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Synergistic effect in treatment of C.I. Acid Red 2 by electrocoagulation and electrooxidation

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ABSTRACT

An aqueous C.I. Acid Red 2 solution was decolorized by electrolysis using iron as anode. The decolorization mechanism was investigated through experimental observations on the electrochemical behavior of C.I. Acid Red 2 on Pt rotating disk electrode, UV–visible spectra of the solution and IR spectra of the coagulated mixtures. It is found that the decolorization efficiency is high, over 98.0% after 40 min, and this high decolorization efficiency can be ascribed to the synergistic effect of electrocoagulation and electrooxidation. The electrocoagulation results from the electrogenerated iron hydroxide and the electrooxidation results from electrogenerated ferric ions. The results obtained from IR spectra shows that the decolorization of C.I. Acid Red 2 by electrooxidation is due to the partial or complete cleavage of C–N bonds in C.I. Acid Red 2.

1. Introduction

Compared with other methods for wastewater treatment, electrochemical technologies have many advantages, convenient, highly efficient and environmentally friendly [1–3], because it does not add extra chemical into the system [4,5]. Added chemical substances might cause the secondary water pollution [6]. Electrocoagulation (EC) as one of the electrochemical technologies has attracted great attention in the wastewater treatment, since it combines oxidation and reduction (indirect or direct), flotation, concentration and collection of the metal hydroxide flocs and adsorbed pollutants by hydrogen gas bubbles formed at the cathode [7–9]. The EC process takes advantage of the binding effect of charge neutralization/surface complexation/adsorption onto the in-situ formed metal hydroxides generated from the oxidation of sacrificial anode materials (e.g. Fe and Al). EC has been used for the treatment of various effluents generated from restaurant [10,11], silicon wafer polishing processes [12] and textile [7,13–17]. It was believed that the removal efficiency of pollutants by the electrochemical coagulation was higher than those by the chemical coagulation [18].

Dye wastewater is an environmental concern due to its huge quantity, variable nature, biologically-difficult-to-degrade chemical composition, and toxicity to aquatic life [19]. EC technology was widely used for the treatment of dye wastewater. Cañizares et al. [20] reported that the dye molecules were removed by the binding of Eriochrome Black T (EBT) molecules to the surface of small iron or aluminum precipitated particles. Golder et al. [21] studied the decolorization of aqueous solutions of methylene blue (MB) and eosin yellowish (EY) using mild steel electrodes and believed that the decolorization resulted from electrocoagulation. Merzouk et al. [22] used aluminum electrodes as anode electrode to treat a synthetic textile wastewater. The decolorization efficiency and the COD abatement were higher than 80%. Raju et al. [23] reported that the wastewater from a textile industry was initially treated by eletrocoagulation and then by electrooxidation. The level of COD of the effluent was high. Szpyrkowicz et al. [24] used electrooxidation technique to treat synthetic textile wastewater containing partially soluble disperse dyes and obtained 39% removal of COD after 40 min of electrolysis and 90% removal of color.

C.I. Acid Red 2 (methyl red) is a representative of organic compounds known as azo-dyes, which is widely used in the textile industries and analytical chemistry. The chemical structure and other characteristics of this dye are shown in Table 1. C.I. Acid Red 2 is resistant to the degradation by light, oxygen and common acids and bases [25]. In this paper, an aqueous C.I. Acid Red 2 solution was treated by electrolysis using carbon steel as anode, with an aim at understanding the mechanism on the decolorization of C.I. Acid Red 2. It was found that there was a synergetic effect of electrooxidation and electrocoaglation in the decolorization of C.I. Acid Red 2, resulting in a high decolorization efficiency.

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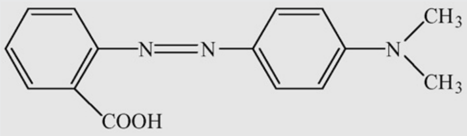
Table 1
Structure and characteristics of C.I. Acid Red 2.

Dye	C.I. Acid Red 2 (methyl red)
Structure	
λ_{max} (nm)	523
Chemical class	Monoazo
C.I. number	13020
M (g/mol)	269.30

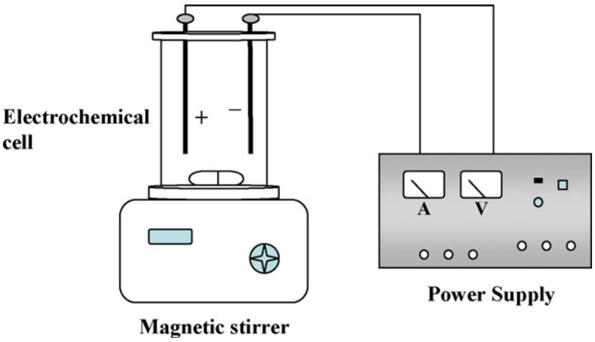


Fig. 1. Schematic diagram of experimental setup.

