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Degradation of methylene blue in a heterogeneous Fenton reaction catalyzed by chitosan crosslinked ferrous complex

Mengfan Gao, Duoduo Zhang, Wenyun Li, Jiali Chang, Qingwen Lin, Dandan Xu, Hongzhu Ma*

School of Chemistry and Chemical Engineering, Shaanxi Normal University, 710119 Xi'an, Shaanxi Province, PR China

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ABSTRACT

A novel heterogeneous Fenton chitosan-Fe catalyst (CS-Fe), the ferrous ions coordinated by amino and hydroxyl groups of CS, was prepared and characterized by FT-IR and XRD. The decolorization of methylene blue (MB) was monitored by UV–vis spectra and chemical oxygen demand (COD). At the optimum reaction conditions, 10000 mg l^{-1} CS-Fe, 1200 mg l^{-1} H_2O_2, 30 °C, original pH, 120 mg l^{-1} MB, up to 99% color removal for MB was achieved at 30 min, superior to other Fenton systems. The study of COD removal and UV–vis spectra suggested that the uncompletely mineralization of MB occurs in the CS-Fe system. The concentration of Fe iron dissolved from CS-Fe was negligible relative to CS-Fe applied and the removal of MB remains as high as 90% after recycled five times, indicating that this novel heterogeneous Fenton catalyst is efficient for MB wastewater treatment. Moreover, almost 90% of color removal obtained after five cycles and low amount of dissolved iron were detected in solution, indicating that the catalyst has good stability.

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1. Introduction

The effluents from textile manufacturing and dyeing processes are highly colored and contain considerable amounts of organic matter which are refractory to remove [1,2]. As an advanced oxidation process (AOP), generated hydroxyl radicals (·OH) that are very effective in degradation organic pollutants because of its strong oxidizing capabilities, Fenton oxidation has been widely applied for treatment of organic contaminants [3]. While for the widely studied homogeneous Fenton process, the optimal pH is verified to be in the range of 2–4 [4,5], severely limits its application. Meanwhile, there are some other shortcomings for the application of this process [6], such as the homogeneous catalyst cannot be easily separated from solution, the generated iron sludge after reaction also cause secondary pollution affecting the quality of the water [7]. In order to solve these problems, some researchers fixed homogeneous Fenton catalysts in the carrier, forming heterogeneous catalysts, which are easy to be separated. However, some of the heterogeneous catalysts are costly and need to introduce energies such as UV light or ultrasonic to promote the reaction [8]. Also, activated component loaded on carriers may dissolve out with reaction proceed, which result in the decrease of catalyst activity.

In recent years, chelate based heterogeneous Fenton reactions can avoid the leaching of iron ions and enhance significantly the degradation efficiency of organic contaminants even at neutral pH. Lu [9] studied the enhancement effects of chelating agents, citric acid monohydrate (CIT), oxalic acid (OA), and glutamic acid (Glu) of Fe(III)-based catalyzed sodium percarbonate (SPC) for stimulating the oxidation of tetrachloroethene (PCE) applied in groundwater remediation, and found that the chelating agents significantly enhanced the degradation of PCE.

As a nature chelating agent and an abundantly natural polymer, chitosan (CS) has been applied in many fields, such as pharmaceutical, environmental and biotechnological [10–12], for its unique properties—biodegradability, non-toxicity and hydrophilicity. Moreover, it has strong ability of chelating with metal, because of the great number of hydroxyl groups (–OH), amino groups (–NH_2) and a flexible structure of polymer chains, that make it easy to chelate with transition metal ions [13–14]. Cu(II)-CS complex and CS supported Pd(II) have been reported that they played a significant role of heterogeneous catalyst in degradation of textile dyes [15], hydroquinone [16], chlorophenol [17], nitrophenol [18], and nitrotoluene [19]. Si et al immobilized laccase onto CS beads to enhance the stability and reusability of enzymes to degrade various synthetic dyes, the immobilized enzyme could be used in many applications [20]. Kandasamy reported the synthesis of an economic and eco-friendly CS-Ag nanocomposite and illustrated the eco-friendly approach for the reduction of silver using CS

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* Corresponding author. Fax: +86 29 81530727.
E-mail address: hzmachem@snnu.edu.cn (H. Ma).

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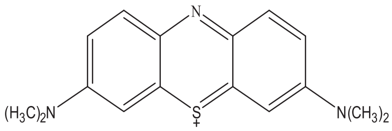
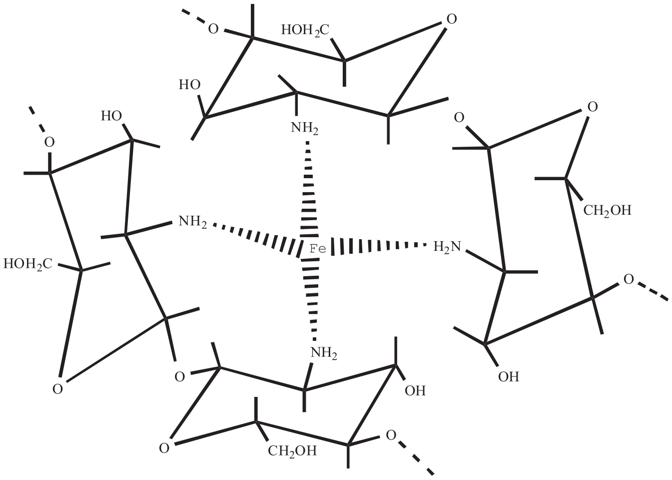
Table 1
Main characteristic of MB.

