

Electrochemical Degradation of Typical Dyeing Wastewater in Aqueous Solution: Performance and Mechanism

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In this study, the degradation of cationic turquoise blue GB (GB) by electrochemical oxidation with typical rare earth doped PbO₂ electrodes was studied. The novel PbO₂ doped with typical rare earth (Ce) electrode was prepared by thermal decomposition-electrodeposition technique. The effects of electrodes applied as anodes in electrochemical oxidation system were carefully studied for GB degradation and the effects of Ce-doped and undoped electrodes were compared. Optimal degradation conditions were explored with Ce-doped by the study the effects of different parameters, such as current densities and electrolyte concentrations. The characteristics of undoped and Ce-doped electrode were analyzed based on the SEM images. The mechanism of GB degradation in electrochemical oxidation with Ce-doped electrode was discussed based on the intermediates analyzed by IC and GC/MS.

Keywords: electrochemical oxidation; degradation; mechanism

1. INTRODUCTION

The pollution of dyeing wastewater received increasing attention for environmental researchers in recent year in China due to the largest dye production in the world. The biological treatment for dyeing wastewater could not meet the ever strict demand of the discharge standard. Therefore, sound way of dyeing wastewater treatment is an urgent demand for environment scientists and the government [1-5].

Advanced Oxidation Processes (AOPs) could receive satisfied results for dyeing wastewater with the formation of hydroxyl radical. As a typical AOP, electrochemical oxidation technology has been applied in many different fields of environmental pollution treatments due to the promising effects at relatively mild reaction conditions [2, 6-8]. However, in traditional electrochemical oxidation

system, the electrode activity is still one of the most important factors which greatly influence of the effect of organic degradation. Due to the special 4f rabbit, rare earth received the increasing attention for the high catalytic activity in environmental catalysis fields [9-10]. So, if relative good results can be achieved when the rare earth introduced, then the PbO_2 electrode would be potential widely used for the degradation of high concentration organic wastewater [9, 11-13].

In this paper, Ce was selected as typical rare earth used for enhancing the activity of the $\beta\text{-PbO}_2$ electrode, the enhancement of rare earth doped for dye degradation was explored. The effects of operational factors in electrochemical oxidation were detailed studied. Based on the intermediates detected by IC and HPLC, the possible degradation mechanism was discussed. This paper can provide basic data for dyeing wastewater pollution control.

2. MATERIALS AND METHODS

2.1 Materials

The rare earth doped electrodes were prepared with thermal decomposition-electrodeposition technology, and used as the anodes in electrochemical system. Pure titanium plate was used as the cathode. Cationic turquoise blue GB (GB) was selected as the model pollutant, which was widely used in dyeing industry. All chemical reagents were of analytical reagent or higher grade.

2.2 Sampling and methods

The concentration of GB was measured by UV detector with the detection wavelength at 653nm (SP-752, Shanghai Spectrum, China). The chemical oxygen demand (COD) was measured by the dichromate method (DRB200, Hach, USA). The organic acids and other intermediates were detected with ion chromatograph (ICS-200, Dionex, USA) and gas chromatography-mass spectrometry (GC7890/MS5975, Agilent Technologies, USA). The surface morphology was examined by scanning electron microscopy (5570, Hitachi, Japan).

3. RESULTS AND ANALYSIS

3.1 Effect of electrode

Electrode played an important role in electrochemical oxidation system [14]. The effect of electrode was investigated for the degradation of 100 mg/L GB on the condition of 0.2 mol/L Na_2SO_4 and 40 mA/cm^2 current density. The result was shown in Fig. 1.

