Treatment of methyl orange dye wastewater by cooperative electrochemical oxidation in anodic–cathodic compartment

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ABSTRACT

Electrochemical oxidation of methyl orange wastewater was studied using Ti/IrO2/RuO2 anode and a self-made Pd/C O2-fed cathode in the divided cell with a terylene diaphragm. The result indicated that the appropriate rate of feeding air improved the methyl orange removal efficiency. The discoloration efficiency of methyl orange in the divided cell increased with increasing current density. The initial pH value had some effect on the discoloration of methyl orange, which became not obvious when the pH ranged from 2 to 10. However, the average removal efficiency of methyl orange wastewater in terms of total organic carbon (TOC) can reach 89.3%. The methyl orange structure had changed in the electrolytic process, and the characteristic absorption peak of methyl orange was about 470 nm. With the extension of electrolysis time, the concentration of methyl orange gradually reduced; wastewater discoloration rate increased gradually. The degradation of methyl orange was assumed to be cooperative oxidation by direct or indirect electrochemical oxidation at the anode and H2O2, ·OH, O2· produced by oxygen reduction at the cathode in the divided cell. Therefore, the cooperative electrochemical oxidation of methyl orange wastewater in the anodic–cathodic compartment had better degradation effects.

Key words | dye wastewater, electrochemical oxidation, methyl orange, Pd/C O2-fed cathode

INTRODUCTION

The electrochemical method for treatment of organic wastewater has attracted a great deal of attention recently, mainly because of its ease of control, amenability to automation, high efficiency and environmental compatibility (Choi et al. 2010). Various electrochemical processes have been developed, among which electrochemical oxidation methods such as anodic oxidation or the oxidation by electrogenerated oxidizing agents might be the earliest and most extensively studied (Chu et al. 2010; Zhu et al. 2010). In previous works on electrochemical degradation of organic pollutant, the role of cathodes, owing to its reductive reaction, has usually been disregarded. However, it is possible to generate useful oxidant species by cathodic reduction of oxygen, such as hydrogen peroxide, and the cooperative electrochemical oxidation including indirect oxidation at anode and indirect oxidation by hydrogen peroxide at cathode has been proved to be an efficient method for the degradation of dye effluents (Raghu et al. 2009). Some kinds of material have been used to make the cathode, including carbon/polytetrafluoroethylene (C/PTFE), carbon nanotube/PTFE, and polypyrrole composite cathode (El-Desokya et al. 2010; Zarei et al. 2010; Zhang et al. 2011). Generated H2O2 can be coupled with Fe2+ to produce hydroxyl radicals (·OH) that are strong enough to non-selectively oxidize most organics (Dhaouadi et al. 2010; Üstüna et al. 2010; Masomboon et al. 2010). Therefore, the process known as ‘electro-Fenton’ is applied. Using Fenton to degrade dye effluents has obtained certain achievements (Fan et al. 2010). The degradation of the acid red 97 dye, Rhodamine B and industrial textile dye effluents using electro-Fenton systems has been investigated and good results have been achieved (Kayan et al. 2010; Yuan et al. 2011; Salazar et al. 2012). However, the disadvantage of electro-Fenton process is the iron sludge formation (Martínez-Huitilea & Brillas 2009). As reported previously (Wang & Wang 2007), we have explored a new electrochemical...
oxidation system to treat aqueous organic pollutant without adding metal catalysts. It was performed in a diaphragm cell with a C/PTFE gas-diffusion cathode. The degradation of organic pollutants was attributed to the cooperative oxidation processes including direct and/or indirect electrochemical oxidations at the anode and by H2O2 and free radicals produced by the reduction of oxygen at the cathode.

In this paper, we report the anodic–cathodic cooperative degradation of methyl orange dye wastewater in a diaphragm cell with an organic synthesized diaphragm, a Ti/IrO2/RuO2 anode and self-made Pd/C O2-fed cathodes. On the basis of pollutant degradation by the anode, the cathode reaction was exploited to enhance the removal efficiency of methyl orange and reduce energy consumption. In addition, the influence of rate of feeding air, current density and initial pH was studied systematically.

