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Mineralization of an azo dye Acid Red 14 by photoelectro-Fenton process using an activated carbon fiber cathode

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ABSTRACT

The mineralization of an azo dye Acid Red 14 (AR14) by the photoelectro-Fenton (PEF) process was studied in an undivided electrochemical reactor with a RuO_2/Ti anode and an activated carbon fiber (ACF) cathode able to electrochemically generate H_2O_2. Anodic oxidation and UV irradiation of AR14 were also examined as comparative experiments. Results indicate that the electro-Fenton process yielded about 60–70% mineralization of AR14, while the photoelectro-Fenton could mineralize AR14 more effectively (more than 94% total organic carbon (TOC) removal) even at low current densities assisted with UV irradiation after 6 h electrolysis. The mineralization current efficiency (MCE) of the PEF process increased with the increasing AR14 concentrations. In addition, the initial solution pH ranging from 1.49 to 6.72 had little influence on the TOC removal probably due to the formation of organic carboxylic acids which balanced the pH increase caused by the cathodic generation of hydrogen gas. The ACF cathode showed a long-term stability during multiple experimental runs for degradation of AR14, indicating its good potential for practical application in treating refractory organic pollutants in aqueous solutions.

1. Introduction

Dyes present in wastewater are of particular environmental concern since they not only give an undesirable color to the waters but also in some cases are themselves harmful compounds and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase [1]. Most dyes are toxic and recalcitrant to biodegradation, causing a decay in the efficiency of biological plants currently used for the treatment of such wastewaters [2]. To avoid the dangerous accumulation of dyes in the environment, there is a need to develop effective methods for the degradation of such organic pollutants, either to less harmful compounds or, more desirable, to their complete mineralization.

Various treatment processes have been investigated to reduce dye concentrations in water and to minimize the potential health risks associated with exposure to the chemicals through consumption of contaminated waters. In recent years indirect electro-oxidation methods with hydrogen peroxide electrogeneration, such as electro-Fenton (EF) and photoelectro-Fenton (PEF) reactions, are being developed for the treatment of toxic and refractory organic pollutants in acid waters [3–30]. In these environmentally friendly electrochemical techniques, hydrogen peroxide is continuously generated in an acidic contaminated solution from the two-electron reduction of O_2 which takes place on graphite [3–5], reticulated vitreous carbon [6–9], mercury pool [10–12], carbon-felt [13–18] O_2-diffusion [19–29] and activated carbon fiber (ACF) [30] cathodes. In acidic aqueous medium the oxidation power will be enhanced by addition of ferrous ions to the solution that allows the production of a very reactive one-electron oxidizing agent hydroxyl radical ($^{\bullet}OH$) ($E^{\circ} = 2.8$ V/NHE) from the well-known Fenton reaction between both species with a second-order rate constant $k_2 = 53\ M^{-1}\ s^{-1}$ [11]. This $^{\bullet}OH$ radical acts as a non-selective, very strong oxidant agent with ability to react with organics giving dehydrogenated or hydroxylated derivatives, until achieving their total mineralization, i.e., their conversion into CO_2, water and inorganic ions [19]. The electro-Fenton process can generate $^{\bullet}OH$ by the simultaneous electrochemical reduction of O_2 in the presence of catalytic amounts of ferrous ions [14]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2, \quad E^{\circ} = 0.69\,\mathrm{V/NHE} \tag{1}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH, \quad k = 63\,\mathrm{L\,mol^{-1}\,s^{-1}} \tag{2}$$

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+}, \quad E^{\circ} = 0.77\,\mathrm{V/NHE} \tag{3}$$

$$H_2O \leftrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-, \quad E^{\circ} = 1.23\,\mathrm{V/NHE}$$

However, a significant drawback is the parasitic reactions, e.g., electrolysis of water often compete with the O_2 reduction and

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lower the energy efficiency [31]. Moreover, under most conditions pollutant impurities are present at such low concentrations that electrochemical processes are diffusion-controlled. The resulting diffusion-limited currents can, however, be enhanced at high-area, porous electrodes at which 2-dimensional electrochemistry is converted to "quasi-3-dimensional" behavior due to the large distributed area [32]. In our laboratory, the large surface area of ACF felt (BET 1297 $m^2 g^{-1}$) was developed for the cathode of electro-Fenton reaction. The mineralization of azo dye Acid Red 14 (AR14) by electro-Fenton reaction was achieved efficiently using the ACF felt cathode, at pH 3.0 and applied current 0.36 A, after 360 min electrolysis the total organic carbon (TOC) removal rate for 500 mL of a 200 mg L^{-1} AR14 in solution was 70% [30].

