

Decolorization of organic dyes by zero-valent iron in the presence of oxalic acid and influence of photoirradiation and hexavalent chromium



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ABSTRACT

In the present study, zero-valent iron (Fe^0) film coated on indium tin oxide (ITO)-coated glass substrate was prepared with electrodeposition. Decolorization of methylene blue (MB) and orange II (OII) by the Fe^0 film in the presence of oxalic acid (OA) and dissolved oxygen (DO) and the influence of photoirradiation and hexavalent chromium (Cr(VI)) has been investigated. The newly developed $\text{Fe}^0/\text{OA}/\text{DO}$ system is more effective in decolorization of MB than its EDTA counterpart, and is of a strong stability in prolonged use. Operating parameters such as pH and OA concentration have significant influence on the decolorization rate for MB in this system, and lower pH value and higher OA concentration are favorable. The low decolorization rate for OII can be dramatically enhanced by introduction of photoirradiation into the system. Coexistence of Cr(VI) has an opposite influence on decolorization of MB and OII in the photo-assisted $\text{Fe}^0/\text{OA}/\text{DO}$ system. In the latter case, Cr(VI) promotes the decolorization of OII, and itself can also be reduced, which allows effective simultaneous removal of OII and Cr(VI) from a mixed solution. Several mechanisms involved in decolorization of MB and OII have also been discussed.

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1. Introduction

Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has been widely used for the treatment of both organic and inorganic pollutants under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning etc. [1]. The process is based on the formation of hydroxyl radical ($\bullet\text{OH}$) able to oxidize almost all organic matters and mineralize them to carbon dioxide and water owing to its high oxidation potential ($E^0 = +2.80\text{V}$ versus NHE) [2]. Introduction of light into Fenton system to form a so-called Fenton-like system or photo-Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UVC}$) increases the efficiency of formation of $\bullet\text{OH}$ [3,4]. In fact, ferric ion (Fe^{3+}) can also catalyze the H_2O_2 decomposition in acidic solution under UVA illumination to form $\bullet\text{OH}$ (known as photo-Fenton-like system, $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UVA}$) [5,6]. The amount of $\bullet\text{OH}$ produced by the homogeneous Fenton process is strongly affected by the pH and the optimum pH value for the Fenton reaction is about 3 [1]. In order to maintain this pH value during the process, large amount of acid needs to be added to the reaction system [7]. Without pH adjustment, large amount of ferric hydroxide sludge would be produced [8]. These drawbacks limit its practical application in environmental remediation.

To overcome the disadvantages of the homogeneous Fenton or Fenton-like process, heterogeneous solid catalysts have been tried to catalyze the decomposition of H_2O_2 . The heterogeneous catalysts include iron oxides [9] and structured silica fabrics loaded with Fe ions [10]. The immobilization of the Fe(III) species into the catalyst allows the mediation of Fenton-like reactions over a wide range of pH values [11] and prevents iron hydroxide precipitation [8]. In recent years, direct use of zero-valent iron (Fe^0) as catalyst in heterogeneous Fenton process has received much attention. Because the corrosion of the Fe^0 generates in situ Fe^{2+} , this process is the cost-saving compared with the conventional Fenton system [12]. Moreover, the concentration of iron ions in the wastewater after the treatment is significantly reduced [13].

Recently, some authors have reported that Fe^0 and dissolved oxygen (DO) can form a new Fenton-like system (Fe^0/DO) to oxidize organic pollutants [14,15]. In such a system, both Fe^{2+} and H_2O_2 are not artificially added. However, the coating of iron oxides on Fe^0 surface will decrease its degradation efficiency [16]. Efforts have been made to enhance the degradation efficiency by addition of EDTA [17,18]. The degradation efficiency of $\text{Fe}^0/\text{EDTA}/\text{DO}$ may be further improved by assistance of ultrasound [19] or microwave [20]. Up to now, little attention has been paid to other ligands and the corresponding influence of photoirradiation. Although Keenan and Sedlak have reported on the enhancement of oxalate for reactive oxidant generation by nanoparticulate Fe^0 and oxygen [21], little information is available on the decolorization of organic dyes using oxalate-enhanced Fe^0/DO system ($\text{Fe}^0/\text{OA}/\text{DO}$). It is

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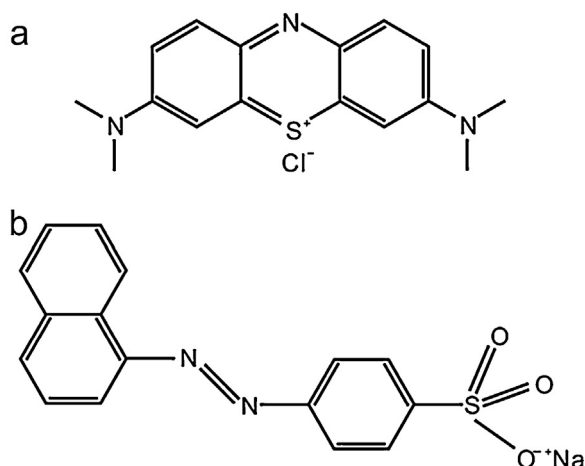


Fig. 1. Molecular structure of MB (a) and OII (b).

noteworthy that the used Fe⁰ is often in the form of powder, whereas Fe⁰ film should be expected to present benefits such as easy separation and avoiding the aggregation of particles.