**METHODS**

**Preparation of Pd/C catalyst and gas-diffusion cathode**

Pd/C catalysts with a Pd load of 0.5 wt% were prepared by hydrogen gas reduction, and characterized by X-ray diffraction (XRD), transmission electron microscopy, and X-ray photoelectron spectroscopy. In the catalyst, Pd particles with an average diameter size of 4.1 nm were highly dispersed in the activated carbon with an amorphous structure; Pd content on the surface of the Pd/C catalyst reached 1.3 at% (atomic concentration). The Pd/C O2-fed cathodes were prepared according to the reported procedure (Wang & Wang 2007).

**Procedures**

Electrolysis was conducted in a terylene diaphragm cell of 100 mL. The anode was a Ti/IrO2/RuO2 net of 16 cm². The cathode was a gas-diffusion electrode of 16 cm². A schematic diagram of the experimental setup is shown in Figure 1.

A laboratory direct current power supply with current-voltage monitor was employed to provide the electric power. Synthetic wastewater was used. The initial methyl orange concentration was 50 mg/L; the current density was 39 mA/cm²; the concentration of supporting electrolyte (Na2SO4) was 0.1 mol/L; the distance between electrodes was 2 cm; the initial pH was 7.0. Before the experiment started, air was fed for 5 min in order to keep dissolved oxygen saturation, and the rate of feeding air was 30 mL/s. Air was fed into the gas compartment during electrolysis.

**Analysis methods**

The presence of the methyl orange dye in the wastewater was tested by a UV/Visible spectrophotometer at the wavelength of 470 nm (the maximum absorbance wavelength of methyl orange dye solution). The TU-1901 UV/Visible scanner was used to analyze the electrolyte in which spectral bandwidth was 2 nm and a quick scanning rate was used. A TOC VCPH/C-PN analyzer was used to analyze the removal of total organic carbon (TOC) at different times.

**RESULTS AND DISCUSSION**

**Rate of feeding air**

Figure 2 shows the effects of the rate of feeding air on methyl orange degradation. It can be seen that the methyl orange removal is little affected by the rate of feeding air. After 60 min electrolysis, the methyl orange removal efficiencies at air-sparging rate of 0, 30 and 40 mL/s were all about 100%. Air-feeding contributes to transfer of reactive products, excludes heat, and provides dissolved oxygen that was reduced to H2O2 in the cathode. It was believed that oxygen generated on the anode can diffuse to the cathode.
where dissolved oxygen is reduced to H$_2$O$_2$. Air-sparging rate of 30 mL/s was selected in the paper.

**Current density**

Figure 3 shows the effects of current density on the discoloration efficiency of methyl orange. It showed that the methyl orange removal efficiency increases with current density. This trend was attributed to the fact that the increase of current density helps to accelerate ion transfer, which contributes to the electrode reactions for the methyl orange removal. On the other hand, the increase of current density enhanced the opportunity for side reactions, such as the formation of hydrogen and oxygen. Therefore, the appropriate current density needed to be controlled during electrolysis.

**Initial pH**

The relationship between the methyl orange removal efficiency and initial pH is shown in Figure 4. Discoloration efficiency tended to be steady after 60 min electrolysis and had little difference with different pH. After the start of the electrolytic experiment, the color of the cathodic and anodic compartments would quickly turn to bright red and orange, respectively. It can be attributed to the fact that the methyl orange is an indicator, and at that moment the solution of the cathodic and anodic compartment was alkaline and acidic, respectively. When pH was 13 or 2, the phenomenon was quite special. When pH was 13, the solution color in the cathodic and anodic compartments was orange, because they were both alkaline. Figure 4 (inset) shows that in the anodic compartment discoloration efficiency was poor and the removal of chromaticity was slow. After 60 min electrolysis the discoloration rate of methyl orange only reached 97.7%. When pH was 2, the solution color in the cathodic and anodic compartments was red, because they were both acid. The anodic compartment was brighter because of lower pH.

