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Degradation Characteristics of Cationic Red X-GRL with Gd, La Co-doped PbO_2 Electrode

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Abstract: *To enhance the degradation efficiency as purpose, the* Gd_2O_3 *and* La_2O_3 *were doped in the lead dioxide electrode by the thermal decomposition and electro-deposition technique for the treatment of simulated wastewater containing cationic red X-GRL (X-GRL). The optimized molar ratio of Pb:Gd:La of 200mol:3mol:1mol, and the optimal degradation conditions of current density 50* mA/cm^2*, 0.1 mol/L* Na_2SO_4*, initial quality concentration of X-GRL 100 mg/L, after 2 h degradation, the X-GRL and TOC removal of reached 97.81% and 51.28%, respectively. The efficiency of combustion (*η_c*) of rare earth co-doped electrode was increased by 0.257 than that of un-doped electrode.*

Keywords: rare earth co-doped; PbO_2 *electrode;* Gd_2O_3*;* La_2O_3*; cationic red X-GRL*

1. INTRODUCTION

The existing processing methods could not obtain satisfied results for azo dyeing wastewater with increasingly strict environmental standard, which had become serious environmental problems [1-3]. Many technologies to remove azo dyes from wastewaters have been developed, such as electrochemical oxidation, photochemical oxidation, ozone oxidation and supercritical water oxidation treatment, etc [3-5]. Among them, electrochemical method offers the prospect of relatively simple equipment, environmental friendliness, and the possibility of high-energy efficiency [6-7]. Furthermore, electrochemical oxidation technology could be used for degradation of refractory pollutants [8-10]. However, there still have some limites due to the disadvantage of traditional electrode with low efficiency and weak stability. Therefore, various kinds of electrode materials including BDD and various metal oxide-film electrodes, e.g., PbO_2, SnO_2 and RuO_2 had been studied [11-14]. Among these, PbO_2 was potential widely used in organic wastewater pollution control because of its higher stability, higher activity and lower cost. But, there are some problems still not completely resolved, such as the lifetime was short and the catalytic activity was shortages [15-17].

The chemical composition and structure of the coating on electrode surface are the major factors of the electrocatalytic characteristics and stability of the dimensionally stable anode (DSA). The introduction of small amounts dopants, such as Fe^{2+}, Co^{2+}, F^-, and so on [18-22], which improve the performance in degradation progress, and minish the size of crystal on the surface of electrode. Rare earth metals, for its special 4f electronic structure, had been successfully applied in the petrochemical industry and in fuel cells. Some reports also indicated that the addition of rare earth, such as Gd, Ce and La [23-27], could get better property in the electrochemical degradation process than pure PbO_2 electrodes [12].

In this work, based on the previous work [7, 26], In order to obtain higher degradation efficiency, the oxides of rare earth (La_2O_3 and Gd_2O_3) were co-doped in lead dioxide anodes to modify the electrode film. According to the degradation of X-GRL and its TOC, the optimized co-doped molar ratio of Gd and La was determined. Furthermore, the degradation efficiency of *X-GRL* with co-doped electrode was analyzed.

2 MATERIALS AND METHODS

2.1. Preparation of electrode

The PbO_2 film of electrodes was prepared by the thermal decomposition and electro-deposition technique[25-27], and the PbO_2 film was composed by α-PbO_2 layer and β-PbO_2 layer. Suitabler quantity of rare earth oxides (Gd_2O_3 and La_2O_3) were added

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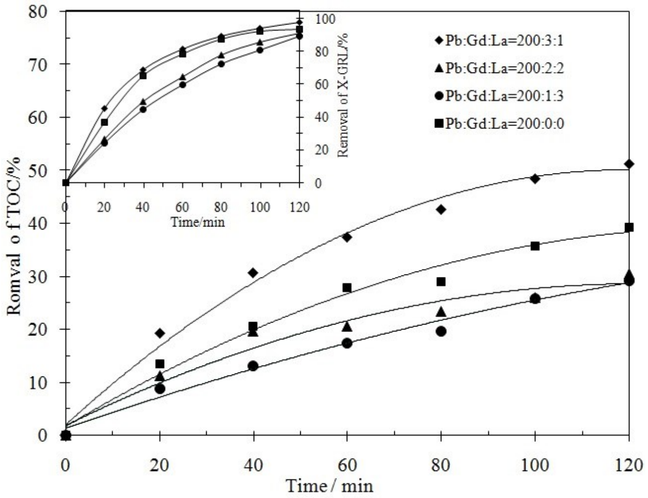

Figure 1. The degradation efficiency of different co-doped ratios of PbO_2 electrode

into the electroplating solution for the electrodeposition of the co-doped PbO_2 electrode. In the experiments, all reagents used were analytic grade and solutions were prepared using ultrapure water purified with a RO system (>18 MΩ·cm).