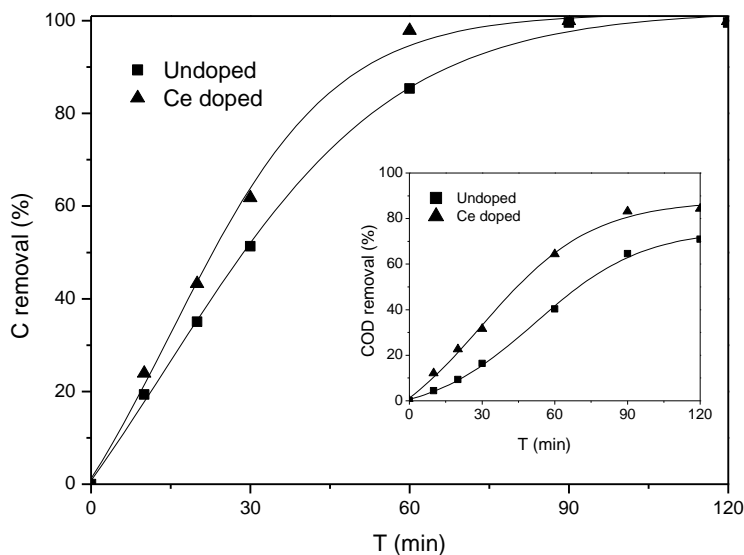


Figure 1. The comparison of dye degradation on different electrode

As was shown in Fig.1, after 60 min treatment, the removal of dye reached 97.89% in electrochemical oxidation system with Ce-doped electrode. Compared with undoped β -PbO₂ electrode, the removal of GB increased from 85.39% to 97.89%, respectively. As for COD removal, after Ce doped, the effect of Ce-doped electrode raised from 40.33% to 64.33% after 60 min treatment. After 120 min, the removal of undoped β -PbO₂ electrode and Ce-doped electrode were 70.95%, 84.27%, respectively. The results showed that after Ce doped, the catalytic effects for the mineralization of the dyeing wastewater could be greatly enhanced, which would be potential widely used in dyeing wastewater treatment.

To further understand the mechanism of the electrode catalytic effect, the characteristic of the electrode was analyzed with the scanning electron microscopy (SEM).

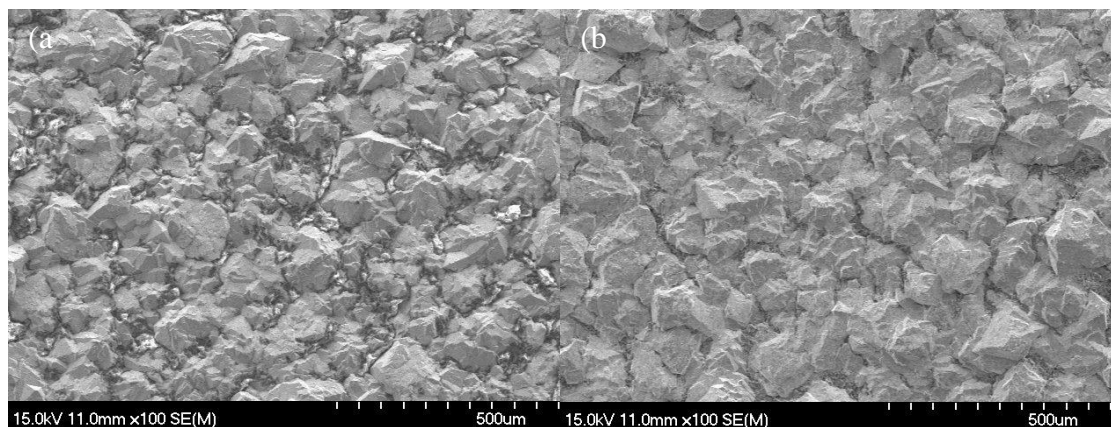


Figure 2. SEM of PbO₂ electrode (a) Undoped (b) Ce-doped

As was shown in Fig. 2, the surface of Ti/PbO₂ electrode had tinier crystal structure, which could efficiently prevent the penetration of fresh oxygen and the formation of TiO₂ insulator layer with Ti base. In addition, compact surface structure composed by tinier crystal structure could improve the distribution of microcurrent on surface to promote the conductivity, catalytic activity and stability of electrode. However, as could be seen in the SEM images of Ti/PbO₂ electrode, the surface of un-doped electrode was uneven and without uniform crystal structure. These shortages would decrease the mass transport between solute and electrode surface, and reduce the degradation efficiency of pollutant by electrode.

Compared with the surface of Ti/PbO₂ electrode, the surface of Ti/Ce-PbO₂ possessed integral crystal form. The morphology of Ce-doped PbO₂ electrode demonstrated that the addition of rare earth (Ce) could effectively improve the crystallinity of PbO₂ crystal on electrode surface in electrodeposition progress. In addition, the morphology of electrode with higher degree of crystallinity, compact unit cell and tinier crystal could enhance the adsorption of electrode for its high specific surface area. Increase in the number of adsorption site and activity site was also help for the improvement of mass transport between solute and electrode surface and the increase of degradation efficiency of pollutant by electrode, finally. The probability of the generation of TiO₂ insulator layer for the contact of fresh oxygen with Ti base would be efficiently decreased for the uniform and compact crystal structure of Ti/Ce-PbO₂ surface. Tinier and even crystal structure could also diminish the surface stress of the PbO₂ grain crystals on electrode to prolong the service life, and improve the distribution of microcurrent on surface to promote the conductivity, stability and catalytic activity of electrode. Electrode with long service life and high degradation efficiency could be widely applied in dye wastewater pollution control in application filed.

