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Electrodeposition of PbO_2 film on stainless steel substrate and application as anode electrode for organic dye degration

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Abstract

The electrodeposition of PbO_2 on stainless stell substrate has been carried out by the anodic oxidation of $Pb(NO_3)_2$ solution at constant current density. The optimum conditions for the electrodeposition of PbO_2 on steel substrate were current density 60 mA/cm^2, 0.4 M $Pb(NO_3)_2$, 0.3 M $Cu(NO_3)_2$, concentrated HNO_3 10 mL/L, the time of the electrodeposition t = 60 min, T = 30 ^oC. The obtained PbO_2 was smooth, good adherent and ratio of β-PbO_2 80 %. The morphology and crytal structure of PbO_2 were investigated by SEM and XRD. The influence of some factors such as organic dye concentration, reaction time, NaCl concentration, pH of solution, current density on the electrochemical oxidation of organic dye on PbO_2 anode has been investigated. The optimal conditions for the electrochemical treatment of organic dyes on a PbO_2 anode are pH = 7, dye concentration of 100 mg/L, electrolysis time of 25 minutes, current density 70 mA/cm^2 and NaCl concentration of 10 g/L. Under these conditions, the dye degradation efficiency exceeds 99 %, while the chemical oxygen demand (COD) removal efficiency is above 90 %.

Keywords: PbO_2; Electrode; Electrodeposition; Electrochemical oxidation; Dye degration

1. Introduction

The electrode material is a critical factor influencing the direction of the electrode reaction, as well as determining the reaction rate, efficiency, and product quality in the electrolysis process. Ideal electrode materials should exhibit the following properties: excellent electrical conductivity, effective electrocatalytic activity for desired reactions, chemical stability, corrosion resistance, mechanical durability, ease of fabrication, and cost-effectiveness [1].

In electrochemical oxidation processes, the selection of anode materials is particularly challenging, as most metals undergo dissolution during anodic oxidation. Certain metal oxides, such as TiO_2, MnO_2, PbO_2, and RuO_2, are commonly used as anode materials due to their high electrical conductivity, excellent corrosion resistance, and significant oxygen evolution potential [2].

Among oxide electrodes, PbO_2 is widely utilized and serves as a cost-effective alternative to precious metal anodes like Pt. PbO_2 anodes are employed in various electrochemical applications, including the production of perchlorates, periodates, hydroquinones, hydroxylamines, and carboxylic acids. Notably, PbO_2 is used as an inert anode in the electrochemical oxidation of organic pollutants in environmental treatment processes [3, 4, 5, 6].

PbO_2 electrodes can be fabricated using chemical methods or by electrodeposition onto substrates such as titanium or graphite under constant potential or cyclic potential scanning conditions [7, 8, 9, 10].

In this study, we electrodeposited PbO_2 film on stainless steel substrates under constant current conditions and explored the application of PbO_2 electrodes in the treatment of organic dyes in aqueous environments.

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2. Material and methods

Stainless steel, $Pb(NO_3)_2$, $Cu(NO_3)_2$, HNO_3, NaCl, NaOH, HCl, gelatin, Alizarin Red S analytical grade.

2.1. Electrodeposition of PbO_2

$Pb(NO_3)_2$ was used as a precursor for the PbO_2 synthesis. The electrodeposition of PbO_2 on stainless stell substrate has been carried out by the anodic oxidation of $Pb(NO_3)_2$ solution at constant current density Before electrodeposition, all the electrodes were mechanically roughened, with grades 600 and 1200 SiC paper.

2.2. Electrochemical oxidation processes of dye solution

Electrochemical oxidation processes of dye solution was carried out in a small glass. The anodic oxidation was performed with a stainless steel plate (8 cm^2) and an PbO_2-coated electrode (8 cm^2) used as the cathode and anode, respectively. In evaluating the efficiency of the electrochemical process, the remaining dye concentration and COD are considered the primary factors.

3. Results and discussion

3.1. Synthesis of PbO_2 Electrode on Stainless Steel Substrate

The PbO_2 film was synthesized in a solution with the following composition and electrolysis conditions: 0.4 M $Pb(NO_3)_2$, concentrated HNO_3 with a ratio of 10 mL/L, temperature of 30°C, electrolysis time t = 60 min, and a current density of 60 mA/cm^2.