2.2. Methods and analyze

The samples were selected depending on the time duration of 0, 20, 40, 60, 80, 100 and 120min. The concentration of cationic red X-GRL was measured by the spectrophotometer (U-2910, Hitachi, Japan). The UV detector was set at 230 nm. The chemical oxygen demand (COD) was measured by dichromate method, and the detection wavelength was 440 nm (U-2910, Hitachi, Japan). Total organic carbon (TOC) was detected by TOC automatic analyzer (TOC-V CPH, SHIMADZU, Japan).

The electrochemical oxidation system was mainly composed by two working electrodes (active area was 70×30 mm^2), and an electrolysis cell (working volume was 250 mL).

3. RESULTS AND DISCUSSION

3.1. Effect of different Gd, La co-doped molar ratio

The effect of different co-doped molar ratio (Pb : Gd : La = 200:0:0, 200:1:3, 200:2:2 and 200:3:1) on the degradation of waste water was investigated at $300mg\cdot L^{-1}$ X-GRL, pH=2, $0.1mol\cdot L^{-1}$ Na_2SO_4 and $50mA\cdot cm^{-2}$ current density. The result was shown in Figure 1.

As could be seen, when the molar ratio was Pb:Gd:La = 200:3:1, the maximum removal of all organic species in solution (indicated by X-GRL and its TOC concentrations) was achieved. The removal of TOC by the co-doped electrode (Pb : Gd : La = 200:3:1) was 51.28%, which was higher than that of un-doped electrode (39.29%) and else. Therefore, it could be concluded that suitable co-doped molar ratio could significantly improve the degradation efficiency. The co-doped electrode (Pb : Gd : La= 200:3 1) possessed an excellent degradation ability on both X-GRL and its TOC as well.

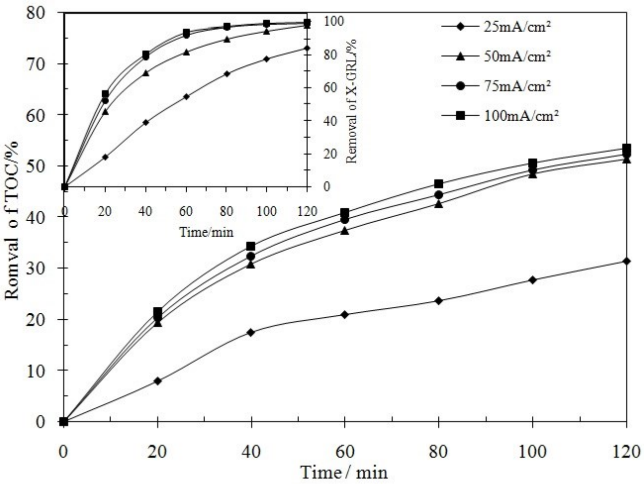

Figure 2. The effects of current density on degradation efficiency of X-GRL

A higher degradation efficiency of TOC could not only avoid the accumulation of intermediates on the surface of electrode ,but also improved the mass transfer condition of the electrochemical oxidation system. The same general trend in the rate of X-GRL removal during the degradation process was observed (see inset in Figure 1). Thus, the co-doped electrode (Pb : Gd : La= 200:3 1) was selected as the working electrode.

3.2. Effect of current density

Different current density (25, 50, 75 and 100 mA/cm^2) on the degradation of 100 mg/L X-GRL was investigated at 0.1 mol/L Na_2SO_4 and suitable Gd doped molar ratio (Pb : Gd : La = 200:3:1). The removal rates of X-GRL and its TOC obtained with different current density conditions were illustrated in Fig. 2.

These results showed that the degradation efficiency increased with the increase of current density from 25 mA/cm^2 to 100 mA/cm^2. This result also indicated that high current density could significantly promote the degradation efficiency. However, with the increase of current density, oxygen evolution reaction, which wasted electric energy and declines the current efficiency, would be intensified. So, appropriate current density should be selected. Combined the results of the removal of X-GRL and its TOC, 50 mA/cm^2 was selected as the suitable one for higher degradation efficiency and better energy utilization ratio.

