Degradation of methyl orange waste water by electrochemical oxidation method

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Abstract. Degradation of methyl orange (MO) waste water was conducted by electrochemical oxidation method with PbO₂/Ti electrode as anode. PbO₂/Ti electrode was fabricated by electrochemical deposition of PbO₂ on Ti foil. The micrograph and crystal structure of PbO₂ show that uniform coating of PbO₂ on titanium foil was obtained and the dominant crystal structure was β-PbO₂. Degradation experiments of MO solution indicate that the degradation rate increased with cell voltage and solution conductivity. In addition, air aeration also improved the degradation of MO solution; but an increase in cell voltage or input energy decreased the energy efficiency of MO removal. The energy efficiency reached over 0.1mg kJ⁻¹ under a cell voltage lower than 15V, and the removal rate could reach 90%.

1. Introduction

Dyes have wide application in textile or cosmetic industries for dyeing fibres, and a considerable percent of the dye is lost during the dyeing process into the effluents [1]. The emission of dyes into surface water reduces its transparency and the dissolved oxygen [2], furthermore, certain dyes and its degradation products are carcinogenic and highly toxic [3], all of these influences pose a great threat to the water aquatic ecosystem. In recent years, besides microbial degradation process of dyes [3], some advanced oxidation processes (AOPs) for degradation of dyes waste water have been developed with more stringent environmental standards [4-7]. In AOPs, hydroxyl radicals are the important oxidative agents for dye pollutants, therefore, some practices including addition of hydrogen peroxide into reaction system for enhancing the production of •OH were often adopted.

Electrochemical oxidation (EO) is one of the effective technologies for degradation of dye waste water, and EO has obtained extensively attentions [5, 8, 9] since it holds the advantages such as the potential of complete oxidation of dyes to CO₂ and H₂O, operation at room temperature and atmospheric pressure, simple process, etc. Since electrode materials have important effect on the life of electrode and the production active species as well as PbO₂ electrode has a good anti-oxidation

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performance. In this paper, we used EO to decolorize methyl orange (a type of acid dye) on Ti/PbO₂ electrode, and the factors influencing the degradation rate of methyl orange were studied.

2. Materials And Methods

2.1. Chemicals
All reagents used in experiments, including methyl orange (C₁₄H₁₄N₃O₃SNa), lead nitrate (Pb(NO₃)₂), sodium sulfate (Na₂SO₄), hydrochloric acid (HCl), were analytically pure, and the titanium substrate for preparation of PbO₂ electrode was ultra-pure with a purity of 99.99%.

2.2. Preparation of Ti/PbO₂ electrode
Ti/PbO₂ electrode was prepared by electrical deposition method. Titanium sheet with a dimension of 30 mm × 30 mm × 0.2 mm was used as the substrate for electrical deposition of PbO₂. Prior to electrical deposition, the Ti substrate underwent five minutes of ultrasonic cleaning in acetone, deionised water in sequence for diminish the grease and acetone, and 30 min of etching in boiling hydrochloric acid with a volume concentration of 10%, and then the Ti substrate was ultrasonically cleaned in deionised water for another 5 min.

Electrical deposition of PbO₂ on the clean Ti sheet was performed at a constant anodic current of 60 mA for about 60 min and then at 120 mA for another 30 min. The micro-morphology and crystal form were tested by SEM and XRD, respectively.

![Figure 1. Micro-morphology of Ti/PbO₂ by SEM.](image)

![Figure 2. Crystal form of PbO₂ electrode.](image)

Figure 1 shows micro-morphology of Ti/PbO₂ electrode. It can be seen that uniform PbO₂ thin film was formed on the surface of Ti sheet. Figure 2 shows the XRD pattern of Ti/PbO₂ electrode. The figure shows that no diffraction peaks of Ti appeared in the sample of PbO₂ electrode, which means that the Ti substrate was completely covered by PbO₂; also the sample hold some strong diffraction peaks at 25.3°, 36.2°, 49.1°, 58.8°, 74.4° and so on, these characteristic diffraction peaks at 25.3°, 36.2°, 49.1°, 58.8° corresponds to (110), (200), (211), and (310) reflections of β-PbO₂, respectively. Furthermore, the sample hold some weak diffraction peaks at 28.5, 23.4, etc, which correspond to that of α-PbO₂.

2.3. Experimental procedures
Electrochemical degradation of methyl orange was carried out in a 300 mL batch electrolytic cell. 200 mL methyl orange solution with a concentration of 2.5-10 mg/L was used as the simulated waste water, and 0.2 g-0.8 g Na₂SO₄ was added into the simulated waste water were used as supporting electrolyte, the conductivity of solution was gauged by a conductivity meter DDSJ-308A (China). The electrolytic
cell was located on a magnetic stirrer to keep the electrolyte well mixed. The Ti/PbO$_2$ electrode was used as anode, and a pure Ti sheet, vertically and parallel to the anode, was used as the counter electrode in the electrolytic cell.