The SEM image (Figure 1) of the obtained PbO_2 shows that the PbO_2 film synthesized on the stainless steel substrate has a uniform structure.

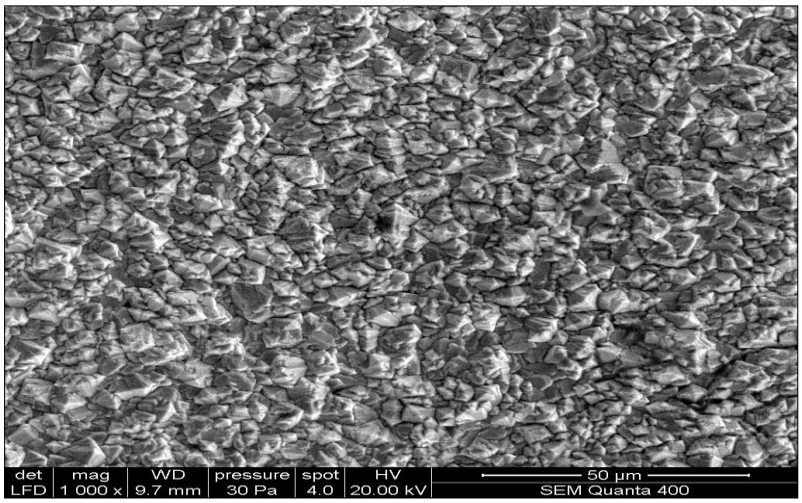

Figure 1 The SEM image of PbO_2 film

The XRD diffraction spectrum of PbO_2 is presented in Figure 2.

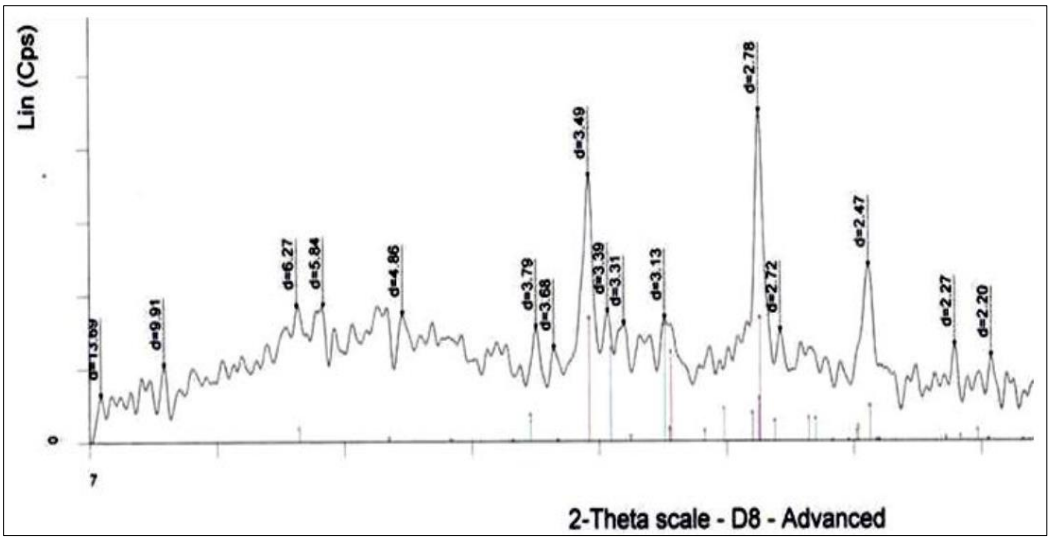

Figure 2 The XRD diffraction spectrum of PbO_2

Table 1 Chemical composition of the PbO_2 synthesized at a current density of 60 mA/cm^2

Mineral composition	Content (%)
β - PbO_2	80
α - PbO_2	8
Pb_3O_4	6
PbO	6

From Table 1, it can be seen that β-PbO_2 accounts for a very high proportion of 80%, opening up the possibility of producing durable β-PbO_2 anode electrodes, providing high efficiency for many industrial electrolysis processes.