**TOC removal**

TOC removal efficiency increased with the electrolysis time in the cathodic and anodic compartment (Figure 5). The mineralization degree of aromatic compounds and TOC removal in the cathodic compartment were better than in the anodic compartment. In the anodic compartment of the diaphragm cell, the mechanism of the electrochemical oxidation of organic compounds at the
metallic oxide Ti/O_{2}/RuO_{2} anode was very complex and not yet fully understood. It was believed that the degradation of aromatic compounds in the anodic compartment was supposed to be oxidized by MOx(OH) or MOx\(^+1\) produced on the anode surface (Canizares et al. 1999). For anodic oxidation, it was difficult to achieve total mineralization because of low MOx(OH) or MOx\(^+1\) concentration on the anode. However, the oxidizing power of H\(_2\)O\(_2\), OH\(^-\) and O\(^2-\) existing in the catholyte during O\(_2\) electro-reduction on the Pd/C O\(_2\)-fed cathode is very strong, and can oxidize organics to smaller molecule intermediates or to CO\(_2\) and H\(_2\)O (Wang & Wang 2007). Therefore, the mineralization of methyl orange in the cathodic compartment was better than that in the anodic compartment. The TOC removal of methyl orange increased with the electrolysis time (Figure 5). The total TOC removal was lower than the corresponding degradation fraction of the target methyl orange. This indicated that most of the methyl orange was oxidized to intermediates, which were not further oxidized to CO\(_2\) and H\(_2\)O.

**Analysis of UV/Visible scanning**

The changes in the UV/Visible absorption spectrum of methyl orange dye wastewater in the cathodic and anodic compartment with electrolysis time are shown in Figure 6. Methyl orange shows two significant and characterized absorption bands at 263 and 470 nm. At the cathodic compartment, after 10 min electrolysis, the absorption peak at 263 nm had almost disappeared. With the extension of electrolysis time, the absorption peak at 470 nm significantly weakened, after 60 min it became not obvious. Processed by electrochemical catalytic oxidation degradation, the electrolyte of the cathode room basically had no significant absorption peaks with spectra at 250–800 nm. It showed that the conjugate system of methyl orange molecules except the benzene had been broken, the structure of the molecule changed a lot and a chromophoric group did not exist. With spectra at 210–250 nm, a new absorption peak appeared. It indicated that the methyl orange in the cathode room had been degraded into small molecular organics. At the anodic compartment, because the methyl orange turns yellow in neutral or alkaline solution, and red in acid solution, the features of the absorption peak at 470 nm had red shift for 508 nm in the electrolytic process. The solution in the anodic compartment became acidic quickly after the electrolytic experiment began. The color of the azo dyes is mainly decided by azo bonds, the related chromophoric group and the secondary color group. With increasing electrolytic time, the characteristic peak of methyl orange at 508 nm became weak and disappeared after 30 min. There were still some aromatic intermediate products. The
intermediate products took longer time to degrade, and caused higher absorption at the anode than the cathode. This is one of the reasons that the anodic compartment has a lower mineralization degree than the cathodic compartment. In addition, in the degradation process of dyes, no other new absorption peaks appeared. Therefore, the degradation of methyl orange is caused by the destruction of the chromophoric group, but not a simple discoloration or spectrum hypochromatic shift. As shown in Figures 2, 3 and 4, the discoloration of methyl orange kinetics follow a pseudo-first order. And the kinetic constants in the anodic and cathodic compartment were 0.1156 min⁻¹ ($R^2 = 0.9846$) and 0.0610 min⁻¹ ($R^2 = 0.9987$) under the appropriate process, respectively.

CONCLUSIONS

In a diaphragm electrolytic system, anodic–cathodic cooperative degradation of methyl orange dye wastewater was very good. The appropriate aeration was beneficial to the degradation of methyl orange. The discoloration increased with the adding of the current density. The initial pH value had slight effect on the methyl orange discoloration, but it was not obvious when the pH ranged from 2 to 10. Controlling experimental conditions, TOC removal rate can reach 89.3% on average. The result of UV/Visible scanning showed that both the destruction of the molecular structure and mineralization happened in the electrolytic process. The discoloration of the anodic compartment was better than that of the cathodic compartment, while the mineralization of methyl orange was better in the cathode compartment. Because of the alkaline conditions of the cathode compartment, $H_2O_2$ produced more $·OH$ and $O_2·$. The free radicals had stronger oxidation to methyl orange than the direct and indirect electrochemical oxidation at the anode. The cooperative electrochemical oxidation of methyl orange wastewater in the anodic–cathodic compartment had better degradation effects.

ACKNOWLEDGEMENTS

This work was supported by the Fundamental Research Funds for the Central Universities (No. TD2011-24, HJ2010-6 and YX2010-32), the National Natural Science Foundation of China (Grant 20903012), Program for New Century Excellent Talents in University (No. NCET-10-0233) and Beijing Natural Science Foundation (No. 8122031), which are gratefully acknowledged.

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