

Electrocatalytic Degradation of Methyl Orange on PbO₂-TiO₂ Nanocomposite Electrodes

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ABSTRACT: The electrocatalytic degradation of methyl orange (MO) on PbO₂-TiO₂ nanocomposite electrodes was studied by cyclic voltammetry and bulk electrolysis. The results reveal that PbO₂-TiO₂ nanocomposite electrodes possess higher oxygen evolution overpotential than PbO₂ electrodes and the electrocatalytic degradation of MO on the electrodes is direct oxidation process. The influence of experimental parameters, such as current density, initial MO concentration, initial pH value and Na₂SO₄ concentration, on the MO removal efficiency was studied in order to optimize the electrochemical oxidation process. The results show that the MO and COD removal efficiency in 0.1 mol/L Na₂SO₄ solution containing 30 mg/L MO could reach 95.5 % and 77.2% with current density 30 mA/cm² after 240 min. Compared with PbO₂ electrodes, the PbO₂-TiO₂ nanocomposite electrodes show higher COD removal efficiency and instantaneous current efficiency with MO degradation. The experimental results demonstrate that electrochemical oxidation on PbO₂-TiO₂ nanocomposite electrodes is a suitable method for treatment of water polluted with organic pollutants.

Key words: Electrocatalytic degradation, Methyl orange, Electrochemical property, PbO₂-TiO₂ Nanocomposite electrodes

INTRODUCTION

The development of dye industry has resulted in an increase in the discharge of dye wastewater containing toxic and refractory organic pollutants into the environment. Traditional treatment technologies, including physical, chemical and biological methods, have been adopted, but verified not to meet the strict discharge standard. Therefore, efficient removal method of dye wastewater is an urgent demand for environment protection. In recent years, electrochemical oxidation method has been proposed as an efficient way for the treatment of wastewater containing toxic or refractory organic pollutants, because of its strong oxidation performance, mild operative condition, environmental compatibility and low operative cost (Elaoud *et al.* 2011; Aquino *et al.* 2011; Flox *et al.* 2009).

For electrochemical oxidation methods, anode material plays an important role on the pollutants degradation. PbO₂ has been regarded as an excellent metal oxide anode due to its easy preparation, low cost, chemical stability and high oxygen evolution overpotential (Tahar *et al.* 2009). In order to further

enhance the electrochemical oxidation activity of PbO₂ electrodes, the incorporation of metal oxides, such as ZrO₂ (Velichenko *et al.* 2012; Velichenko *et al.* 2008), Co₃O₄ (Dan *et al.* 2011) and TiO₂ (Amadelli, *et al.* 2009; Li *et al.* 2006), into the lead dioxide matrix was examined. These research works indicate that the performances of PbO₂ electrodes are influenced significantly by the codeposition of metal oxides particles. PbO₂-TiO₂ nanocomposite electrodes is a novel anode material, the lifetime of this electrode was twice as long as that of pure PbO₂ electrodes (Velichenko *et al.* 2009). However, the electrocatalytic property of PbO₂-TiO₂ composite electrodes on treatment of organic pollutants have not been discussed in detail.

In this study, PbO₂-TiO₂ nanocomposite electrodes were used as anodes to treat organic pollutants. Methyl orange (MO) was chosen as model pollutants, and the electrocatalytic property of PbO₂-TiO₂ nanocomposite electrodes was studied by cyclic voltammetry and bulk electrolysis. Systematical

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experiments were conducted to investigate the effects of operating parameters, such as initial MO concentration, applied current density, initial pH value and Na₂SO₄ concentration on MO removal efficiency over PbO₂-TiO₂ nanocomposite electrodes, which was important for enhancing our understanding of this process on the novel anode.