3.2. Treatment of organic dye in water by electrooxidation on PbO_2 Anode

3.2.1. Effect of dye concentration

The effect of dye concentration on the conversion process was investigated in a solution with the following composition and conditions: temperature of 30°C, NaCl concentration of 10 g/L, electrolysis duration of 15 minutes, pH = 7, and dye concentration ranging from 50 to 300 mg/L. The results are shown in Figure 3.

Figure 3 shows that the dye conversion rate decreases as the concentration increases. However, this conversion rate reaches over 99% when the concentration is ≤ 100 mg/L, while concentrations of 100 mg/L or higher show a significant drop in conversion. Therefore, a concentration of 100 mg/L was chosen to investigate the subsequent factors.

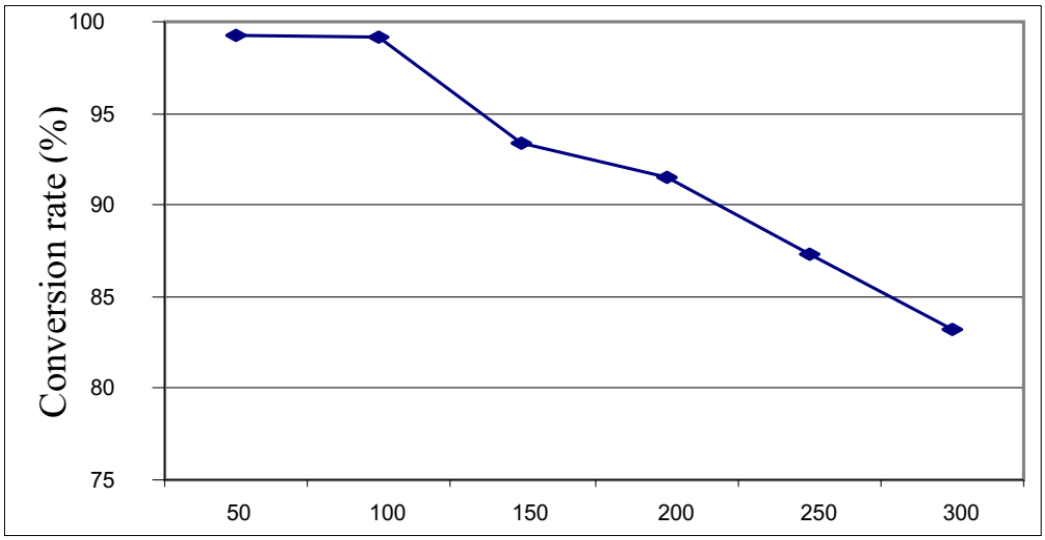

Figure 3 Dye conversion rate at different concentrations

3.2.2. Effect of electrolysis time on dye conversion

The effect of electrolysí time on the dye conversion process was investigated under the following conditions: dye concentration of 100 mg/L, temperature of 30°C, NaCl concentration of 10 g/L, with electrolysis time varying from 5 to 30 minutes. The results are shown in Figure 4.

