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Dyes and Pigments 74 (2007) 647–652
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process

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Received 7 January 2006; received in revised form 16 February 2006; accepted 20 April 2006
Available online 6 June 2006

Abstract

The degradation of an azo dye Amido black 10B in aqueous solution by Fenton oxidation process has been investigated. The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_0$), the initial ferrous concentration ($[Fe^{2+}]_0$), the initial Amido black 10B concentration ($[dye]_0$) and the temperature on the oxidative degradation of Amido black 10B have been assessed. The optimal reacting conditions were experimentally determined and it was found to be initial pH = 3.50, $[H_2O_2]_0 = 0.50$ mM, $[Fe^{2+}]_0 = 0.025$ mM for $[dye]_0 = 50$ mg/L at temperature = 25 °C. Under optimal conditions, 99.25% degradation efficiency of dye in aqueous solution was achieved after 60 min of reaction. The UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process were studied. It was easier to destruct the azo linkage (–N=N–) group than to destruct the aromatic rings of Amido black 10B by Fenton oxidation. The experimental results showed that the Fenton oxidation process was an effective process for the degradation of azo dye Amido black 10B at low H_2O_2 and Fe^{2+} concentrations.

Keywords: Amido black 10B; Fenton process; Advanced oxidation technologies (AOTs); Hydroxyl radical; UV–vis spectra

1. Introduction

Azo dyes are widespread environmental pollutants associated with textile, cosmetic, food colorants, printing, and pharmaceutical industries. Yearly, 800,000 tonnes of dyes are produced in the world and about 50% of them are azo dyes [1]. Estimates indicate that approximately 10–15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations [2,3]. The effluents are strongly colored which not only created environmental and aesthetic problems, but also posed a great potential toxic threat to ecological and human health as most of these dyes are toxic and carcinogenic.

The strong electron-withdrawing character of the azo group stabilizes these aromatic pollutants against conversions by oxygenases. Therefore, azo dyes are not readily degraded under aerobic conditions [4,5]. Under anaerobic conditions, azo dyes are readily cleaved via a four electron reduction at the azo linkage generating aromatic amines. The aromatic amines cannot be regarded as environmentally safe end products as they are suspected to be carcinogens and mutagens [6–9]. Nowadays, various chemical and physical processes, such as elimination by adsorption onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method, etc. are applied for the treatment of dye waste effluents [10–12]. Nevertheless, these methods are usually non-destructive, inefficient, costly and resulted in the production of secondary waste products. Therefore, purification of azo dye wastewater is becoming a matter of great concern and it is necessary to develop novel and cost-effective technologies to treat azo dye wastewater.

Advanced oxidation technologies (AOTs) are innovative methods for water treatment and are extremely useful in the case of substances resistant to conventional technologies.

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0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.04.006

AOTs are oxidation processes which generate hydroxyl radicals ($^{\bullet}OH$) that are very effective in degrading organic pollutants because of their strong oxidant power ($^{\bullet}OH + H^+ + e^- \rightarrow H_2O$; $E^0 = 2.80$ V) and nonselective species [13,14]. O_3/H_2O_2, O_3/UV, H_2O_2/UV, TiO_2/air/UV, Fe(II)/H_2O_2 (Fenton's reagent), Fe(III)/H_2O_2 (Fenton-like reaction), an oxidant (H_2O_2, O_3) and ultrasonic irradiation are the main types of AOTs that have been suggested in recent years [15–19]. Various combinations of them are employed for the complete mineralization of pollutants. Among these AOTs, Fenton's reagent is particularly attractive because of the low costs, the lack of toxicity of the reagents (i.e., Fe(II) and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology [20]. Early studies have shown that the Fenton reaction is efficient in the degradation of organic compounds. The active species can be generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions according to Eqs. (1) and (2) [21,22], the $^{\bullet}OH$ radical can attack and initiate the oxidation of organic pollutant molecule (R) by several degradation mechanisms as shown below (Eqs.(3)–(5)) [23]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad k_1 = 76\ M^{-1}\,s^{-1} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad k_2 = 0.01\text{–}0.02\ M^{-1}\,s^{-1} \tag{2}$$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad k_3 = 10^7\text{–}10^{10}\ M^{-1}\,s^{-1} \tag{3}$$

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R^+ \tag{4}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + {}^{\bullet}OH \tag{5}$$

For economic degradation of dye wastewater by Fenton oxidation, there is a need to determine the optimal conditions of experimental parameters. The aim of the present work is to investigate the influence of various parameters on the degradation of a classical azo dye, called Amido black 10B, in aqueous solution by the Fenton oxidation process. The effects of pH, dosages of hydrogen peroxide and ferrous, the concentration of Amido black 10B and the temperature were examined. The optimal reacting conditions were evaluated. In addition, the UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process were also studied.

2. Materials and methods

2.1. Reagents

Amido black 10B was obtained from Beijing Chemical Reagents Co. (Beijing, China), the molecular structure of it is displayed in Fig. 1. Hydrogen peroxide (30% w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sulfuric acid and sodium hydroxide were all obtained from Shanghai Chemical Reagents Co. (Shanghai, China). All chemicals were of analytical grade and were used without any further purification. Deionized water was used throughout this study.

2.2. Experimental procedures

All experiments were carried out in 500 mL beakers, which were placed in a thermostat water bath with constant temperature and stirred by a magnetic stirrer. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of ferrous ion and dilution with deionized water to 200 mL. Solution pH values were adjusted to the desired level using dilute sulfuric acid and sodium hydroxide, which were measured by a pH meter (PHS-3C). The reactions were initiated by adding hydrogen peroxide to the beaker. Samples were taken out from the beaker periodically using a pipette and were immediately analyzed and then returned back to the beaker. Each experiment was replicated three times or more.

2.3. Analytical methods

The UV–vis spectra of dye were recorded from 200 to 800 nm using a UV–vis spectrophotometer (Lambda 17, Perkin–Elmer) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of Amido black 10B could be found at 618 nm from the spectra. Therefore, the concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at $\lambda_{max} = 618$ nm and from a calibration curve. The degradation efficiency of Amido black 10B was defined as follows (Eq. (6)):

$$\text{Degradation efficiency}\ (\%) = (1 - C_t/C_0) \times 100\% \tag{6}$$

where C_0 is the initial concentration of Amido black 10B, and C_t is the concentration of Amido black 10B at reaction time t (min).

3. Results and discussion

3.1. Effect of pH

The pH of the solution is an important parameter for Fenton oxidation process, which controls the production rate of hydroxyl radical and the concentration of Fe^{2+}. It is also an

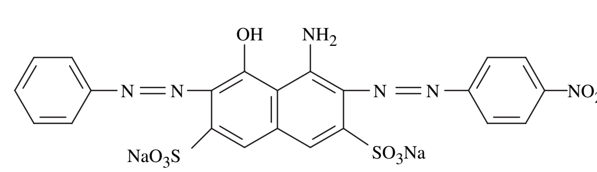

Fig. 1. Molecular structure of Amido black 10B.