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ScienceDirect

Journal of Hazardous Materials 145 (2007) 100–108

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Electrochemical degradation and toxicity reduction of C.I. Basic Red 29 solution and textile wastewater by using diamond anode

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Received 17 August 2006; received in revised form 31 October 2006; accepted 31 October 2006
Available online 7 November 2006

Abstract

Electrochemical oxidation of Basic Red 29 (BR29) was studied in a bipolar trickle tower (BTT) reactor by using Raschig ring shaped boron-doped diamond (BDD) electrodes, which were originally employed by the present researchers, in a recirculated batch mode. The model solution was prepared with BR29 using distilled water. The effects of initial dye concentration, Na_2SO_4 concentration as supporting electrolyte, current density, flow rate and initial pH on the removal efficiency were investigated, and practically, complete BR29 removal (over 99%) was obtained in all the studies. After optimum experimental conditions were determined, textile wastewater has also studied by monitoring the destruction of color and COD. With the textile wastewater, 97.2% of color and 91% of COD removal were, respectively, achieved at the current density of 1 mA/cm^2. Microtox toxicity tests were performed in both BR29 solution and textile wastewater under optimum experimental conditions, and relatively good toxicity reductions were obtained with respect to the initial values. According to the results, BDD anode was seen to be a unique material for the degradation of BR29 and COD and also the reduction of toxicity simultaneously.

Keywords: Electrochemical oxidation; Dye; Textile wastewater; Boron-doped diamond; Toxicity; Bipolar trickle tower reactor

1. Introduction

Textile wastewater is characterized by strong color, large amount of suspended solids, broadly fluctuating pH, high chemical oxygen demand (COD) and biotoxicity and causes coloring of the receiving water environment [1]. Different dyes result in wastewater with different colors and the variations in color induce variation in chemical oxygen demand (COD) of the wastewater [2]. The pH change is primarily caused by different kinds of dye stuffs used in the dyeing process. The pH value of the wastewater can range from 2 to more than 12. Textile wastewater, depending on dye used, can have a toxic effect on the living organisms in the receiving water, affects the ecosystem adversely, and reduces the assimilative capacity of the environment. The temperature of textile wastewaters is unusually high (typically 40 °C because of hot rinse waters and the temperatures up to 90 °C used in various steps in the dyeing process) in comparison with most industrial wastewaters [3]. For all these reasons, textile wastewater needs to be treated to satisfy discharging standards.

Textile wastewater is typically treated by conventional methods. During chemical precipitation, although additives increase treatment efficiency, a sludge disposal problem is created [3]. Ozone and hypochlorite oxidation are efficient decolorization methods, but they are not desirable due to the high investment and operational cost, and the secondary pollution arising from the residual chlorine [1]. The wide range of pH and elevated temperatures are also additional problems encountered when textile wastewaters are treated by conventional methods [3]. Azo dyes like BR29 (contain –N=N– bonds) are resistant to biodegradation under aerobic conditions whereas anaerobic treatment is applied successfully. However, textile wastewater is not proper to use anaerobic process because the breakdown of azo dye leads to the formation of aromatic amines, which may be more toxic than the dye molecules themselves [4]. Electrochemical methods are also used successfully for the degradation of dyes and treatment of textile wastewaters.

In recent years there has been an increasing interest in the use of electrochemical methods for the destruction of toxic and biorefractory organic pollutants. These methods use the electron

Abbreviations: BDD, boron-doped diamond; BR29, basic red 29; BTT, bipolar trickle tower; COD, chemical oxygen demand; HF CVD, hot filament chemical vapor deposition

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2006.10.090

as the main reagent, but also require the presence of supporting electrolytes. In general, the supporting electrolytes exist in the wastewaters to be treated, but not always in sufficient concentrations. These processes can operate at ambient temperature without a need of temperature control [5].

Decolorization can be achieved either by electrooxidation with insoluble anodes [1,5–12] or by electrocoagulation using consumable materials [13–18]. The degradation products in the oxidation of azo dyes are typically carbon dioxide, nitrate and sulfate, with the possible formation of aromatic esters, phenols, aromatic carboxylic acids, cyclic and aliphatic hydrocarbons, etc., as intermediates. Usually, the oxidation of azo group occurs, followed by the oxidation of the decomposition products [5].

Electrode material can influence the mechanism and consequently the products of anodic reaction. Electrode material is the most important parameter in the electrochemical oxidation of organics. BDD has a great potential for electrochemical applications, especially for the treatment of wastewater and drinking water because of the extraordinary chemical inertness offering the opportunity to use such electrodes (anodes as well as cathodes) in very aggressive media. The electrochemical properties of diamond provide a wide range of applications due to the extreme electrochemical window (>3 V) for almost any reaction at the surface, before hydrogen forms at the cathode and oxygen at the anode [19,20].