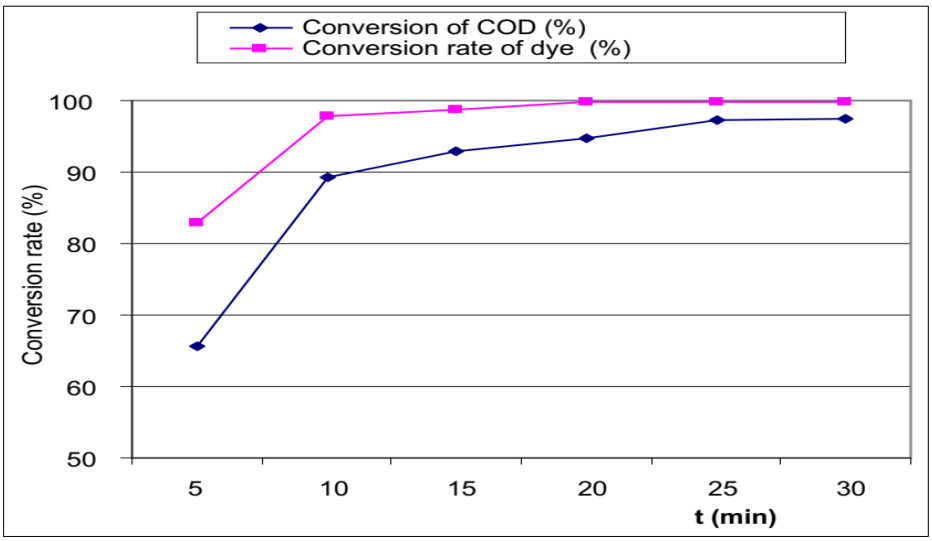

Figure 4 Effect of electrolysis time on dye conversion (%) and COD conversion (%)

Figure 4 shows that when the electrolysis time increases, the dye conversion rate increases. Therefore, the optimal time of t = 25 minutes was selected to examine the subsequent factors.

3.2.3. Effect of NaCl concentration

The effect of NaCl concentration was investigated under the conditions: dye concentration of 100 mg/L, temperature of 30°C, electrolysis time of 25 minutes, and NaCl concentration varying from 4 to 14 g/L. The results are shown in Figure 5.

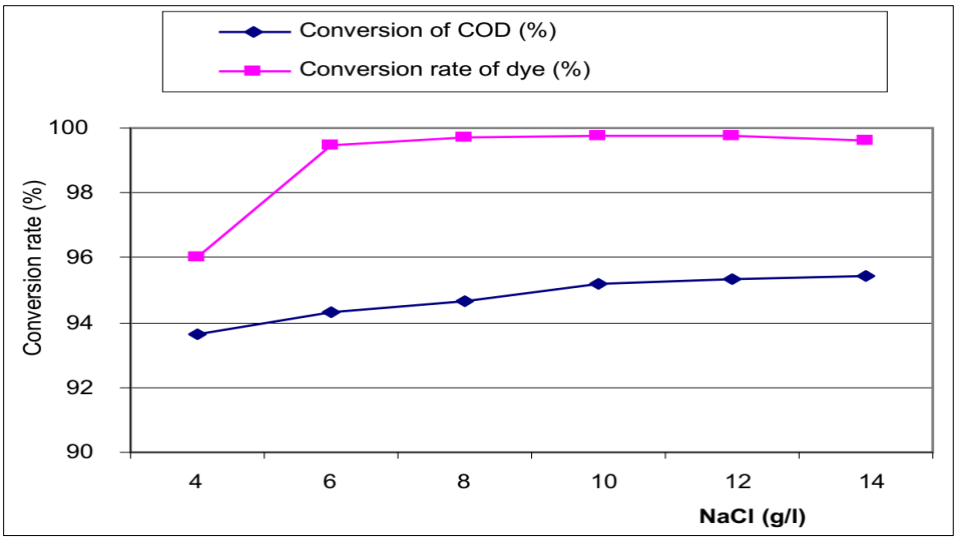

Figure 5 Effect of NaCl concentration on dye conversion (%) and COD conversion (%)

Figure 5 shows that as the NaCl concentration increases, both dye conversion and COD conversion increase. This can be explained by the occurrence of indirect electrooxidation through the following reactions:

$$2Cl^- \rightarrow Cl_2 + 2e \quad .....(1)$$

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl \quad .....(2)$$

$$HClO \rightleftharpoons H^+ + ClO^- \quad .....(3)$$

Cl_2 and ClO^- participate in the oxidation process of the dye and convert back into Cl^-. The biggest drawback of the indirect electrolysis process is the formation of chlorine-containing organic compounds. However, a COD conversion rate of over 93% indicates that the amount of chlorine-containing organic compounds is negligible. Figure 5 also shows that at an NaCl concentration of 10 g/L, the dye conversion rate is the highest, and the degree of mineralization reaches over 95%. Therefore, an NaCl concentration of 10 g/L was chosen for the dye treatment process.

3.2.4. Effect of pH

With a dye concentration of 100 mg/L, electrolysis time of 25 minutes, NaCl concentration of 10 g/L, pH was varied from 3 to 8. The results are shown in Figure 6.