MATERIALS & METHODS

Ti plates (99.5%, 20 mm×50 mm) were degreased in absolute ethanol for 20 min and polished by 320-grit paper strips with water. The plates were cleaned using ultrasound for 10 min, then treated in boiling aqueous 20% oxalic acid for 2 h until TiO₂ was thoroughly dissolved. The SnO₂-Sb₂O₃ interlayer deposited on Ti plates was prepared by thermal decomposition. In this step, 20.0 g SnCl₄, 2.0 g SbCl₃ and 13.2 mL concentrated HCl were dissolved in 100 mL isopropanol. The Ti plates were dipped in this solution for 5 min, then dried at 100 °C for 15 min, and the same procedure was repeated four times. At last, Ti plates were thermally treated in a muffle furnace at 500 °C for 2 h.

PbO₂-TiO₂ nanocomposite electrodes were prepared from the lead nitrate solution containing TiO₂ nanoparticles. The composition of the plating bath was: 0.2 mol/L Pb(NO₃)₂, 0.1 mol/L HNO₃, 0.01 mol/L NaF and 6 g/L TiO₂ nanoparticles. The Pb electrode was used as the cathode, the anode was Ti/SnO₂-Sb₂O₃ interlayer. Prior to plating, ultrasonic agitation was applied to mix the TiO₂ nanoparticles and the electrolyte for 3 h. The TiO₂ nanoparticles (VK-TG01, purity>99.5%) were purchased from Wanjing Int. The average size of TiO₂ nanoparticles was estimated to be 5 nm. All chemicals and reagents were analytic grade and used without purification, purchased from Yuda Int. All solutions were prepared with deionized, doubly distilled water. The operating conditions were current density 30 mA/cm², stirring rate 150 rpm and bath temperature 30 °C. The PbO₂ electrodes were obtained under the same condition from the lead nitrate plating bath without TiO₂ nanoparticles.

Surface morphology of PbO₂ electrodes and PbO₂-TiO₂ nanocomposite electrodes was examined by SUPRA 55VP field emission scanning electron microscope (FESEM). The structure of PbO₂ electrodes and PbO₂-TiO₂ nanocomposite electrodes was analyzed by BRUKER X-ray diffraction (XRD). The grain size of lead dioxide was estimated by Scherrer equation.

A conventional three-electrode cell was used to do the electrochemical experiments. PbO₂-TiO₂ nanocomposite electrode (10mm×10mm) was used as the working electrode, a platinum sheet (15mm×20mm) as the counter electrode, and a saturated calomel

electrode (SCE) as the reference electrode in a separate compartment with a Luggin capillary. Electrochemical measurements were conducted at 25 °C using CHI 660D electrochemical workstation.

The electrolysis of aqueous solutions containing MO was carried out in a 200-mL one-compartment Pyrex glass cell. The anode (PbO₂-TiO₂ nanocomposite electrode) was supported vertically and parallel to the stainless steel cathode. The distance between the cathode and the anode was 1 cm. 100mL simulated wastewater containing MO was used in each experiment. Initial MO concentrations of 10, 20, 30, 40 and 50 mg/L were used to examine the effect of the initial concentration on the MO removal efficiency. The current density was done at 10, 20, 30, 40 and 50 mA/cm². The supporting electrolyte (Na₂SO₄) concentration was 0.01, 0.05, 0.1, 0.15 and 0.20 mol/L, respectively. The electrolysis conditions were temperature at 25 °C. During the experiments, samples were drawn from the reactor at certain intervals and then analyzed. The variation of MO concentration was determined by measuring the absorbance at a fixed wavelength (465 nm), which corresponded to the maximum absorption wavelength using INESA L5 UV-visible spectrophotometer (Shanghai, China).

Chemical oxygen demand (COD) was measured by a titrimetric method using dichromate as the oxidant. The COD removal efficiency (η) was calculated by the following formula:

$$\eta = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100\%$$

where COD₀ is the COD of initial concentration and COD_t is the COD at given time t. The instantaneous current efficiency (ICE) during MO degradation process was calculated using the following equation by measuring COD at different time intervals:

$$\text{ICE} = \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}]FV}{8I\Delta t} \times 100\%$$

Where COD_t and COD_{t+Δt} are the COD at time t and t+Δt (g O₂/L), respectively; F is the Faraday constant (96487 C/mol); V is the volume of the electrolyte (L); and I is the current (A).