The oxidation power can be enhanced by introduced UV light into electro-Fenton process. UV light can accelerate the mineralization process by: (i) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids, e.g., oxalic acid. That is, at acidic pH, oxalic acids behave as photo-active complexes in the presence of ferric ions which undergo photo-decarboxylation reaction [33]:

$$\mathrm{Fe(III)(RCO_2)^{2+}} + h\nu \rightarrow \mathrm{Fe^{2+}} + \mathrm{CO_2} + \mathrm{R^{\bullet}} \tag{5}$$

and (ii) the regeneration of more Fe^{2+} from the additional photoreduction of $Fe(OH)^{2+}$, which is the predominant Fe^{3+} species in acid medium [20]:

$$\mathrm{Fe(OH)^{2+}} + h\nu \rightarrow \mathrm{Fe^{2+}} + {}^{\bullet}\mathrm{OH} \tag{6}$$

The objective of this work is to investigate the photoelectro-Fenton process based on ACF felt cathode for degradation of AR14 so as to compare the oxidative capability with electro-Fenton process. We focused on systematically investigating the degradation of AR14, a model chemical throughout the study to represent toxic contaminants with aromatic structures, by photoelectro-Fenton process. The effect of UV light, pH, Fe^{2+} concentration, initial AR14 concentration, iron ion type and applied current were also studied in detail in the experimental runs.

2. Experimental

2.1. Materials

The activated carbon fiber felt was obtained from Xuesheng Technology Co. Ltd. (Shandong, China), and its BET surface area, total pore volume, and mean micropore size of ACF, measured from N_2 adsorption using Micromeritics Model ASAP 2000, were shown in our another paper [30].

Acid Red 14(AR14), a commercial azo dye, whose chemical structure was given in Fig. 1, was used without further purification. Sulfuric acid, anhydrous sodium sulfate and heptahydrated ferrous sulfate were of analytical grade. Deionized and double distilled water was used throughout this study.

2.2. Electrolytic system

The experiments were conducted in an open, undivided cell with a capacity of about 0.5 dm^3 including an 11 W low pressure mercury lamp was positioned in a hollow cylindrical quartz tube (Fig. 2). The experiments were performed at constant currents supplied by a DC power supply. The 20 cm^2 (4 cm × 5 cm) area ACF felt was selected as cathode. A titanium grid, on the ACF felt, ensured the electric contact. The same solid surface area RuO_2/Ti mesh was selected as anode. The electrode distance was 4.5 cm. The solution was continuously stirred with a magnetic bar.

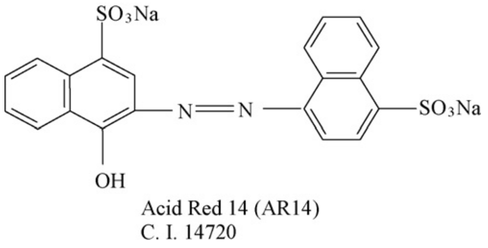

Fig. 1. Chemical structure for Acid Red 14 (AR14).

Prior to each electrolysis, the ACF felt cathode was first presaturated with 400 mg L^{-1} AR14 solution for 12 h to preclude the TOC decrease due to AR14 adsorption on ACF felt. AR14 was comparatively degraded in an acidic aqueous medium containing 0.05 M Na_2SO_4 as supporting electrolyte and 0.2 M H_2SO_4 was added to adjust its initial pH to 3.0 using an Orion model 720APLUS Benchtop pH meter (Thermo Orion Co., USA). Solutions of 450 mL with 200 mg L^{-1} of initial AR14 concentration were electrolyzed at constant current. During the electrolysis, O_2 was sparged near the cathode surface to ensure the essential oxygen for electrochemical reactions. A catalytic quantity of ferrous ion was introduced into the solution before the beginning of electrolysis.

2.3. Analytical method

Samples were withdrawn from the reactor at regular time intervals (0, 30, 60, 120, 180, 270, and 360 min, etc.). UV–vis spectra of the samples were recorded, between 190 and 650 nm, on a U-3010 UV–vis spectrophotometer (Hitachi Co., Japan) equipped with 10 mm quartz cuvettes. The decolorization of the solution was achieved by measuring the absorbance of the diluted samples (typically 1:4 in water) at 514 nm. The total organic carbon of the initial and electrolyzed samples was determined with Phoenix 8000 TOC analyzer (Tekmar–Dohrmann Co., USA).

The mineralization current efficiency (MCE) at a given time for the above solutions was then comparatively estimated from the following equation [23]:

$$\mathrm{MCE} = \frac{\Delta(\mathrm{TOC})_{\mathrm{exp}}}{\Delta(\mathrm{TOC})_{\mathrm{theo}}} \times 100 \tag{7}$$

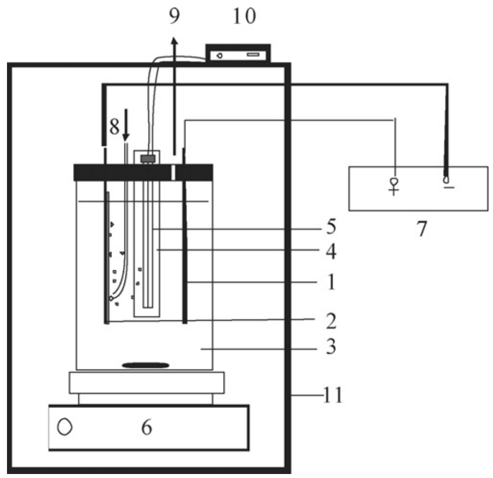

Fig. 2. Experimental set-up of the photoelectro-Fenton reactor. (1) RuO_2/Ti anode; (2) ACF cathode; (3) AR14 solution; (4) quartz tube; (5)11 W low-pressure Hg lamp; (6) magnetic stirrer; (7) DC supply; (8) O_2 in; (9) sampling; (10) UV switch; and (11) dark box.