Figure 6 shows that at different pH values, both the dye conversion rate and COD conversion rate do not vary significantly. The highest COD conversion efficiency of 96.20% was achieved at pH = 7.

Experimental observations showed that at lower pH, the dye conversion process occurs faster, but both the dye conversion rate and COD conversion rate are lower than in a neutral environment. This might be due to equilibrium (3) shifting to the left, creating a large amount of Cl_2 and simultaneously generating a certain amount of chlorine-containing organic compounds. When pH > 7, a portion of the generated Cl_2 reacts with OH^-, reducing both the COD conversion and dye conversion. Therefore, pH = 7 was chosen to examine the next influencing factor.

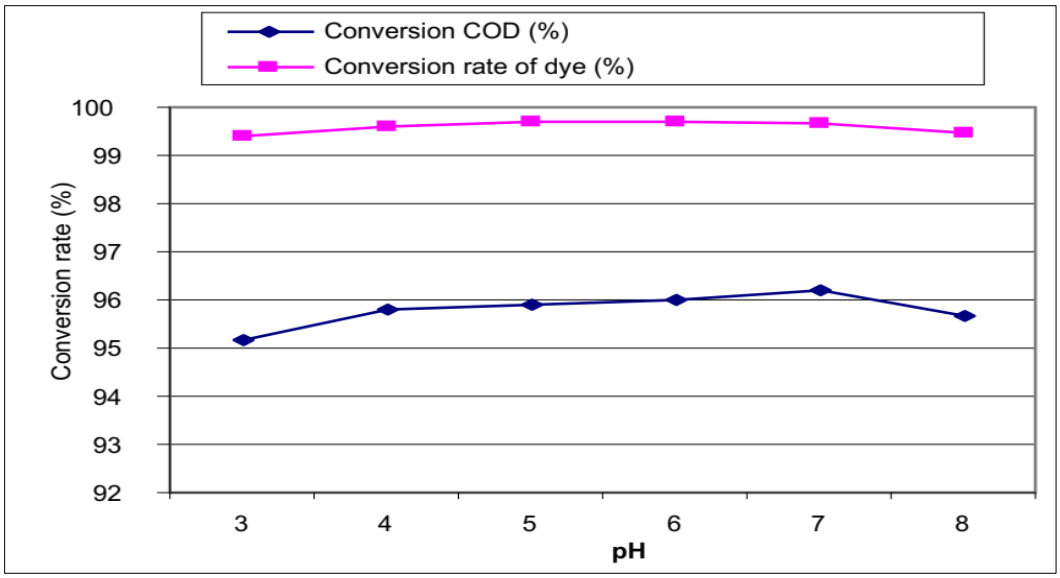

Figure 6 Effect of pH on dye conversion (%) and COD conversion (%)

3.2.5. Effect of current density

In the electrochemical redox process, current density is an important factor influencing the speed and efficiency of the process. The effect of current density on dye conversion and COD conversion was studied under the following conditions: dye concentration of 100 mg/L, electrolysis time of 25 minutes, NaCl concentration of 10 g/L, pH = 7, with current density (i_a) varying from 50 to 100 mA/cm^2. The results are shown in Figure 7.