Dye	Structure	Chemical formula	Molecular weight ($g\,mol^{-1}$)	Maximum absorbance wavelength
MB		$C_{16}H_{18}ClN_3S$	319.9	665 nm



Scheme 1. Structure of CS-Fe complex.

as a reducing agent, and it can be applied in dye decay and microbial contaminants [21]. Liu developed an efficient catalyst of a CS–metal complex through the chelation of CS polymer with bimetals Cu(II) and Fe(III) and found the enhanced catalytic ability of chitosan–Cu–Fe bimetal complex for the removal of dyes in aqueous solution [22]. Therefore, CS was selected and should be cross-linked with Fe ions to form CS-Fe complex (Scheme 1) [14], which can catalyze H_2O_2 decomposition to produce hydroxyl radicals. However, the application of CS-Fe complex in the Fenton oxidation of dye pollutants is limited.

In the present investigation, the objective was to demonstrate the feasibility of the heterogeneous Fenton oxidation processes with chitosan-Fe(II) (CS-Fe) in the degradation of dye and the optimal operational conditions in methylene blue (MB) degradation was also investigated.

2. Experimental

2.1. Materials

CS with a deacetylation degree of 85%, obtained from Gold shell pharmaceutical Co. Ltd. Ammonium ferrous sulfate obtained from Tianjin tianli chemical reagent Co. Ltd. Hydroxylamine hydrochloride and hydrogen peroxide (30%) obtained from Sinopharm Co. Ltd. Methylene blue (MB) obtained from Paini chemical reagent factory, China. All of the reagents were analytical grade. The main characteristics of MB are shown in Table 1.

2.2. Preparation of catalyst CS-Fe

A certain amount of CS was dissolved into 2% acetic acid solution, ammonium ferrous sulfate solution containing hydroxylamine hydrochloride was added slowly with stirring at room temperature for 40 min. Then filtered, immersed the precipitate with ethanol and acetone (1:1 in volume), subsequently washed several times by ethanol to remove excess ammonium ferrous sulfate. The obtained solid were dried at 60 °C, mechanically grinded and obtained CS-Fe complex.

2.3. Heterogeneous Fenton oxidation of MB

The heterogeneous oxidation of MB in solution catalyzed by CS-Fe was performed at ambient temperature. A certain amount of catalyst was dispersed in a 200 ml reactor containing 100 ml of MB, and the reaction was initiated with the addition of H_2O_2. The effect of dosage of CS-Fe (2500–15,000 $mg\,l^{-1}$), concentration of H_2O_2 (800–1400 $mg\,l^{-1}$), reaction temperature (20–45 °C), pH (2–11), and initial concentration of MB (90–360 $mg\,l^{-1}$) on MB color removal were carried out to determine the optimum conditions for the oxidation of MB. The pH of MB wastewater was adjusted to the desired pH level by NaOH (10%) or H_2SO_4 (10%), and then magnetically stirred during the procedure. Samples were withdrawn at predetermined reaction intervals for analysis.

The oxidation process of MB was monitored by UV–visible spectrophotometer (T6 New Century, Beijing, China). COD was analyzed by a COD detector (5B-3C, Lianhua Tech, Lanzhou, China). The color removal of MB was calculated as follows:

$$\text{Color Removal}(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where A_0 and A_t are absorbance of MB at time 0 and t min at 665 nm, respectively.

2.4. Analytical methods

The structure and crystallinity of CS and CS-Fe before and after reaction were characterized using an X-ray diffraction (XRD, D/max-3c Deffractometer, Rigalcu Corporation, Japan) with Cu Kα radiation (D/Max2550VB+/PC, λ = 1.5406 Å) at 40 KV/100 mA in the range of 3–60° (2θ) with scanning rate of 8°/min. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 instrument (Bruker, Germany) in the transmission mode using KBr pellets of the samples in the range of 400–4000 cm^{-1}.

3. Results and discussion

3.1. Characterization of catalyst

The basic FT-IR characteristics of CS and CS-Fe were shown in Fig. 1. 3441 cm^{-1} was typical for O–H and N–H stretching vibration. 1657, 1566 cm^{-1} attributed to C=O stretching and N–H deformation vibrations in –NH–C=O group [23,24], 1416 cm^{-1} attributed to C–H bending vibration, 1071 cm^{-1} attributed to C–O–C and C–OH bond stretching vibrations [25], 659 cm^{-1} attributed to –OH bond plane bending vibration. Compared with CS (a) and Fresh CS-Fe (b), a shift from 3435 to 3441 cm^{-1} occurs, demonstrating that $-NH_2$ and –OH group of CS involved in CS-Fe. And the peak at 1416 cm^{-1} shifted to 1439 cm^{-1}, suggesting that –OH of $-CH_2-OH$ group cross-linked with Fe ion [26]. Meanwhile slight shifts from 1566 to 1555 cm^{-1} and 659 to 615 cm^{-1} occur, indicating that $-NH_2$ and –OH group cross-linked with iron ion. The

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