Chemosphere 171 (2017) 332–338

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Electrochemical oxidation of COD from real textile wastewaters: Kinetic study and energy consumption

Jiaxiu Zou [a], Xiaolan Peng [a], Miao Li [b], Ying Xiong [a, *], Bing Wang [b], Faqin Dong [c], Bin Wang [c]

[a] State Key Laboratory Cultivation Base for Non-metal Composites and Functional Materials, Southwest University of Science & Technology, Mianyang 621010, PR China
[b] School of Materials Science & Engineering, Southwest University of Science & Technology, Mianyang 621010, PR China
[c] Key Laboratory of Solid Waste Treatment and Resource Recycle of Ministry of Education, Southwest University of Science & Technology, Mianyang 621010, PR China

HIGHLIGHTS

- Real textile wastewaters were electrooxidized using BDD anode.
- COD oxidation could be well fitted using a modified kinetic model.
- High COD removal rates were attained with adding NaCl and in acidic media.
- Low energy consumption and short electrolysis time could be obtained under the optimizing conditions.

ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form
8 December 2016
Accepted 15 December 2016
Available online 19 December 2016

Handling editor: Enric Brillas

Keywords:
Textile wastewaters
Electrochemical oxidation
Kinetic study
BDD anode
Energy consumption

ABSTRACT

In the present study, the electrochemical oxidation of real wastewaters discharged by textile industry was carried out using a boron-doped diamond (BDD) anode. The effect of operational variables, such as applied current density (20–100 $mA \cdot cm^{-2}$), NaCl concentration added to the real wastewaters (0–3 $g \cdot L^{-1}$), and pH value (2.0–10.0), on the kinetics of COD oxidation and on the energy consumption was carefully investigated. The obtained experimental results could be well matched with a proposed kinetic model, in which the indirect oxidation mediated by electrogenerated strong oxidants would be described through a pseudo-first-order kinetic constant *k*. Values of *k* exhibited a linear increase with increasing applied current density and decreasing pH value, and an exponential increase with NaCl concentration. Furthermore, high oxidation kinetics resulted in low specific energy consumption, but this conclusion was not suitable to the results obtained under different applied current density. Under the optimum operational conditions, it only took 3 h to complete remove the COD in the real textile wastewaters and the specific energy consumption could be as low as 11.12 $kWh \cdot kg^{-1}$ COD. The obtained results, low energy consumption and short electrolysis time, allowed to conclude that the electrochemical oxidation based on BDD anodes would have practical industrial application for the treatment of real textile wastewater.

1. Introduction

Synthetic organic dyes have been extensively used in many industries such as textile, cosmetic, paper, pharmaceuticals and food, thus producing large volumes of wastewaters with high concentration of dyes and other organic and/or inorganic compounds (Martínez-Huitle and Brillas, 2009; Brillas and Martínez-Huitle, 2015; Zhao et al., 2016). The discharge of these colored wastewaters in the environment, without meeting required standard, would result in considerable non-aesthetic pollution and serious health-risk factors (Forgacs et al., 2004). Thus, it is necessary to apply reliable and effective treatment technologies, capable of dealing with these organic dyes, before they are entered into the surface and groundwater. Conventional treatments, such as

* Corresponding author.
E-mail address: xiongying@swust.edu.cn (Y. Xiong).

http://dx.doi.org/10.1016/j.chemosphere.2016.12.065
0045-6535/

physical adsorption, separation, chemical and microbiological oxidation, have encountered hard difficulties to solve when facing to these dyes effluents, thus cannot completely degrade the majority of these contaminated dyes (Robinson et al., 2001; Forgacs et al., 2004; Santos et al., 2007; Ulson de Souza et al., 2007). Over the past 10 years, the application of conductive BDD anode in the abatement of *synthetic or simulated dyes wastewaters* have received great attention, because of several technologically important characteristics of BDD anode including high O_2 evolution overvoltage, an inert surface with low adsorption properties, remarkable corrosion stability (Sáez et al., 2007; Panizza and Cerisola, 2008; Andrade et al., 2009; Palma-Goyes et al., 2010; Migliorini et al., 2011; Petrucci and Montanaro, 2011; Aquino et al., 2012; Abdessamad et al., 2013; Rocha et al., 2014; Garcia-Segura et al., 2015; Fan et al., 2016; Migliorini et al., 2016). But until now, there are only a few reports about the electrochemical treatment of *real textile wastewaters* using BDD anode (Aquino et al., 2011; Zhu et al., 2011; Martínez-Huitle et al., 2012; Tsantaki et al., 2012; Solano et al., 2013).