Hexavalent chromium (Cr(VI)) is a carcinogenic contaminant in waste waters arising from industrial processes such as electroplating, leather tanning, or paint manufacture [22]. There are a number of methods for Cr(VI) removal from contaminated aqueous systems, such as membrane filtration, extraction, ion exchange, adsorption and chemical reduction followed by precipitation [23]. The preferred treatment is reduction of Cr(VI) to the less harmful Cr(III), which can be precipitated in neutral or alkaline solutions as Cr(OH)₃ and removed as a solid waste [24]. The reducing agent in this process is chiefly a salt of either S(IV) or Fe(II) [25]. In addition, Fe⁰ and organic acids as reductants for transformation of Cr(VI) to Cr(III) have also been widely studied [26,27]. It has been found that the coating of iron oxide significantly impedes the reduction activity of Fe⁰ [28], and the reduction of Cr(VI) by organic acids is a slow process [29]. Fortunately, reduction of Cr(VI) by Fe⁰ can be accelerated by some organic acids [30], and reduction of Cr(VI) by some organic acids can be photocatalyzed by Fe(III) species [31]. In a previous work [32], we have reported that Cr(VI) can be reduced effectively by Fe⁰ and oxalic acid under photoirradiation. It is of interest to investigate the simultaneous removal of Cr(VI) and organic dyes in photo-assisted Fe⁰/OA/DO system, because they may co-exist in some industrial effluents [33].

In the present study, Fe⁰ film was prepared with electrodeposition and used to fabricate Fe⁰/OA/DO system. Two common dyes, methylene blue (MB, anthraquinone dye) and orange II (OII, azo dye), were selected as the model pollutants (molecular structure of the dyes is shown in Fig. 1). The study aims: (i) to examine the feasibility of the Fe⁰/OA/DO system in decolorization of the dyes; (ii) to evaluate the enhancement of photoirradiation for the Fe⁰/OA/DO; (iii) to investigate the simultaneous decolorization of the dyes and reduction of Cr(VI) in the photo-assisted Fe⁰/OA/DO system.

2. Experimental

All chemicals were of analytic reagent grade and used as received. Except potassium dichromate (from Tianjin Damao Chemical Reagent Factory, China), EDTA (disodium salt) and other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All solutions were prepared with distilled water. Cr(VI) stock solutions (0.02 M) was prepared by dissolving K₂Cr₂O₇ into distilled water.

Fe⁰ film was fabricated on indium tin oxide (ITO)-coated glass substrates by cathodic deposition in an ordinary cell with an iron

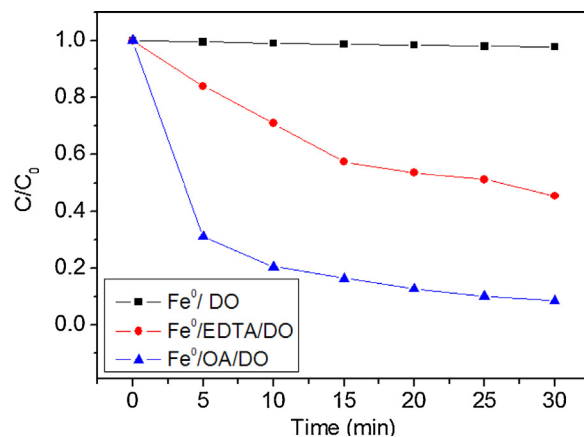


Fig. 2. Decolorization of MB in different systems. Experimental conditions: [MB] = 9 mg/L, [AO] = [EDTA] = 2.4 mM, pH = 3.0.

plate used as counter electrode. The bath was composed of 0.2 M ferrous sulfate, 0.5 M sodium sulfate and 0.4 M boric acid [34]. The applied current density and the deposition time were 3 mA cm⁻² and 30 min, respectively [32]. The prepared Fe⁰ film was immediately used after washing with distilled water.

The decolorization experiments were carried out in a cylinder quartz tube (containing 15 mL of reaction solution). The concentration of both MB and OII was 28 μM (i.e. 9 and 10 mg/L, respectively). In some cases, EDTA of 2.4 mM or OA with different concentrations (0.8, 1.6, 2.4 and 3.2 mM) was added into the solution. The initial pH of the solution was adjusted by sodium hydroxide (1 M) or sulfuric acid (0.2 M). The decolorization was initiated by placing Fe⁰ film (efficient area: 4 cm²) into the dye solution. The experiment on reuse of Fe⁰ film was performed as follows: after every 30 min of reaction the content of the tube was replaced with fresh MB or OII solution containing OA.

In the photo-assisted experiments, a 300 W metal halide lamp was used as photoirradiation source, which was 10 cm away from the reactor. The intensity of photoirradiation (I) available in the solution was measured to be about 14 mW/cm². For the experiments on simultaneous decolorization of MB or OII and reduction of Cr(VI), concentration of Cr(VI) and MB (or OII) was 0.2 mM and 28 μM, respectively, in a mixed solution. All the experiments were conducted at room temperature with the reactor open to the air.

The concentration of MB, OII and Cr(VI) during the reaction period was determined by measuring the absorbance at 486, 664 and 349 nm [32], respectively, using a spectrophotometer. The decolorization rate of MB or OII was obtained from the following formula:

$$\text{Decolorization rate (\%)} = \frac{C_0 - C}{C_0}$$

where C₀ and C are the concentration of MB or OII before and after reaction, respectively. Similarly, reduction rate of Cr(VI) was obtained.

3. Results and discussion

3.1. Decolorization of MB in different systems

The results of decolorization of MB in different systems are given in Fig. 2. It can be seen that the MB concentration remains nearly constant in Fe⁰/DO system during the reaction period (decolorization rate being 2.0% after 30 min, which may be attributed to the adsorption of MB on Fe⁰ surface). Noradoun et al. observed a similar result in degradation of chlorophenols using Fe⁰ [35]. Several reports have indicated that Fe⁰ corrosion in the presence of DO

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