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Electrochemical degradation of reactive brilliant red X-3B with the (CeO_2/C)-β-PbO_2-PTFE composite electrode

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Abstract: The (CeO_2/C)-β-PbO_2-PTFE composite electrodes modified by graphite powder, cerium oxide powder, polytetrafluoroethylene (PTFE) and the homemade β-PbO_2 powder were prepared by the high pressure molding technique. The X-ray diffraction (XRD) was used to test the purity of the homemade β-PbO_2 powder. The surface structure and electrical property of electrodes were characterized by using scanning electron microscopy (SEM) and the cyclic voltammetry curves (CV). Those images indicated that in electrolysis the (CeO_2/C)-β-PbO_2-PTFE composite electrodes had higher activity than the β-PbO_2-PTFE electrodes, as good as the excellent catalytic performance. In the electrode system the composite electrodes were applied to treat reactive brilliant red (RBR) X-3B solution and we studied the degradation influence factors and the reaction mechanism. The results showed that the electrode system was well in treating RBR X-3B solution with the 20%(CeO_2/C)-β-PbO_2-PTFE composite electrodes at the initial 100 mg/L RBR X-3B concentration, Na_2SO_4 concentration of 0.35 mol/L, the constant current density of 30 mA/cm^2 and electrolyte pH=2. After electrolytic time of 90 min, the maximum decolorization and chemical oxygen demand (COD) removal rates reached 88.92% and 54.54%. And the decolorization rate of RBR X-3B was in conformity with pseudo-first-order kinetics equation. The RBR X-3B degradation mechanism in the electrochemical oxidation system was used with LC-MS to analyze the possible intermediates and degradation pathway.

Keywords: CeO_2; PbO_2; reactive brilliant red X-3B; chemical oxygen demand; decolorization; rare earths

In recent years, with the rapid growth of the economy in our country, the dyeing and printing industry is rapidly developing. The types of the printing and dyeing wastewater are dramatically increasing, and the colored organic pollution has caused serious environmental problems[1]. All over the world, over half of the production and consumption of total dyes have been polluted and are deemed as azo dye[2]. Reactive brilliant red (RBR) X-3B is a kind of azo dye and considered to be stable[3]. So choosing economic and efficient wastewater treatment technology has become the key to the problem that the printing and dyeing industry must solve. Printing and dyeing wastewater is very complicated and difficult to be degradation. The traditional wastewater treatment technology has difficulty in dealing with it. And development of new wastewater treatment technology has become the research hot spot. Now as a kind of green production processing technology and a kind of efficient methods of the organic pollutants degradation, electrochemical oxidation technology has gradually become a new research direction of printing and dyeing wastewater treatment technology and the governments have paid attention to it[4]. The anode material is the important factor of electrochemical oxidation for treating organic wastewater[5]. Thus the choice of anodic materials depends on high efficiency, reliability and electro-catalysis for the electrochemical destruction of organic compounds. In the electrochemical water treatment technology, lead dioxide as a kind of anode material has good conductivity, high oxygen evolution potential, good stability and the advantages of low price important anode materials[6,7]. So lead dioxide of anodic materials is widely researched and applied. Currently the dimensionally stable anodes (DSA) is an important direction of research on lead dioxide electrode[8]. But electrode coating is easy to fall off and the question has not been solved. Using high pressure molding technique is simple in the process and fundamentally solves the problem of the coating[9]. Some similar work has been done. Cao et al.[10] compared the β-PbO_2 electrode with the graphite electrode and indicated that the degradation effect of the β-PbO_2 electrode was better than that of graphite electrode and β-PbO_2 electrode had very good application prospect. The rare-earth modification mixed by TiO_2[9] and La[11] could generate very good activity. Shan et al.[12] and Li et al.[13] found that the electrode had good degradation effect with doping some manganese mineral powder. Some other researchers[11,14–16] also made electrodes by doping nonmetal of

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graphite and activated carbon and changed the physical and chemical properties of the electrodes. In this paper, the (CeO_2/C)-β-PbO_2-PTFE composite electrodes were successfully prepared by using high pressure molding technique. RBR X-3B dye wastewater treatment was studied to explore the optimal operating conditions and provided the theoretical basis on its application in industry. And the composite electrode was used as the anode on the electro-catalytic degradation to dispose of RBR X-3B simulated wastewater. The effect of doping amount, initial RBR X-3B concentration, current density, solution pH value, and electrolyte concentration on RBR X-3B degradation was systematically studied. In order to provide theoretical and technical foundation in the industry, the degradation kinetics of RBR X-3B was preliminarily discussed.