Electrochemical treatment was an energy-intense process and its efficiency was usually assessed in terms of energy consumption (E_c, kWh/m³). This could be defined as the amount of energy consumed per unit volume of wastewater treated as shown in the following equation:

$$E_c = \frac{U_{\text{cell}}It}{3600V}$$

where U_{cell} was the average cell voltage (V), I is the

current (A), t is the electrolysis time (s) and V is the volume (L).

RESULTS & DISCUSSIONS

SEM morphology of PbO_2 electrodes and PbO_2 - TiO_2 nanocomposite electrodes are shown in Fig. 1. From Fig 1a, it can be observed that PbO_2 electrodes display typical pyramidal shape. The crystallinity of PbO_2 - TiO_2 nanocomposite electrodes is smaller and the structure is more compact than that of PbO_2 electrodes, and the TiO_2 nanoparticles are distributed in the lead dioxide matrix.

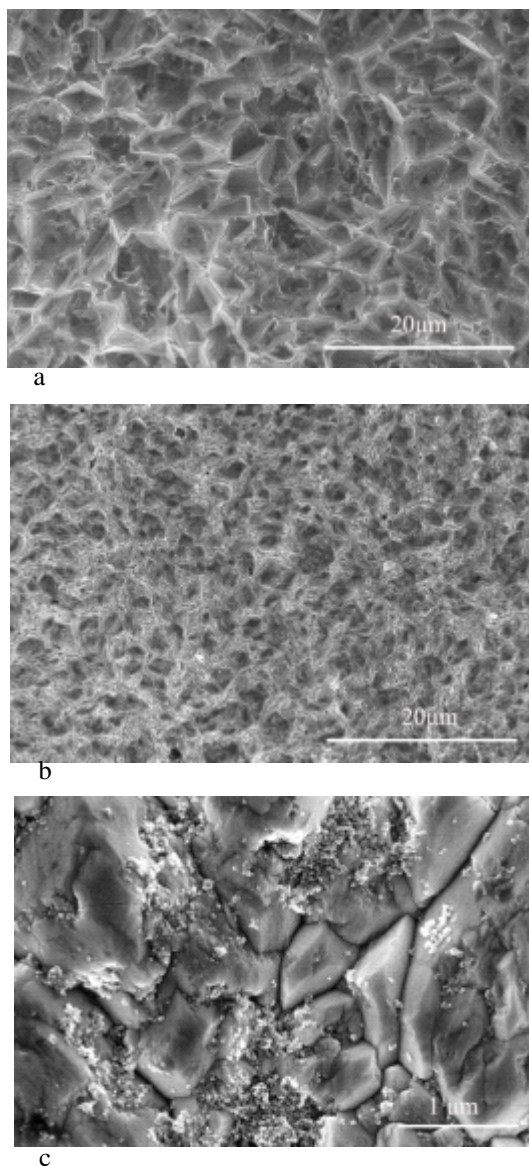


Fig.1. SEM images of (a) PbO_2 electrodes, (b) PbO_2 - TiO_2 nanocomposite electrodes and (c) the magnified image of (b)

Fig. 2 presents the XRD patterns of PbO_2 electrodes and PbO_2 - TiO_2 nanocomposite electrodes.

It can be seen that the main diffraction peaks of PbO_2 electrodes is 32.1° , 49.2° and 62.5° corresponding respectively to (101), (211) and (301) crystal planes of β - PbO_2 . The codeposition of TiO_2 could change their preferred orientation, the main diffraction peaks are (101) and (301) crystal planes of β - PbO_2 . The crystal size of PbO_2 - TiO_2 nanocomposite electrodes (13.5 nm) calculated by Scherrer's formula is smaller than that of PbO_2 electrodes (22.9 nm).

