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Enhanced Mineralization of Cationic Red X-GRL with Rare Earth doped materials: Gd for example

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In order to improve the degradation efficiency, the lead dioxide electrode doped with Gd was prepared 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 was 200 mol:4 mol for the X-GRL and TOC removal. The optimal degradation conditions were achieved by investigating on the effects of different parameters, such as current density, electrolyte concentration and X-GRL initial concentration. Under 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 hours degradation, the removal of X-GRL and TOC reached 99.71% and 55.07%, respectively. Based on the analysis of scanning environmental microscopy (SEM), the surface of electrode had a dense structure and the preferred crystalline orientation, which was helpful to improve the catalytic activity of electrode and finally enhance the mineralization of X-GRL. In addition, with the help of cyclic voltammograms (CVs), it could be concluded that Gd doped electrode has high oxygen evolution potential and electrochemical activity.

Keywords: electrocatalysis; lead dioxide electrode; cationic red X-GRL; Gd

1. INTRODUCTION

Highly concentrated dyeing wastewater was a challenge of environmental concern in China for its large emission and poor biodegradability. Traditional biological treatment methods could not reach satisfied results for dyeing wastewater with increasingly strict discharge standard. Therefore, novel way for the dyeing wastewater treatment is an urgent demand for the environmental workers and the government [1-4].

Alternatives had also been studied, such as electrochemical oxidation, ozone oxidation, photochemical oxidation and supercritical water oxidation treatment, etc [5-7]. Among them, electrochemical oxidation was known as the most promising alternative technology for its environmental friendly properties [8, 9]. However, the application of electrochemical oxidation in industrial organic wastewater treatment is still limited 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., SnO_2 and RuO_2 were studied [10, 11]. With the successful development of dimensionally stable anodes (DSA) for nearly 30 years, many researches were focused on preparing novel DSA anodes for higher stability, higher activity and lower cost [12-13]. The introduction of small amounts dopants, such as Co^{2+}, Fe^{2+}, F^-, and so on [14-19], could improve the conductivity of electrodes and its performance in degradation progress. Rare earth metals and PTFE were applied in the petrochemical industry and showed a potential application in fuel cell area [20-24].

In this work, considering the rare earth with special 4f electronic structure, Gd was used and co-doped with PTFE to cover the advantages both catalytic efficiency and stability. According to the degradation of X-GRL, the optimized doped molar ratio of Gd was also determined. The electrocatalytic activity of modified anode was also investigated by means of cyclic voltammetric experiments. Furthermore, SEM was used to analyze the morphologies and structure of covering films.

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 [19]. Rare earth oxide (Gd_2O_3) was added into the electroplating solution for the electrodeposition of the Gd-doped PbO_2 electrode.

2.2. Methods

The samples were selected depending on the time duration of 0, 10, 20, 30, 60, 90 and 120 min. The concentration of X-GRL was measured by the spectrophotometer (U-2910, Hitachi, Japan). 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). SEM (5570, Hitachi, Japan) was used to analyze the morphology and the crystalline structure of films.

Electrochemical workstation (660C, CHI, USA) was employed to analyze the electrochemical property. In the three-compartment cell (with a working volume of ca. 120 mL), the self-made electrode was employed as the working electrode, the Pt plate electrode was used as the counter electrode, and the Ag/AgCl electrode was employed as the reference electrode.

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 &ANALYSIS

3.1. Effect of degradation condition

3.1.1. Effect of different Gd doped molar ratio

The effect of different Gd doped molar ratio (Pb : Gd = 200 mol:0 mol, 200 mol:0.2 mol, 200 mol:0.4 mol, 200 mol:2 mol, 200 mol:4 mol) on the degradation of 100 mg/L X-GRL was investigated at 0.1 mol/L Na_2SO_4 and 50mA/cm^2 current density. The result was shown in Fig. 1.

As could be seen, when the molar ratio was Pb : Gd = 200 mol:4 mol, the maximum removal of all organic species in solution (indicated by X-GRL and its TOC degradation efficiency) was achieved. The removal of TOC by the co-doped electrode (Pb : Gd = 200 mol:4 mol) reached to 55.07%, which was higher than that of un-doped electrode (39.29%), after 2h degradation. This suggested that suitable Gd doped molar ratio has a positive influence on the catalytic activity of PbO_2 electrode. The Gd-PbO_2 electrode (Pb : Gd = 200 mol:4 mol) possessed an excellent degradation ability on both X-GRL and its TOC as well. In electrochemical oxidation degradation system, for the high concentration organic wastewater, the oxidation and reduction processes on electrode surface would produce a polymer film, which could lead to the reduction of electrode activity and the increase of power consumption [18, 25]. And then, the degradation efficiency of electrochemical oxidation system would decrease for the low mass transfer rate of organic in solution [26]. A higher degradation efficiency of TOC could avoid the accumulation of intermediates on the surface of electrode and improve the mass transfer condition of the electrochemical oxidation system. Therefore, Gd-PbO_2 electrode (Pb : Gd = 200 mol:4 mol) was selected as the working electrode.