3.2 Effect of current density

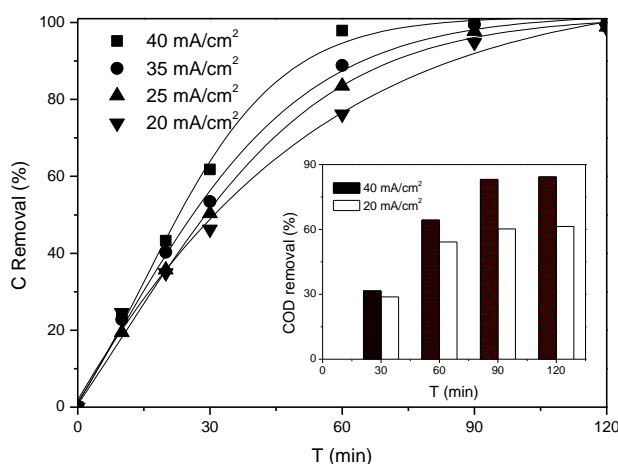


Figure 3. The effect of current density on dye degradation

Current density was an important factor which could influence the energy of consumption. The influences of current density on the degradation of GB were carried out on condition of 0.2 mol/L Na_2SO_4 and 100 mg/L GB.

As was shown in Fig.3, the effect of current density 20 mA/cm^2 , 25 mA/cm^2 , 35 mA/cm^2 and 40 mA/cm^2 were studied for dye degradation. The dye removal rose at a higher current density [15]. At the current density of 20 mA/cm^2 , the dye removal was 76.17% after 60 min treatment, while it was at 97.89% at the current density of 40 mA/cm^2 . Compared with the results of COD removal, at the current density of 20 mA/cm^2 , the COD removal was 50.23% after 60 min treatment, while it was at 64.33% at the current density of 40 mA/cm^2 . After 120 min treatment, the COD removal was 84.27% and 69.02%, respectively. The results also showed that at higher current density would enhance the dye mineralization [16-17].

3.3 Effect of electrolyte concentration

Na_2SO_4 was selected as the supporting electrolyte due to the relative stable characteristic [18-19]. And the effect of electrolyte (Na_2SO_4) on the GB degradation were studied under the condition of 0.1, 0.2 and 0.5 mol/L Na_2SO_4 , 100 mg/L GB and 40 mA/cm^2 . As was shown in Fig. 4, at different concentration of electrolyte, after 60 min treatment, the dye degradation were 94.11%, 97.89% and 93.42% at the condition of 0.1, 0.2 and 0.5 mol/L Na_2SO_4 , respectively. The varied little, which showed that the concentration contributed little for dye degradation. As for dye COD removal, after 60 min treatment at the condition of 0.1, 0.2 and 0.5 mol/L Na_2SO_4 , the COD removal was 59.68%, 64.33% and 63.62%, respectively. However, after 90min treatment, the COD removal at the condition of 0.1, 0.2 and 0.5 mol/L Na_2SO_4 reached 64.41%, 83.15% and 66.12%, respectively. The results showed that dye COD removal at 0.2 mol/L Na_2SO_4 was obviously higher than those of other conditions. This was probably due to low concentration of electrolyte could not supply enough ions for the generation of active species, and thus caused poor degradation efficiency of pollutant. And, too much electrolyte would cause a supersaturated solution, which might lead to a decrease in dye degradation. So, 0.2 mol/L Na_2SO_4 showed an optimized dye COD removal.