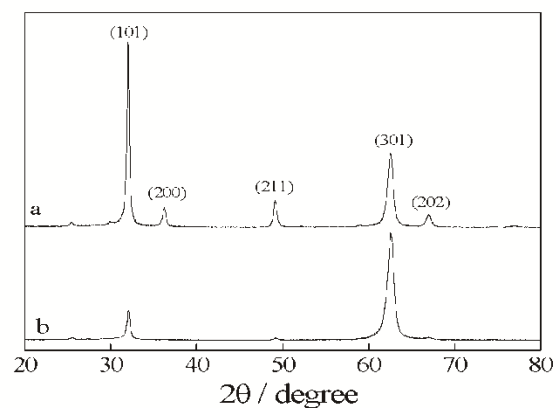


Fig.2. XRD patterns of (a) PbO_2 electrodes and (b) PbO_2 - TiO_2 nanocomposite electrodes

Fig. 3 shows the cyclic voltammograms of PbO_2 electrodes (curve a) and PbO_2 - TiO_2 nanocomposite electrodes (curve b) in 0.1 mol/L Na_2SO_4 solution at the scan rate of 10 mV/s. It can be observed that the oxygen evolution overpotential of PbO_2 - TiO_2 nanocomposite electrodes is 1.56 V (vs. SCE) at 20 mA/cm, and oxygen evolution overpotential of PbO_2 electrodes is 1.46 V (vs. SCE). The result shows that PbO_2 - TiO_2 nanocomposite electrodes possess the higher oxygen evolution overpotential than PbO_2 electrodes, which is favorable to organic oxidation by hydroxyl radicals (Amadelli *et al.* 2011). So the PbO_2 - TiO_2 nanocomposite electrodes should be more suitable for the degradation of organic pollutants than PbO_2 electrodes.

The cyclic voltammogram of PbO_2 - TiO_2 electrodes in 0.1 mol/L Na_2SO_4 solution containing 30 mg/L MO at the scan rate of 10 mV/s is shown in Fig. 3 (inset). During scanning toward positive direction, an oxidation peak can be observed at 0.95-1.35 V (vs. SCE), which is absent in the blank solution. The process at this potential can be attributed to the direct electrochemical oxidation of MO on PbO_2 - TiO_2 nanocomposite electrodes. The electrooxidation of MO and oxygen evolution are in different overpotential region, the overpotential of MO oxidation is lower than the oxygen evolution overpotential, which implies that the oxidation process is caused by direct electron transfer (Amadelli *et al.* 2000).

Fig. 4 shows the effects of current density on the MO removal efficiency. It can be seen that the MO removal efficiency increases with the increase of current density. This could be attributed that higher current density could produce more strong oxidation free hydroxyl radicals, which eventually enhance the MO degradation. When current density reaches 30 mA/cm², MO removal efficiency are 95.5% after 240 min. However, the increase of MO removal efficiency becomes more slowly when the current density is higher than 30 mA/cm². This result is because at higher current density, some undesirable side reactions, such as water electrolysis and oxygen evolution reaction, should compete with the electrooxidation of the contaminant (Song *et al.* 2010).

The industrial wastewater usually involves different concentrations of MO, it is very significant to analyze the effect of initial concentration on the electrochemical oxidation process of MO. Fig. 5 shows that the influence of the initial MO concentration on the removal efficiency. It can be seen that the MO removal efficiency decreases with the increase of initial MO concentration. The results is favored for diffusion control reaction (Martinez-Huitle & Brillas 2009). Therefore, it is inferred that the electro-generated hydroxyl radicals should play an important role for the MO degradation. Additionally, the amounts of generated hydroxyl radicals should be similar at the same operating conditions (except initial MO concentration) in electrolysis. When the initial MO concentration increases, the more hydroxyl radicals is needed. It is possible that competitive consumption of hydroxyl radicals is present and parts of hydroxyl radicals are used to oxidize the intermediates generated from MO degradation (Lucas & Peres 2006). So the removal efficiency would decrease with the increase of initial MO concentration.