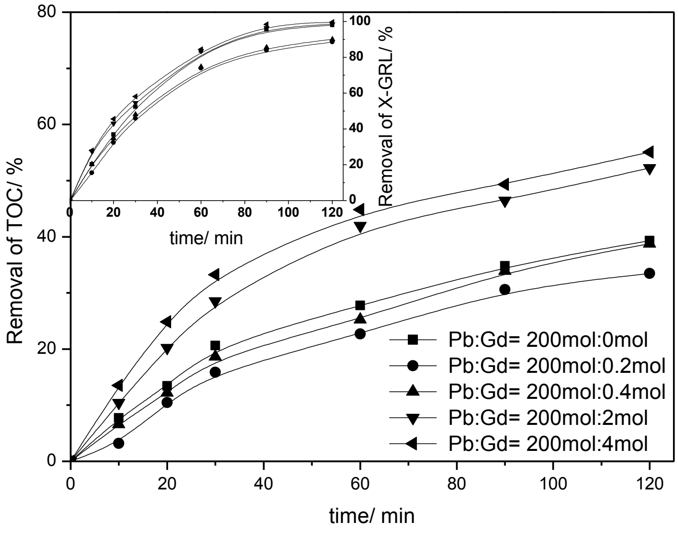

Figure 1. The effects of Gd-doped ratios on degradation efficiency of X-GRL

3.1.2. Effect of current density

The effect of 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 = 200 mol:4 mol). The result was shown in Fig. 2.

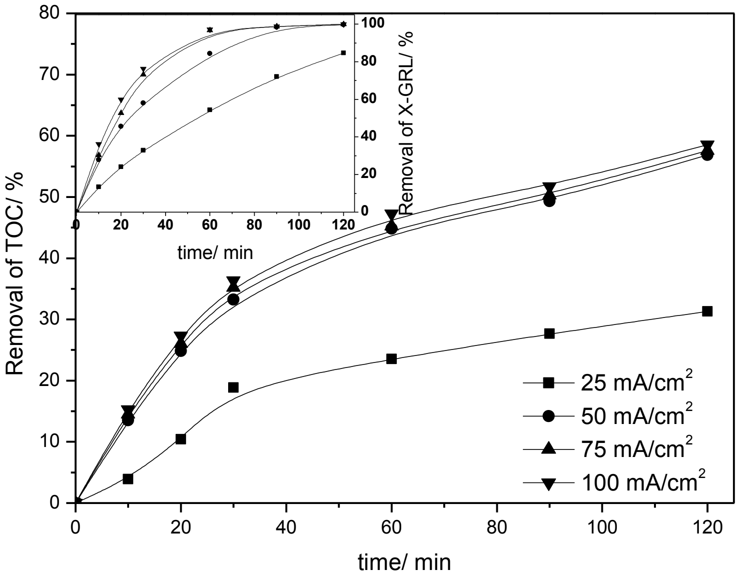

Figure 2. The effects of current density on degradation efficiency of X-GRL

Fig.2 illustrated the removal rates of X-GRL and its TOC obtained with different current density conditions. 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. Therefore, appropriate current density should be selected. Combining 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.

3.1.3. Effect of concentration of electrolyte

Strong electrolyte (Na_2SO_4) was needed to promoting the conductivity of X-GRL solution for the low conductivity of X-GRL. Therefore, the effect of electrolyte (Na_2SO_4) concentration on the X-GRL degradation should was also evaluated. In order to evaluate the influence of electrolyte (Na_2SO_4) on the X-GL degradation, the concentration of 0.05, 0.1, 0.2 and 0.4 mol/L Na_2SO_4 were tested under the condition of 100 mg/L X-GRL by Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol). The result was shown in Fig. 3.

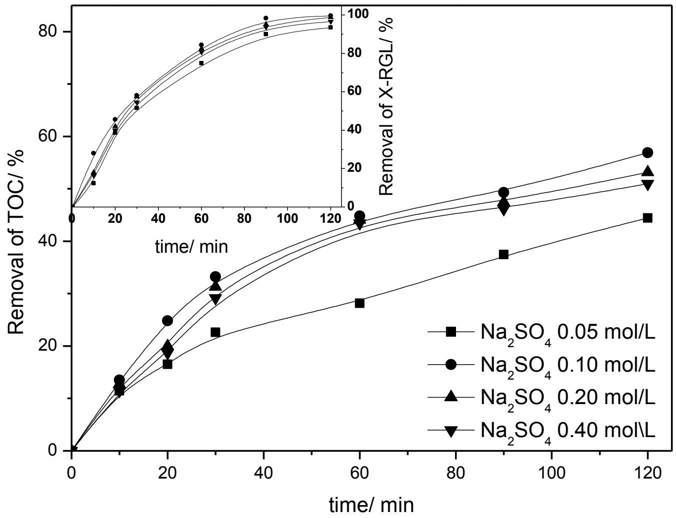

Figure 3. The effects of Na_2SO_4 concentration on degradation efficiency of X-GRL