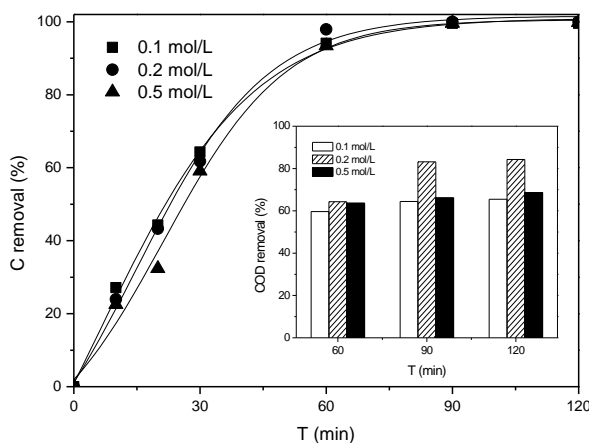


Figure 4. The effect of electrolyte concentration on dye degradation

3.4 Degradation mechanism

The intermediates of dye degradation were analyzed with IC and GC/MS. Typical intermediates were showed in Fig. 5, the most organic acids acetated were benzoic acid and acetic acid. After 60 min treatment, the concentration of benzoic acid and acetic acid increased with the maximum concentration of 110.23 mg/L and 124.65 mg/L. Then, the amount of benzoic acid and acetic acid became to decrease with the concentration of 65.24 mg/L and 94.24 mg/L after 120 min treatment. This was the same variation trend of oxalic acid with the maximum concentration of 26.45 mg/L after 60 min treatment. As for formic acid, the maximum concentration was 96.23 mg/L after 90 min treatment. There was also detected low concentration NO_3^- , which was part of the intermediate containing nitrogen during the dye mineralization.

Thus, it could be concluded that GB firstly was degraded into kinds of organic intermediates, which including kinds of organic acids. After that, dye could be further mineralized into CO_2 and H_2O .

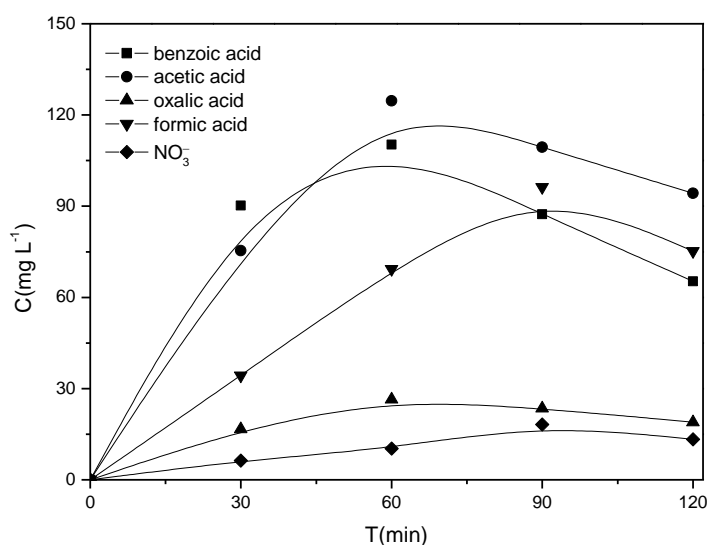


Figure 5. Variation of different kinds of intermediates

4. CONCLUSIONS

A novel PbO_2 doped with a typical rare earth (Ce) electrode was prepared by thermal decomposition-electrodeposition technique. The results showed that the addition of rare earth (Ce) could effectively improve the crystallinity of PbO_2 crystal on electrode surface. In addition, the morphology of electrode with higher degree of crystallinity, compact unit cell and tinier crystal could enhance the adsorption of electrode for its high specific surface area. Increase in the number of adsorption site and activity site was also help for the improvement of mass transport between solute and electrode surface and the increase of degradation efficiency of pollutant by electrode. So after Ce doped, it could improve the distribution of microcurrent on surface to promote the conductivity, stability and catalytic activity of electrode.

Electrode with long service life and high degradation efficiency could be widely applied in dye wastewater pollution control in application filed.

The effects of electrode applied as an anode in electrochemical oxidation system were carefully studied for GB degradation and the effect of Ce-doped and undoped electrodes were compared. Optimal degradation conditions were explored with Ce-doped by the study the effects of different parameters. The results showed that at higher current density would enhance the dye mineralization and the optimized current density was 40 mA/cm². The electrolyte analysis results showed that optimized dye mineralization was achieved when 0.2 mol/L Na₂SO₄ was selected as the supporting electrolyte with the results of 83.15% COD removal after 90 min treatment. The intermediates of dye degradation were analyzed with IC and GC/MS, and the most organic acids acetated were benzoic acid and acetic acid. After 60 min treatment, the concentration of benzoic acid and acetic acid increased with the maximum concentration of 110.23 mg/L and 124.65 mg/L. Then the amount of organic acids became to decrease. Thus, it could be concluded that GB firstly was degraded into kinds of organic intermediates, which including kinds of organic acids. After that, dye could be further mineralized into CO₂ and H₂O.

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