3.3. Effect of concentration of electrolyte

Strong electrolyte (Na_2SO_4) could upgrade the conductivity of X-GRL solution for the low conductivity of X-GRL. Therefore, in order to evaluate the influence of electrolyte (Na_2SO_4) on the X-GRL degradation, different concentration of Na_2SO_4 (0.05, 0.1, 0.2 and 0.4 mol/L) were tested under the condition of 300 mg/L X-GRL by co-doped PbO_2 electrode (Pb : Gd : La = 200:3:1). The result was shown in Fig. 3.

Fig.3 presented the degradation rates of X-GRL and its TOC with the different electrolyte concentration in electrochemical oxidation system. After 2 h degradation, the degradation rates of X-GRL were 93.55%, 97.81%, 96.57% and 95.17%, and its TOC

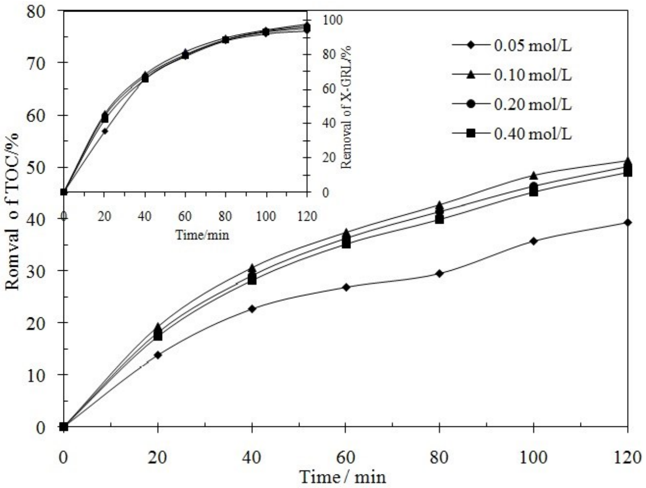

Figure 3. The effects of Na_2SO_4 concentration on degradation efficiency of X-GRL

removal rates were 39.33%, 51.28%, 50.08% and 48.99% at electrolyte concentration of 0.05, 0.1, 0.2 and 0.4 mol/L, respectively, showing that an increase in electrolyte concentration could not always mean an promotion in the degradation efficiency.

When the electrolyte (Na_2SO_4) was high concentration, with the same current density, the electric voltage between the anode and the cathode would decrease, which would influence the occurrence of some chemical oxidation reactions. Therefore, too high concentration of electrolyte would lead to the decrease of the degradation efficiency. The result showed that the electrolyte concentration conditions, 0.1 mol/L Na_2SO_4 was an optimized factor with higher degradation on both X-GRL and its TOC.

3.4. Effect of initial concentration of pollutant

The effect of the different initial concentrations of X-GRL (100 mg/L, 200 mg/L, 400 mg/L, 800 mg/L and 1200 mg/L) on the degradation efficiency was investigated by co-doped PbO_2 electrode (Pb:Gd:La = 200:3:1) under the conditions of 50 mA/cm^2 and 0.1 mol/L Na_2SO_4. The result was shown in Fig. 4.

The trend of X-GRL and its TOC removal rate increased with the decrease of X-GRL initial concentration could be observed in Fig. 4. The removal rates of X-GRL were 100%, 99.71%, 97.81%, 93.15% and 95.17%, and its TOC removal rates were 57.53%, 56.87, 51.28%, 43.39% and 36.54% at initial concentration of pollutant (100, 200, 300, 400, 800 mg/L), respectively, after 2 h degradation. Suitable initial concentration of pollutants (X-GRL) can get the best degradation efficiency and The biggest total removal amount of pollutant in the electrochemical oxidation system. According to the results above, 300mg/L X-GRL initial concentration was the optimal one.

3.5. The degradation efficiency of *X-GRL* with co-doped electrode

The efficiency of combustion (ηc) was introduced to estimate the degradation efficiency and the accumulation of intermediates above surface of the rare earth co-doped electrode in this experimental.