Potentiostatic electrolyses were carried out in the range of 10 V to 20 V. All the experiments were operated at room temperature. The pH value of methyl orange were measured by a pH meter PB-10 (Sartorius, Germany), since the solution was not buffered, the pH value changed in the range of 6.2-6.7, which depended on the degradation level and the concentration of methyl orange. The concentration of methyl orange was determined by testing the absorbance of the samples at regular intervals of 15 min or 30 min. The absorbance of methyl orange were monitored at 466 nm by a UV-vis spectrophotometer UV-1800 (Shimadzu, Japan). The degradation rate of dye waste water was calculated according to the equation below:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

Where $\eta$ is the degradation rate of methyl orange; $C_0$ is the initial concentration of methyl orange, and $C$ is the concentration of methyl orange at sampling after electrolysis.

In this paper, the initial concentration of MO was 2.5 mg/L, and the cell voltage was fixed at 15 V if not specified.

3. Results and Discussion
Electrochemical oxidation of methyl orange was conducted in an electrolysis cell with Ti/PbO$_2$ electrode as anode. The influence of air aeration, cell voltage, solution conductivity on degradation of MO was examined.

The influence of air aeration on the degradation rate of MO was shown in figure 3. The flow rate of air was about 0.3 L min$^{-1}$. Figure 3 indicates that air aeration improved the degradation rate of MO by 11%-25% comparing with that only under magnetic agitation. When air was bubbled into MO solution, the mass transfer of MO to electrode surface can be improved; in addition, oxygen content in solution increased by aeration, and more active species such as H$_2$O$_2$, O$_3$ could be produced and these species could effectively enhanced the decomposition of MO. So in our experiments, air with a flow rate of 0.3 L min$^{-1}$ was always bubbled into the MO solution if not specified.

![Figure 3. Influence of aeration on degradation rate of MO.](image)

Cell voltage had great influence on COD removal of azo dye, and COD removal increased with cell voltage since the increased production of ClO$^-\,$ species [9]. In our experiments, the degradation of MO
also increased with the cell voltage. Figure 4 indicates that the decolorization of MO at electrolysis time of 60 min reached over 85% under the cell voltage beyond 15 V; but in the same interval, the degradation rate of MO reached 34% under the cell voltage of 10 V. When the cell voltage increased from 10 V to 15 V, and 20 V, the degradation rate increased with voltage, but the averaged power also increased from 0.3 W, to 1.2 W, and 2.7 W, that means a big increase in the energy consumption. In order to find a balancing point on the energy efficiency and the removal rate of MO, the energy efficiency of MO removal was also calculated in figure 5. The energy efficiency of MO removal was defined as the removal mass of MO per input energy (kJ). Figure 5 shows that energy efficiency of MO removal decreased with the input energy and the cell voltage. Considering the energy efficiency, the degradation of MO and the treatment time, electrolysis of MO at 15 V was selected in our experiments.

Figure 4. Influence of cell voltage on degradation rate of MO.

Figure 5. Removal efficiency of MO degradation rate of MO.

Conductivity of MO solution influenced the current density of electrode, so influenced the energy input. The conductivity of solution was regulated by the addition quantity of Na₂SO₄. Figure 6 shows that the degradation of MO increased with the conductivity of solution. When the conductivity increased from 1490 μs cm⁻¹ to 2340 μs cm⁻¹, and 4240 μs cm⁻¹, the current increased from 50 mA, to 80 mA, and to 140 mA, which means higher energy was inputted into the electrolytic cell and more
active species for oxidation of MO were produced, so MO removal rate increased with the solution conductivity.

Degradation rate of MO under different concentration of MO was shown in figure 7. Figure 7 indicates that degradation rate of MO decreased with the increase of concentration of MO. When the initial concentration of MO was 2.5 mg L\textsuperscript{-1}, the degradation rate of MO reached 97% after 30 minutes, but the degradation rate decreased correspondingly to 80% and 53% when MO concentration increased to 5 mg L\textsuperscript{-1} and 10 mg L\textsuperscript{-1}, respectively. Because the generation of active species is the same under the same experimental conditions including cell voltage and solution conductivity, so the oxidation of MO has an upper limit, which maybe leads to the decrease in the removal rate of MO solution.

4. Conclusions
The results of electrochemical oxidation of MO solution indicate that an increase in cell voltage and solution conductivity within a certain range was advantageous to increase the degradation of methyl orange solution, but an increase in cell voltage or input power decreased the energy efficiency of MO removal. Compared with no air aeration in solution, air aeration could significantly improve the electrochemical oxidation of methyl orange by 11% and 25%. But the removal rate of MO solution decreased with the initial concentration of MO.

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