Na₂SO₄ was selected as the supporting electrolyte to avoid the production of toxic and carcinogenic chlorinated species. In order to clarify the effect of Na₂SO₄ concentration on the electrochemical degradation of MO, the experiments were performed at different Na₂SO₄ concentration. As shown in Fig. 6, MO removal efficiency increases firstly with the increase of Na₂SO₄ concentration, and then decreases to lower value when Na₂SO₄ concentration surpasses 0.1 mol/L. When the concentration of Na₂SO₄ increases from 0.01 to 0.1 mol/L, the increasing persulphate ions, originated from the oxidation of SO₄²⁻ ions over the anode, can react with MO and hence cause the increase in MO removal efficiency. However, when the Na₂SO₄ concentration increases further, too much SO₄²⁻ ions could contribute to H₂O₂ generation resulted from the generation of S₂O₈²⁻. The electro-generated H₂O₂ could

be oxidized into O₂ at the anode to generate HO₂• as an intermediate, a radical much less oxidant than hydroxyl radicals (Wang *et al.* 2010). Therefore, the increase of Na₂SO₄ concentration promotes the generation of H₂O₂, the decrease tendency in MO removal efficiency can be observed.

The effect of initial pH values on the MO removal efficiency was examined by adjustment of the solution pH from 3 to 11, and the results are shown in Fig. 7 H₂SO₄ or NaOH solutions were used for pH adjustments. It can be found that the initial pH values have a great impact on MO removal efficiency and the removal efficiency is higher in acidic solution. The results can be attributed that the oxidation of organic compounds is more favorable in acidic media, because lower pH values restrict the oxygen evolution reaction and favor organic compound oxidation (Neto & Andrade 2009).

Fig. 8 compared the COD removal efficiency and ICE of PbO₂ electrodes and PbO₂-TiO₂ nanocomposite electrodes in 0.1 mol/L Na₂SO₄ solution containing 30 mg/L MO with current density at 30 mA/cm and pH value at 3. It can be noted that the COD removal efficiency increases with the increase of electrolysis time, indicating that they could be further removed if given much more time. Compared with PbO₂ electrodes, higher COD removal efficiency can be observed for PbO₂-TiO₂ nanocomposite electrodes whose COD removals after 240 min are 77.2% and the COD removal increases by 14%.

The variation of ICE with reaction time is shown in Fig. 8b. It can be observed that the ICE decreases with time, the decrease can be attributed to the complexity of the intermediates formed, especially some hard-to-treatment products (Song *et al.* 2010). This fact suggests that this method is more suitable for the pretreatment of refractory pollutants in wastewater rather than mineralize the pollutants. And the ICE of PbO₂-TiO₂ nanocomposite electrodes is always higher than that of PbO₂ electrodes. The higher COD removal efficiency and ICE of PbO₂-TiO₂ nanocomposite electrodes can be attributed to the high oxygen evolution overpotential (Liu & Liu 2008). So, we conclude that PbO₂-TiO₂ nanocomposite electrodes are more suitable for decomposition of MO than PbO₂ electrodes.

It is very important to estimate the treatment costs in large industrial application, the variation of energy consumption (E_c) as function of MO removal efficiency is shown in Fig.9. For low MO removal efficiency, E_c of both electrodes increases slowly and later it has an exponential increase. This behavior can be probably explained by the formation of more intermediates. The

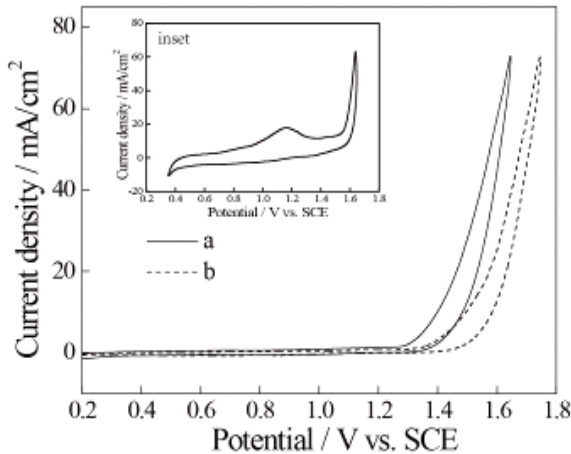


Fig. 3. Cyclic voltammogram of (a) PbO_2 electrodes and (b) $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes in 0.1 mol/L Na_2SO_4 solution and (inset) in the presence of 30 mg/L MO at a scan rate of 10 mV/s at 25 °C

