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Cu(II)–Fe(II)–H_2O_2 oxidative removal of 3-nitroaniline in water under microwave irradiation

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HIGHLIGHTS

- Coexistence of Cu(II) and Fe(II) in MW-Fenton-like process was studied in detail.
- 3-Nitroaniline was removed effectively by MW-Cu(II)-Fenton process.
- Experimental parameters were optimized by kinetics study.
- Relationship between reaction rate constant and reactant concentration was determined.
- Probable Cu(II) effect in MW-Cu(II)-Fenton process was examined preliminarily.

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ABSTRACT

Cu(II)–Fe(II)–H_2O_2 process was studied through degrading 3-nitroaniline (3-NA) in water under microwave (MW) irradiation. The experimental conditions were studied by investigating the removal rates and reaction rate constants of 3-NA at different levels of influence factors. The removal rates and reaction rate constants both increased with the increase of Cu(II), Fe(II) and H_2O_2 dosages when they were at reasonable concentration ranges ([Cu(II)] 0.0016–0.0094 mmol L^{-1}, [Fe(II)] 0.051–0.205 mmol L^{-1} and [H_2O_2] 4.34–17.34 mmol L^{-1}). Under the examined conditions (initial pH = 5.3, [Cu(II)], [Fe(II)] and [H_2O_2] were 0.0078, 0.205 and 17.37 mmol L^{-1}, respectively, P_{MW} = 100 W, $V_{3\text{-NA}}$ = 400 mL), more than 92% of 3-NA was removed at 8.5 min and the reaction rate constant reached 0.310 min^{-1}. Furthermore, the mathematical relationship between reaction rate constants and reactants concentrations was obtained via kinetic study, the result was $k = 43.9 \cdot e^{-\frac{2905.2}{T}} \cdot [H_2O_2]^{1.675} \cdot [Fe(II)]^{0.908} \cdot [Cu(II)]^{0.080}$. Finally, the probable effect of Cu(II) in Cu(II)-Fenton process under MW irradiation was speculated according to the comparison result of 2-hydroxyterephtalic acid (generated by the reaction between hydroxyl radicals and terephthalic acid) intensity, the study of synergetic effects of Cu(II) and Fe(II) in Cu(II)-Fenton process and the comparative analysis of reaction mechanisms in Fenton process and Cu(II)–H_2O_2 process.

1. Introduction

Fenton/Fenton-like processes, as a kind of well-known organic wastewater treatment method, was always composed of transition metal ion (such as Fe ion, Cu ion et al.) as the catalyst and H_2O_2 as the oxidant. The common feature of Fenton/Fenton-like processes is the generation of hydroxyl radicals (OH·) which can degrade most of refractory organic pollutants because of its strong oxidation. Fenton process (i.e. Fe(II) and H_2O_2), as the research foundation of other Fenton-like process, has been studied profoundly and the mechanism of Fenton process can be concluded as follows [1,2]:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\cdot} + OH^{-} \quad (1)$$

$$Fe(III) + H_2O_2 \rightarrow FeOOH^{2+} + H^{+} \quad (2)$$

$$FeOOH^{2+} \rightarrow Fe(II) + \frac{1}{2}O_2 + OH^{\cdot} \quad (3)$$

$$Fe(II) + OH^{\cdot} \rightarrow Fe(III) + OH^{-} \quad (4)$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \quad (5)$$

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$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad (6)$$

$$OH^{\cdot} + \text{Organics} \rightarrow \text{intermediates} \rightarrow \text{Inorganics} \quad (7)$$

Microwave (MW), as an important wave band (300 MHz–300 GHz) of electromagnetic wave, can exert influence over many aspects of chemistry reaction, such as the activation energy, the vibration of chemical bonds, and the reaction rate [3,4]. The thermal and non-thermal effects are the two main characteristics of MW. In contrast to conventional heating, microwave can penetrate into the sample and cause heating throughout the volume of the product [5]; In addition, the non-thermal effect of MW could cause the excitation of reactant molecules to higher vibrational and rotational energy levels [6]. MW irradiation has been proved to have an obvious enhancement to many chemical reactions [7–9], especially in the wastewater treatment using physical–chemical methods.

Recent years, in order to combine the advantages of Fenton/Fenton-like process and MW irradiation, the MW-Fenton/Fenton-like process have been studied widely from many aspects (such as the kinetic and mechanism study) in the organic wastewater treatment [3,10–12]. However, until now just one kind of transition metal ion (such as Fe(II), Fe(III), or Cu(II) et al.) was applied as the catalyst in the MW-Fenton/Fenton-like process [3,10,13,14], the study of combined-catalyst composed of two kinds of transition metal ions in homogeneous MW-Fenton-like reaction has attracted little attention.