BDD anodes allow the direct production of hydroxyl radicals ($OH^{\bullet}$) from aqueous electrolysis with very high current efficiencies as dominant degradation mechanism in dye oxidation [21,22] according to Eq. (1).

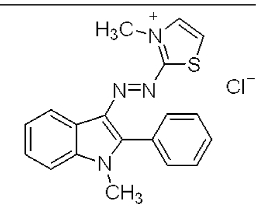
$$H_2O \rightarrow OH^{\bullet} + e^- + H^+ \quad (1)$$

Dissimilarity of this study from the others in the literature is the shape (Raschig ring) of BDD electrodes and BTT reactor used. Furthermore, toxicity studies performed in both model solution and textile wastewater could be a remarkable contribution to the literature.

2. Materials and methods

Aqueous solution of BR29 was chosen as the model wastewater. BR29 has been reported by the manufacturer as the mutagenic to the microorganisms and mammalian somatic cells at the chronic exposure [23]. The chemical structure and other characteristics of BR29 are shown in Table 1.

Table 1
Properties of Basic Red 29 (BR29)

Structural formulae (chemical structure)	
Synonym	Basacryl Red GL
Molecular formula	$C_{19}H_{17}ClN_4S$
MW (g/mol)	368.88
λ_{max} (nm)	511
Source/purity	Aldrich/19%

Experimental setup is illustrated in Fig. 1. BTT reactor had a volume of 125 mL and consisted of two concentric glass pipes with the inner diameters of 4 and 2.5 cm. The distance between the feeding electrodes was about 22.5 cm. BDD Raschig rings were used as working electrode and placed in the inner glass pipe at the bipolar electrode configuration. Raschig rings employed in the reactor had a height of 8 mm, and inner and outer diameters of 6 and 8 mm, respectively. Total surface area of BDD electrodes was 352 cm^2. BDD electrodes were provided from Magneto Special Anodes B.V. (Schiedam, The Netherlands) shaped as Raschig rings had an outer diameter of 0.8 cm and a height of 0.8 cm. The BDD electrodes consisted of thin (2–7 (m), highly conductive (<0.1 (cm) BDD films, deposited on niobium substrates via the hot filament chemical vapor deposition technique (HF CVD) from a gaseous feed of methane and a boron doping agent in dihydrogen.

Experiments were carried out in a recirculated batch mode at ambient temperature and wastewater was fed to the reactor by means of a peristaltic pump. Model solution was recirculated through the electrochemical reactor with the flow rates of 24.83, 36.3 and 47.8 mL/min (1.5, 2.2 and 2.9 L/h). Current densities of 0.25, 0.5, 0.75 and 1 mA/cm^2 were studied to observe their effects. pH values of 3, 5.8 (original pH of the BR29 solution) and 11 were studied to investigate the effect of initial pH of the solution. In addition, supporting electrolyte concentration was also studied using the solutions of 0.01, 0.03, 0.04 and 0.05 M Na_2SO_4. pH of the working solution was monitored throughout the studies.

Wastewater characteristics of textile wastewater which was provided from a local plant are given in Table 2.

2.1. Analysis

BR29 (ALDRICH) was preferred to prepare the model solution and, Na_2SO_4 (MERCK) for the formation of the supporting electrolyte solution. pH of the solutions were adjusted with H_2SO_4 (MERCK) and NaOH (MERCK). All chemicals used were analytical grade.

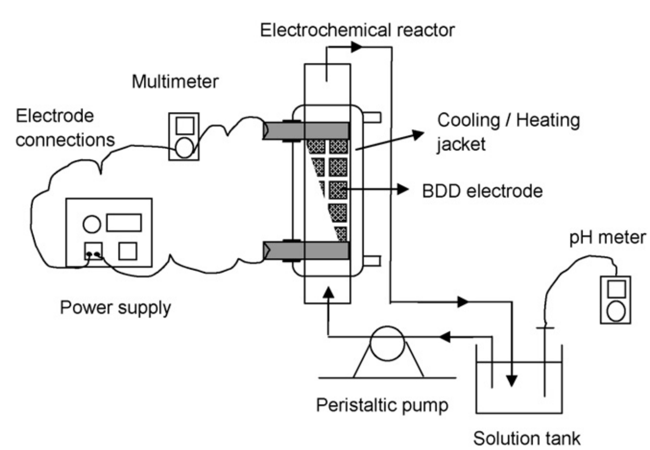


Fig. 1. Experimental setup used in the studies.