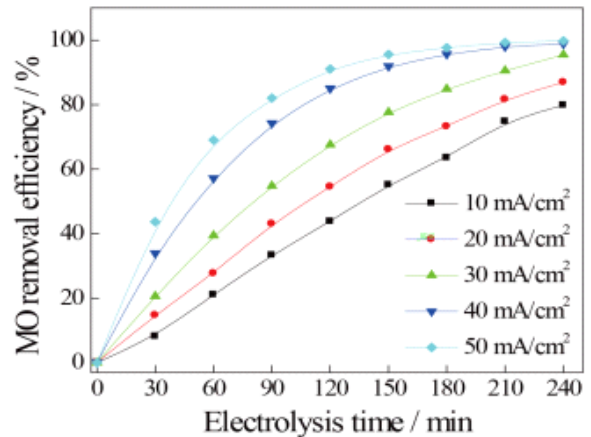


Fig. 4. Influence of the current density on the MO removal efficiency: initial MO concentration 30 mg/L; initial pH value 3.0; Na_2SO_4 concentration 0.1 mol/L

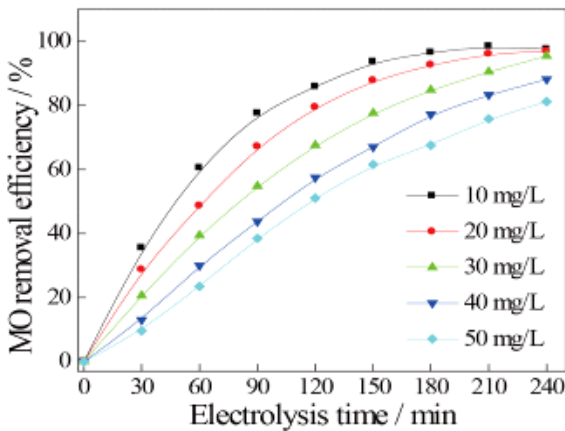


Fig. 5. Influence of the initial MO concentration on the MO removal efficiency: current density 30 mA/cm²; initial pH value 3.0; Na_2SO_4 concentration 0.1 mol/L

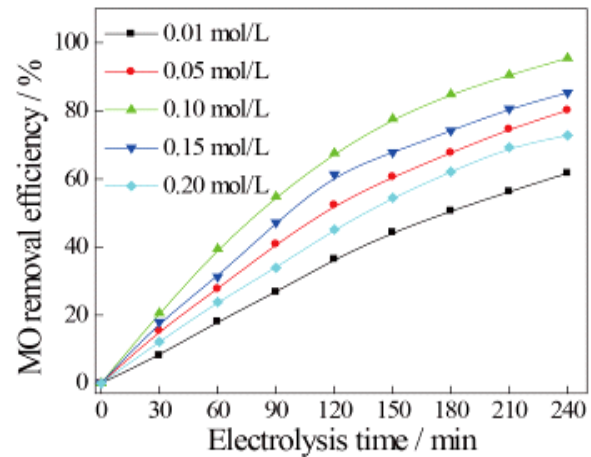


Fig. 6. Influence of the Na_2SO_4 concentration on the MO removal efficiency: initial MO concentration 30 mg/L; current density 30 mA/cm²; initial pH value 3.0.

