is a three-dimensional, crosslinked polymer that can swell in water but do not dissolve [31]. It can swell greatly by absorbing water and shrink after de-swelling. Several terms have been coined for hydrogel, such as “intelligent gel” or “smart hydrogel” [32]. This material can undergo changes in phase, shape, surface energy and permeation rate in response to changes in environmental conditions such as pH, temperature, ionic strength, and electric field [33–36]. In recent years, the use of pH-sensitive hydrogels in drug

delivery applications is increasing because the pH varies widely among different organs and therefore, polymeric micelles that are responsive to pH can be designed to selectively release their payload in the targeted organs or locations inside the body [37–39]. However, the issue of fabricating controllable hydrogel coating on MNPs for catalysis has not been addressed in previous study.

Herein, we prepared a composite catalyst by coating pH-sensitive copolymer hydrogel on Fe_3O_4 MNPs. Carboxymethyl cellulose (CMC), which was used as the hydrogel matrix, is a polysaccharide possessing both carboxylate and hydroxyl groups that allow this “green” and inexpensive polysugar to exert strong interactions with metal particles [40,41]. Poly(partially neutralized acrylic acid) (PNaA), an anionic polymer, was grafted onto CMC backbone to give pH-responsive property and improve the hydrophilicity of the polymeric network [42]. The environmentally responsive Fe_3O_4 magnetic composite nanospheres (MCNs) were synthesized by a facile *in situ* approach.

The goals of the present research are to fabricate controlled release catalyst delivery system, evaluate the role of pH-responsive hydrogel in hydrogel-magnetite nanocomposites, and investigate the catalytic reactivity of Fe_3O_4 MCNs in Fenton reaction.

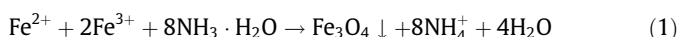
2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%, w/w), H_2SO_4 , NaOH, H_2O_2 (30%, w/w) and high purity nitrogen were purchased from First Chemical Reagent Manufactory (Tianjin, China). Carboxymethyl cellulose sodium (CMC), acrylic acid (AA), N,N'-methylene bisacrylamide (MBA) and ceric ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) were obtained from Beijing Chemical Works (Beijing, China). Phenol was supplied by J&K China Chemical Ltd. (Beijing, China). All of the reaction medium was deionized water.

2.2. Preparation of nanoscale catalyst

Fe_3O_4 nanoparticles were synthesized by coprecipitation method. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (6 mmol) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (6 mmol) were dissolved in 100 mL aqueous solution, then 40 mL of 2.5% ammonia solution was added dropwise into the $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixed solution under stirring. After 40 min reaction at room temperature, the generated black nanoparticles were collected by magnetic separation, washed with deionized water to neutral pH, and then vacuum-dried for use (referred to as the Fe_3O_4 MNPs). The possible reaction for the formation of Fe_3O_4 MNPs is shown below:



Grafting vinyl monomers onto polysaccharides and in-site compounding with inorganic nanoscale particles was the selected method to derive Fe_3O_4 /hydrogel nanocomposites. Hydrogel was synthesized by graft copolymerization of CMC and partially neutralized acrylic acid (NaA) using $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ as an initiator and MBA as a cross-linker. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were firstly added into aqueous solution containing CMC (100 mL, 14 mmol L^{-1}). After reacting with $\text{NH}_3 \cdot \text{H}_2\text{O}$ for 40 min, the resulted suspension was mixed with 100 mL of NaA (AA was partially neutralized by 0.15 mol L^{-1} NaOH solution), 2.7 mg of MBA and 10 mL of 2 mmol L^{-1} $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ solution. The mixture was maintained at 70 °C for 3 h. The whole reaction was performed under nitrogen atmosphere. The obtained products, PNaA-co-CMC/ Fe_3O_4 nanocomposites, were collected, washed and vacuum-dried. The samples were assigned as Fe_3O_4 MCNs.

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