Fig.4 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%, 99.71%, 98.82% and 96.67%, and its TOC removal rates were 44.45%, 55.07%, 53.17% and 50.99% 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 imply an promotion in the degradation efficiency. With a high concentration of electrolyte (Na_2SO_4), 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 for the reduction of contact area between the pollutant and the surface of electrode. In all studied electrolyte concentration conditions, 0.1 mol/L Na_2SO_4 was an optimized factor with higher degradation on both X-GRL and its TOC.

3.1.4. Effect of initial concentration of pollutant

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

As could be observed in Fig. 4, the trend of X-GRL and its TOC removal rate increased with the decrease of X-GRL initial concentration. The highest value of X-GRL removal rate (99.71%) was obtained with 100 mg/L initial concentration of X-GRL, and the highest removal rate of its TOC reached 55.07% with 100 mg/L of X-GRL, after 2 h degradation. The mass transportation in the electrochemical oxidation system would be decreased for the low concentration of X-GRL in solution. Depend on the results above, 100mg/L X-GRL initial concentration was the optimal one.

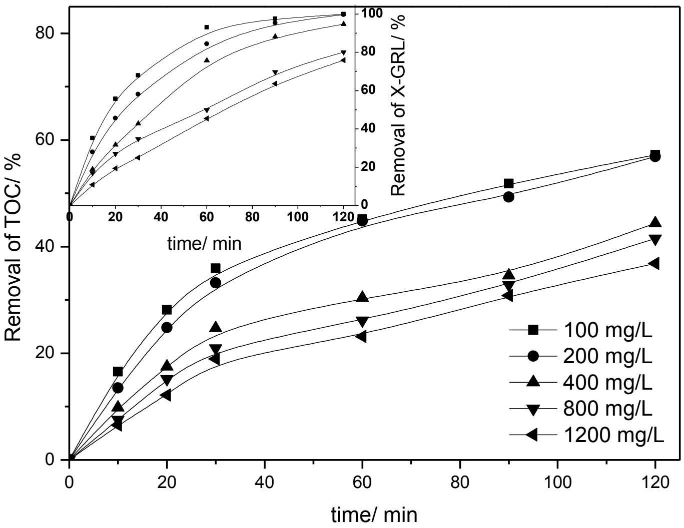

Figure 4. The effects of initial concentration on degradation of X-GRL

3.2 The analysis of SEM

Fig.5 (A) and (B) showed the SEM images of PbO_2 electrode and Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol), respectively. As could be observed in Fig.5 (A), the particles on the electrode surface were relatively small but without a perfect crystal structure. Under the same magnification, Fig. 5 (B) showed a well-crystallized surface of the Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol). Furthermore, compared with the particles in PbO_2 electrode, the Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol) possessed a well-crystallized surface, which composed by tinier crystal structure and lower size crystal cell. What's more, the morphology of the Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol) was beneficial to decreasing the internal stress between two different layers and extending the lifetime of electrode [27].

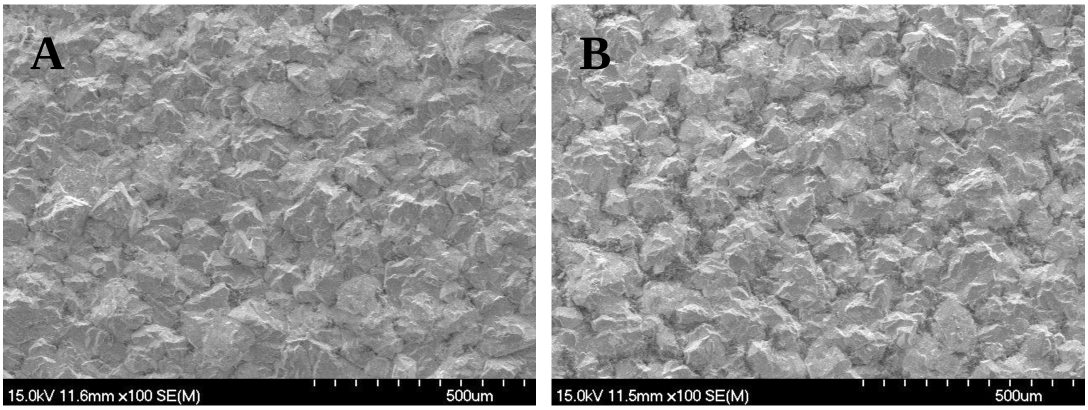

Figure 5. The SEM of electrodes
(A) PbO_2 electrode; (B) Gd-PbO_2 electrode

In addition, the crystal structure of the Gd doped electrode could improve the distribution of surface microcurrent to promote the conductivity of electrode. The surface of electrode with a perfect crystal morohology, which composed by tiny and low size crystal cell, could also help to reduce the resistance of mass transport between solute and electrode surface, and form the high surface area electrode which would enhance the catalytic activity and stability in electrochemical oxidation system.