1 Experimental

1.1 Chemicals and instruments

1.1.1 Chemicals

Reactive brilliant red X-3B used in this work was purchased from Shanghai Dyestuffs Co., Ltd. in China. The structure formula and general characteristic of RBR X-3B are given in Table 1. The deionized water was used to prepare the solution throughout this study. All other chemicals were analytical grade reagent.

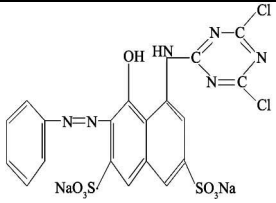
1.1.2 Electrochemical characterization analytical instruments

Electrochemical workstation (CHI 660 C, Shanghai Chen Hua Instrument Co., Ltd.), DC Power Supply (RXN-605D, Shenzhen Qiqilin Electric Manufacturing Co., Ltd.), COD JRY (5B-1F, Shanghai Lian Hua Tech Co., Ltd.), pH meter (PHS-3C, Shanghai Truelab Instrument Co., Ltd.), Tablet press machine (HY-12, Tianjin), UV-Visible spectrophotometer (TU-1900, PERSEE), Electromagnetic stirring (S-25, IKA Topoline), scanning electron microscope (S-3400N, HITACHI), atomic absorption spectrometer (TAS-990F, Beijing PERSEE Instrument Co., Ltd.).

1.1.3 Physical characterization analytical instruments

The surface morphologies of samples were characterized by a HITACHI S-3400N SEM at an accelerating voltage of 15 kV.

Table 1 General characteristic of RBR X-3B

Name	RBR X-3B
Chemical structure	
Molecular formula	$C_{19}H_{10}O_7N_6S_2Cl_2Na_2$
Molecular mass/(g/mol)	615
Solubility in water/(g/L, 20 ºC)	80

A PANalytical X'Pert PRO X-ray diffractometer analyzer with Cu Kα (λ=0.15418 nm) incident radiation was used to test the crystal structure in materials. The X-ray diffraction (XRD) patterns were obtained for 2θ angles from 20º to 90º. The tube voltage is 40 kV. In the experiment the scanning rate is set as 6 (°)/min and sampling interval is 0.02(º)/min.

Cyclic voltammetry curve was tested with standard three-electrode cell. The homemade electrode served as target electrode. Pt was used as auxiliary electrode. Meanwhile standard saturated calomel electrode was used as reference electrode.

In electrochemical oxidation system degradation products were studied by using a liquid chromatography mass spectrometer (LC-MS). To do the analysis, 1 μL aliquots were used with the Millipore filter of 0.22 μm and injected into LC, using the acetonitrile/water (*v*/*v*)=50/50 of the mixture. It was used with 0.2 mL/min as mobile phase.

1.2 Electrode preparation

1.2.1 β-PbO_2 powder preparation[17]

10 g lead acetate was dissolved in 20 mL water. 0.5 g solid sodium hydroxide was added into the solution for adjusting pH value in a certain range from 9.0 to 10.0. After being dissolved completely, sodium hypochlorite of 80 mL was added. Then this was stirred well. And at the temperature of 90 ºC, the solution reaction continued for 6 h. Through the reaction solution filtered and at the same time the solid was washed and dried, and brown powder was obtained. The filtrate was observed with potassium chromate solution and the testing did not find yellow lead chromate precipitate generated, which indicated that the reaction was complete.

1.2.2 (CeO_2/C)-β-PbO_2-PTFE composite electrodes preparation

Take several copies of a certain quantity of homemade powder. Then separately mixed them with the same rare earth material of cerium oxide powder and graphite powder, and stir well. Then add the PTFE emulsion in the mixture. Straight after those being stirred and dried well, put them into the mold and maintain a certain pressure in 2 min. Finally we could get the (CeO_2/C)-β-PbO_2-PTFE composite electrodes.

1.3 Experimental set-up

Electrochemical oxidation reacted in an electrochemical system with effective electrolyte volume of 60 mL within the anode and cathode cells. The electrolytic cell was fabricated by PTFE material. The homemade electrodes (radius: 11 mm; thickness: 2 mm) served as the working electrodes. The effective electrodes area was 3.14 cm^2 and the distance between the anode and cathode was 1 cm. In all tests, the effective electrodes area was