Compared to the synthetic dyes effluents, real textile wastewaters are more complex and usually contain organic dyes with high concentration, inorganic ions such as chloride and sulfate, as well as many other soluble compounds. During the electrochemical oxidation of real textile wastewaters, competitive reactions may occur at the anode surface and/or in the homogeneous phase, and the different species obtained may interact creating complex scenarios that are difficult to describe, which is disadvantage to further take the new technique into practice (Anglada et al., 2009). Therefore, it is necessary to have a better understand on the electrochemical oxidation process using consistent mathematical models that can describe the reactions involved in the electrooxidation of multicomponent mixtures of various pollutants. In the last decade, several mathematical models have been successively proposed to describe the processes occurring in the anodic oxidation of organic compounds at BDD anode (Panizza et al., 2001; Cañizares et al., 2004; Mascia et al., 2010; Tissot et al., 2012; Hems et al., 2016). These models can reproduce the experimental results obtained from *synthetic wastewaters* with a wide variety of organic substrates with great precision, but they still have to be validated for *real wastewaters* with complex and unknown detailed composition. Recently, several groups have focused their attention on clarifying the relationship between the operating variables and the kinetic behaviors of electrochemical removal of ammonium, nitrites and COD from *various real wastewaters*, such as landfill leachates, rubber manufacturing wastewaters and recirculating aquaculture saline solutions (Díaz et al., 2011; Pérez et al., 2012; Urtiaga et al., 2012, 2014). However, the kinetic study of electrochemical treatment of *real textile wastewaters* has been few reported using BDD anode.

For these reasons, the aim of this study is to investigate the viability of electrochemical oxidation using BDD anode as an alternative to treat *real textile wastewaters*. Particular attention has been devoted to the effect of several operating variables, such as applied current density (j), NaCl concentration, and pH value, on the kinetic behavior of COD oxidation. Finally, by optimizing the operational variables, the energy consumption for the COD removal has been also assessed.

2. Material and methods

2.1. Chemicals

All analytical reagents including NaCl, NaOH, H_2SO_4 (98%), $K_2Cr_2O_7$ and $(NH_4)_2Fe(SO_4)_2$ were bought from Sinopharm Chemical Reactant Co. Ltd, and used as received. Deionized water (Millipore Milli-Q system, resistivity $\geq$ 18.2 MΩ·cm) was used for the preparation of all solutions.

2.2. Characteristics of real textile effluent

The wastewater samples were provided by a local textile plant in Santai county, Sichuan province, and directly collected at the entrance reservoir. As-received textile wastewater was mainly composed of dyes and various organic/inorganic additives. The exact composition could not be obtained due to possible commercial secret. It has high COD concentration (2154 mg/L) and poor biodegradability ($BOD_5/COD_{Cr} = 0.13$). Its conductivity was 11.6 mS/cm and the pH was around 12.6. Ion chromatography measurements revealed the textile wastewaters contained chloride (731 ppm) and sulfate ions (1690 ppm). It should be noted here that no physical-chemical treatment were performed for the textile wastewaters before the electrochemical oxidation.

2.3. Electrochemical oxidation experiments

The oxidation experiments were performed in a Diacell®201 commercial electrolytic cell (WaterDiam, Switzerland), which are formed by two parallel flow-by compartments separated by a central bipolar boron-doped diamond electrode, working as anode for one compartment and as cathode for another one (Urtiaga et al., 2014). The mono- and bipolar BDD electrodes supported by monocrystalline Si substrate, with the thickness of 2 μm and the working surface of about 70 cm^2, were bought from NeoCoat SA Co. The doping concentration of boron atoms in BDD electrodes was about 5000 ppm, and the sp^3/sp^2 ratio was about 200. The electrode distance was kept to be 1 mm. A feed tank with water-cooled system and the capacity of 10 L was used to store the textile wastewaters that were circulated by a centrifugal pump with a constant flow-rate of 400 L/h. Before the electrochemical oxidation of textile wastewaters, the anodic polarization procedure of Si/BDD electrodes was carried out in the diluted H_2SO_4 solution by applying 60 mA/cm^2 for 30 min. It should be stressed that in each electrochemical oxidation the volume of textile wastewater was kept at 5 L. The main operational variables included applied current density j, NaCl concentration added into the wastewaters, and pH value. At given time intervals, liquid samples were withdrawn from the feed tank. The electrochemical effectiveness in the oxidation of real textile wastewaters was assessed by the COD removal of the collected sample.

2.4. Analytical methods

The COD values were determined by the standard dichromate method on 10 mL samples. After refluxed at 150 °C for 2 h and then returned to ambient temperature, ammonium ferrous sulfate ($(NH_4)_2FeSO_4$) solution was used to titrate the residual dichromate ions. The pH and conductivity were detected with the pH-201 pH meter and the DDS-307 conductivity meter.

3. Results and discussion

Electrochemical oxidation of organics at BDD anode has been achieved through three possible mechanisms: direct electron transfer from the anode to organics, oxidation mediated by hydroxyl radicals (•OH) occurring in a thin layer close to the anodic surface, and oxidation mediated by electrogenerated strong oxidizing species such as active chlorine, hydrogen peroxide and peroxidisulfate, often appearing in the homogeneous phase (named as indirect oxidation) (Scialdone and Galia, 2011; Araújo et al., 2015). In the model proposed by Comninellis et al., kinetics