3.3 Cyclic voltammetry

To investigate the quality of the un-doped PbO_2 electrode and the Gd doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol) during the electro-oxidation process, a series of cyclic voltammogram experiments were carried out in 0.5 mol/L H_2SO_4 + 0.5 mol/L Na_2SO_4 solution, at the scan rate of 10 mV/s and potential range from 1.1 to 2.2 V. The cyclic voltammogram experiments carried on with the self-made electrodes as working electrodes, platinum electrode as the counter electrode, Ag/AgCl electrode as the reference electrode. The results were given in Fig. 6.

As could be observed in Fig. 6, an anodic peak appeared at about 1.7V versus Ag/AgCl prior for the oxygen evolution reaction. PbO_2 was known as a kind of non-stoichiometric compounds [28]. This implied that, for the lower valence in the lattices, some Pb atoms could be further oxidized by the adsorbed hydroxyl radicals [29]. The physically adsorbed oxygen could also been transferred to the chemically adsorbed oxygen in this process [30]. Furthermore, the potential of CVs curve began to rise after the first the anodic peak of Gd-doped electrode (Pb : Gd = 200 mol:4 mol) was lower than that of un-doped electrode. This implied that the Gd co-doped PbO_2 electrode (Pb : Gd = 200 mol:4 mol) possessed an improved ability on electrochemical oxidation. What's more, the oxygen evolution potential was also enhanced after the doping with Gd_2O_3. The higher oxygen evolution potential was helpful to restrain the reaction of oxygen evolution, which would reduce the current efficiency and waste the electric energy.

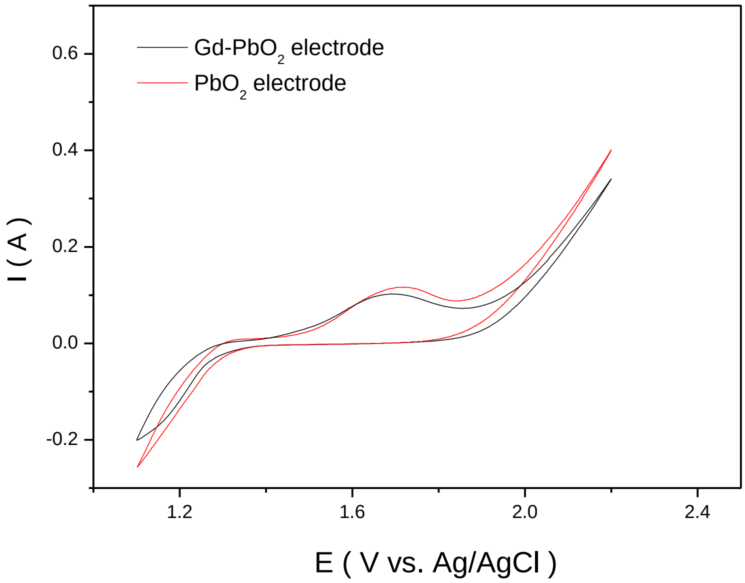

Figure 6. Cyclic voltammogram of Gd-PbO_2 electrode and PbO_2 electrode

4. CONCLUSION

(1) The PbO_2 electrode doped with Gd (Gd-PbO_2) was prepared by electrodeposition technique. The maximum degradation efficiency was achieved by Gd-PbO_2 electrode (Pb : Gd = 200 mol:4 mol) with 100 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 99.71% and 55.07%, respectively, after 2h treatment.

(2) According to the SEM images analysis of Gd-PbO_2 electrode, it was indicated that Gd doped electrode possess a dense structure and a preferred crystalline orientation, which was beneficial to pollutant degradation. Therefore, rare earth dopant (Gd) could modify the surface of electrode effectively. The porous film of Gd-PbO_2 could also help to improve the specific surface area, expose more active sites, promote mass transportation and enhance the efficiency of electro-catalysis, finally.

(3) CVs test illustrated that, comparing with the traditional PbO_2 electrode, electrode doped with rare earth dioxides Gd_2O_3 have a higher oxygen evolution over potential. This implied that the Gd-PbO_2 electrode possesses an improved ability to restrain the reaction of oxygen evolution, and finally promote the current efficiency.

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