2. Experimental

2.1. Electrolysis

Electrolysis experiments were carried out in a batch electrolytic cell, as shown in Fig. 1. Carbon steel was used as anode and stainless steel (grade 316) was used as cathode. The distance between two electrodes during electrolysis was 1 cm and the effective area of the electrodes was 129.2 cm^2. Before experiment, the electrodes were immersed in 1.0 M HCl solution for 5 min and then rinsed by water. The electrolysis was carried out on a DC power supply under constant current density in the solution containing 100 mg L^{-1} C.I. Acid Red 2 and 0.005 mol L^{-1} Na_2SO_4, pH 3.10, at room temperature and under stirring. Na_2SO_4, instead of NaCl which has higher pollutant abatement efficiency, was used as electrolyte because it does not generate adsorbable organically bound halogens (AOX) that can be formed in chloride containing solution [26]. The current density was 2.2 mA/cm^2. The electrode distance, the concentrations of C.I. Acid Red 2 and Na_2SO_4, the pH of the solution, and the current density were selected based on the highest decolorization efficiency. More detailed information on the relation of the decolorization efficiency with electrolysis conditions will be reported in another paper.

2.2. Sweeping voltammetry

Sweeping voltammetric measurements were performed on a Pt rotating disc (d = 3 mm) by an Autolab PGSTAT-30 (Eco Echemine BV Inc.), in 0.1 mol L^{-1} Na_2SO_4 solution with and without 100 mg L^{-1} C.I. Acid Red 2 at room temperature. A platinum wire was used as the counter electrode and an Ag/AgCl electrode as a reference electrode. The potentials in this paper were with respect to this reference. Before sweeping voltammetric measurements, the working electrode was polished with 0.05 μm alumina, cleaned by ultrosonicating in acetone and distilled water successively, and then cycling in 0.5 M H_2SO_4 between 0.2 and 0.9 V at 100 mV s^{-1}.

2.3. Chemical and spectroscopic analyses

For the decolorization efficiency analyses, the solution was filtered through 0.45 μm millipore membrane filter to remove iron hydroxide flocs. The concentration of C.I. Acid Red 2 was determined from the UV absorbance recorded at 523 nm (λ_{max}) by a Shimadzu model UV-1700 double-beam spectrophotometer and the decolorization efficiency (%DE) was calculated from [27]:

$$\%\mathrm{DE} = \frac{A_o - A_t}{A_o} \times 100\% \qquad (1)$$

where, A_0 and A_t are the absorbance of the solution initially and at time t, respectively. The molar extinction coefficient of Acid Red 2 in the acidic (working) pH range at 523 nm was 1.48×10^3 L mol^{-1} cm^{-1}.

The chemical oxygen demand (COD) in the solution was determined by the standard method involving potassium dichromate. The COD reduction rate of the solution was obtained by the following equation:

$$\%\mathrm{COD\ reduction} = \frac{[(\mathrm{COD})_o - (\mathrm{COD})_t]}{(\mathrm{COD})_o} \times 100\% \qquad (2)$$

where $(\mathrm{COD})_o$ and $(\mathrm{COD})_t$ are the chemical oxygen demand of the solution before treatment and after treatment for a certain time, respectively.

Fourier Transform Infrared Spectroscopy (FT-IR) was recorded from 4000 to 450 cm^{-1} on Perkin Elmer instruments (Spectrum One FT-IR Spectrometer). The coagulated mixture was isolated from the tank and then dried at 40 °C (vacuum) to a constant weight. At last, the coagulated mixture was mixed with KBr and pressed into a disk for FT-IR analysis.

3. Results and discussion

3.1. Decolorization efficiency

The decolorization efficiency as a function of treatment time was obtained with a constant current of 2.2 mA/cm^2, in the solution containing 100 mg/dm^3 C.I. Acid Red 2 and 0.005 M Na_2SO_4, pH 3.10. The result is shown in Fig. 2. It can be seen from Fig. 2 that the decolorization efficiency drastically increases in the first 20 min, reaching over 80%. In the later 20 min, the decolorization efficiency increases slightly but reaches 98.0% after 40 min. The decolorization of C.I. Acid Red 2 should be related to the electrocoagulation because the mild steel is used as the anode. In fact, the coagulated mixture

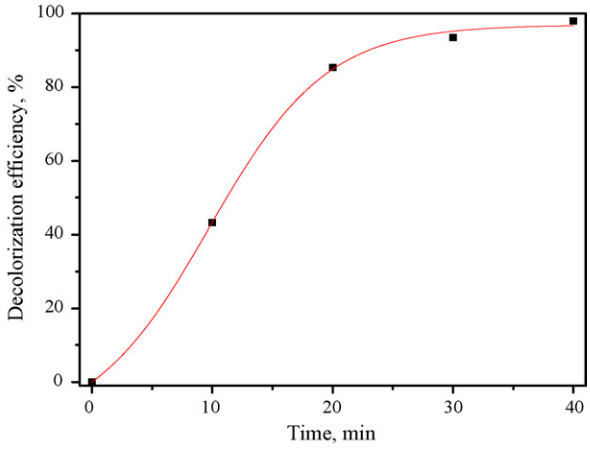


Fig. 2. The decolorization efficiency as a function of treatment time. Conditions: 0.005 M Na_2SO_4, initial pH 3.10, initial C.I. Acid Red 2 100 mg/dm^3, applied current density 2.2 mA/cm^2.