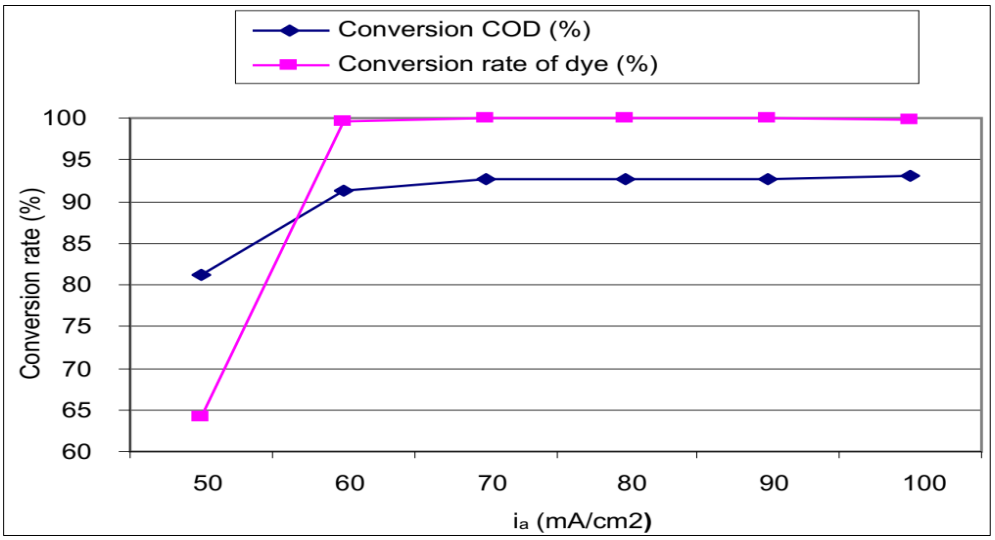

Figure 7 Effect of current density on dye conversion (%) and COD conversion (%)

Figure 7 indicates that increasing the current density enhances the dye electrooxidation capacity. This may be due to the intermediate organic products generated during dye oxidation continuing to be oxidized as the current density increases, facilitating conversion to CO_2 and H_2O. However, when the current density exceeds 70 mA/cm^2, both dye conversion and COD conversion increase only slightly. This could be due to the high current density causing competing water oxidation reactions, generating oxygen, which affects the dye oxidation process and the durability of the PbO_2 electrode. Therefore, a current density of i = 70 mA/cm^2 provides the best efficiency for the dye oxidation process.

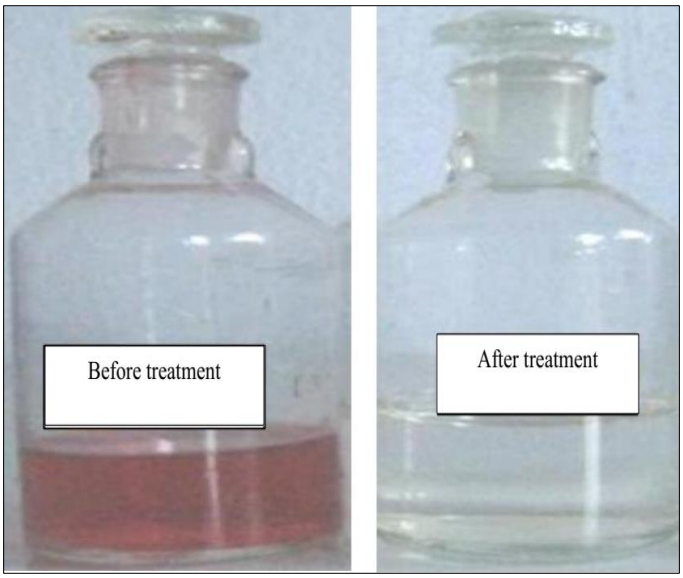

Figure 8 Color change of dye solution before and after treatment

4. Conclusion

- The optimal conditions for the electrolysis process to create a PbO_2 film are: constant current density i = 60 mA/cm^2, solution containing 0.4 M $Pb(NO_3)_2$, 0.3 M $Cu(NO_3)_2$, concentrated HNO_3 10 mL/L, electrolysis time t = 1 hour, temperature 30°C. The resulting PbO_2 electrode is smooth, thick, and dense.
- X-ray diffraction analysis shows that the synthesized PbO_2 film has a β-PbO_2 structure with a very high proportion of 80 %, presenting the potential to produce durable β-PbO_2 anode electrodes, offering high efficiency for many industrial electrolysis processes.
- The dye treatment process using the PbO_2 anode depends on factors such as current density, pH, NaCl concentration, electrolysis time, and dye concentration. The optimal conditions for this process are pH = 7, dye concentration 100 mg/L, electrolysis time 25 minutes, current density 70 mA/cm^2 and NaCl concentration 10 g/L. Under optimal conditions, the dye conversion rate exceeds 99 %, and COD conversion is above 90 %.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors declare that they have no conflicts of interest.

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