3-Nitroaniline (3-NA), as one kind of isomer of nitroanilines, is the critical precursor and intermediates to produce pesticides, azo dyes, antioxidants, cosmetics and fuel additives [15]. With the growing use of 3-NA in different industries, it has been obtained in large amount of industrial wastewater. However, the discharge of wastewater containing 3-NA to environment has caused serious environmental pollution because of the poor biodegradability, toxicity and accumulative effect of 3-NA [16]. In addition, due to the highly mutagenic and carcinogenic property of 3-NA [17], human health is also seriously threatened after 3-NA is absorbed by human bodies. It has been included in the US Environmental Protection Agency (EPA) blacklist of priority pollutants [18]. Thus, the removing of 3-NA from industrial wastewater has become the primary task of scientists.

In this work, Fenton process with the addition of Cu(II) (that is Cu(II)–Fe(II)–H_2O_2 process) was investigated in detail under the MW irradiation by degrading 3-NA. Firstly, the experimental parameters were studied by the comparison of removal rates and reaction rate constants (k) of 3-NA. Next, the mathematic relationship between pollutant removal rate constant (k) and reactants concentrations (C) was investigated and obtained by the study of Arrhenius equation. Finally, the probable Cu(II) effect in Cu(II)-Fenton process under MW irradiation was speculated according to the comparison result of 2-hydroxyterephtalic acid intensity, the study of synergetic effects of Cu(II) and Fe(II) in Cu(II)-Fenton process and the comparative analysis of the reactions in Fenton and Cu(II)–H_2O_2 system under MW irradiation.

2. Materials and methods

2.1. Chemical and reagents

3-NA (analytical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd., China, and was used as received without any further purification. Hydrogen peroxide (30%, w/w), Ferrous sulfate ($FeSO_4$), cupric sulfate ($CuSO_4$) and all other chemicals used here were analytical grade unless noted otherwise. All solutions were prepared with distilled water.

2.2. Treatment procedure

A diagram of the experimental setup is shown in Fig. 1. The treatment of 3-NA was conducted in a modified microwave oven (EM-202MS1, SANYO, Japan). During the reaction process, reaction solution was sampled at certain time interval. After that, NaOH solution was added into the sample immediately to stop the generation of $OH^{\cdot}$ [2] because of the inhibition effect of OH^- to reaction between Fe(II) and H_2O_2 (see Eq. (1)). After the complete decomposition of H_2O_2 and the complete transformation of Fe(II) to Fe(III) in all samples, nitrite and *N*-(1-Naphthyl)-ethylenediamine-Dihydrochloride were added into these samples to react with 3-NA. After 30 min of color reaction, the concentration of 3-NA was measured.

Temperature-controlled (TC) experiments were also performed in the modified microwave oven (Fig. 1), and the settled temperature of wastewater was adjusted by intermittent MW irradiation and air chilling via turning on the air pump under the optimal MW power. In this way, different temperatures could be achieved under MW irradiation. In detailed, the realization of a determined temperature is related to the interval time of MW irradiation and the volume flow rate of cold air. The corresponding operations among them (the determined temperature, the interval time of MW irradiation and the volume flow rate of cold air) could be determined by pre-experiment.

All experiments were carried out three times to diminish experimental errors. The standard deviations were calculated and shown as error bars in every figure.

2.3. Analytical methods

The 3-NA removal rate was monitored by measuring the absorbance of amaranth dye generated by the color reaction among 3-NA, nitrite and *N*-(1-Naphthyl)-ethylenediamine-Dihydrochloride at 545 nm under acid condition by means of a UV–vis spectrophotometer (T-6, PERSEE, China) [19].

Due to the short life and strong oxidation of $OH^{\cdot}$, it is difficult to determine $OH^{\cdot}$ concentration directly, so indirect methods should be used. In this work, $OH^{\cdot}$ was determined by a photoluminescence technique with terephthalic acid as a probe molecule. The intensity of the peak of product (2-hydroxyterephtalic acid, which is generated during the reaction between $OH^{\cdot}$ and terephthalic acid) is in proportion to the amount of $OH^{\cdot}$ in aqueous solution. Terephthalic acid solution was prepared according to the paper of Yu [20].

The 3-NA removal efficiency was calculated by Eq. (8),

$$\text{Removal efficiency}\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (8)$$

where C_0 and C_t are initial and instantaneous concentrations of 3-NA (mmol L^{-1}).

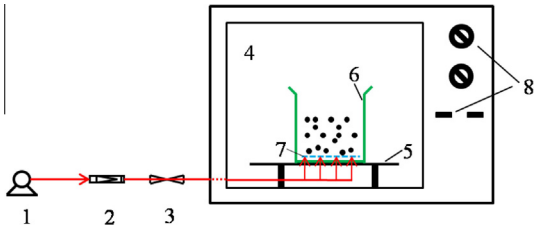

Fig. 1. Schematic diagram of experimental setup with temperature-controlled device (1, air pump; 2, gas flow meter; 3, throttle valve; 4, a modified microwave oven; 5, glass platform; 6, reactor; 7, gas distributor; 8, switch and control knob).