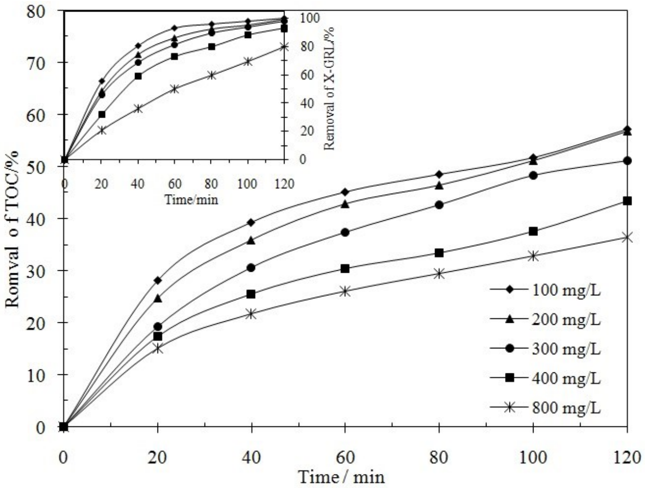

Figure 4. The effects of initial concentration on degradation of X-GRL

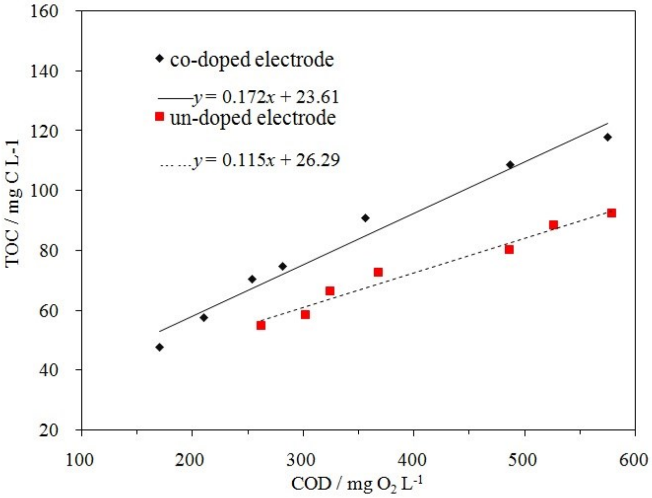

Figure 5. TOC *vs*. COD evolution at 50mA·cm^{-2}, 0.2 mol·L^{-1} Na_2SO_4 and 300mg·L^{-1} X-GRL by co-doped electrode (Pb:Gd:La = 200:3:1)

And, ηc could be calculated from the rate of decrease of total organic carbon (TOC) compared to that of chemical oxygen demand (COD), by determining the *d*TOC/*d*COD ratio [28]. The combustion efficiency was given by:

$$\eta c = \frac{32}{12}\left(\frac{n}{4x}\right)\frac{dTOC}{dCOD} \qquad (1)$$

where n is the number of electrons transferred in the process of the pollutant complete combustion. And, x is the number of carbon atoms of the organic compound. TOC and COD are expressed in mg·C·L^{-1} and mg·O_2·L^{-1}, respectively.

In this case, n and x can be achieved from the following equation:

$$C_{18}H_{21}N_6Cl_3Zn + 54H_2O \rightarrow \\ 18CO_2 + 6NO_3^- + 3Cl^- + 129H^+ + 122e^- + Zn^{2+} \qquad (2)$$

The change of *d*TOC/*d*COD ratio for assays conducted at $50\text{mA}\cdot\text{cm}^{-2}$, with $300\text{mg}\cdot\text{L}^{-1}$ X-GRL solutions, at both anodes (undoped and rare earth co-doped electrodes) were shown in Figure 5. The ηc was calculated with the slopes from Figure 5 (0.115 for undoped electrode and 0.172 for co-doped electrode) and a value of 4.518 for the parameter of Eq. (1) (32/12)(*n*/4*x*). When the current density was 50 $\text{mA}\cdot\text{cm}^{-2}$, the combustion efficiency was higher for the rare earth co-doped electrode (0.777) than the un-doped electrode (0.520). The results implied that metabolites could be mineralized effectively and formation of polymer film would be finally avoided on the co-doped electrode surface during the degradation process.

4. CONCLUSIONS

1) The novel PbO_2 electrode co-doped with rare earth oxides (La_2O_3 and Gd_2O_3) (La-Gd-β-PbO_2) was prepared by electrodeposition technique. Based on the comparison of degradation efficiency of X-GRL and its TOC by electrodes with different co-doped molar ratios, the optimized co-doped molar ratio was Pb:Gd:La of 200:3:1.
2) The maximum degradation efficiency was achieved by co-doped PbO_2 electrode(Pb : Gd : La = 200:3:1) with 300 mg/L X-GRL, 0.1 mol/L electrolyte (Na_2SO_4) and 50 mA/cm^2, in the electrochemical oxidation system. And the maximum degradation efficiency of X-GRL and its TOC reached to 97.81% and 51.28%, respectively, after 2h treatment.
3) According to the degradation of *X-GRL*, the combustion efficiency (η_c) of rare earth (La and Gd) co-doped electrode was enhanced 0.257 than that of un-doped electrode. This result was confirmed that co-doped rare earth in PbO_2 films could enhance the capability of oxidation which was beneficial for the entirely mineralization of intermediates.

5. ACKNOWLEDGMENTS

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