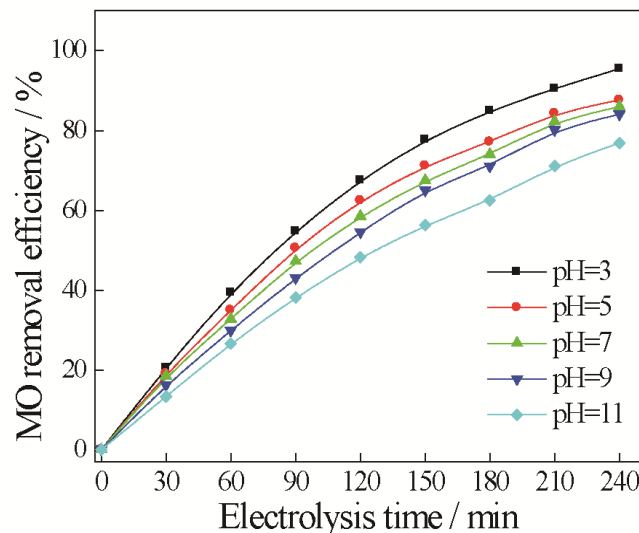


Fig. 7. Influence of initial pH on the MO removal efficiency: initial MO concentration 30 mg/L; current density 30 mA/cm²; Na_2SO_4 concentration 0.1 mol/L

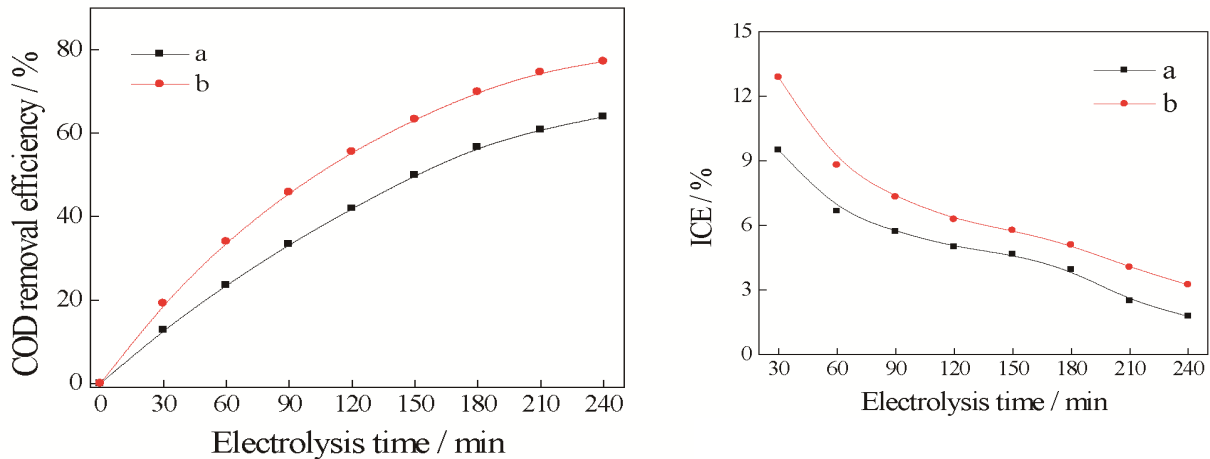


Fig. 8. Variation of (a) COD removal efficiency and (b) ICE as a function of electrolysis time at the (a) PbO_2 electrodes and (b) $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes

results show that $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes consumed less energy than PbO_2 for the higher oxygen evolution overpotential, that is 6.9 kWh/m^3 and 9.2 kWh/m^3 after 240 min for $\text{PbO}_2\text{-TiO}_2$ and PbO_2 , respectively. Although electrocatalytic oxidation is very effective way, its energy consumption is relatively high for practical application as the only treatment process. This fact suggests that this method is more suitable for the pretreatment of refractory pollutants wastewater rather than mineralize the wastewater.

In order to obtain more qualitative information about the electrocatalytic degradation process of MO on $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes and PbO_2 electrodes, the UV-vis absorption spectra of the MO solution in different reaction times are shown in Fig. 10. The strong absorbance band at 465 nm originates

from a conjugated structure formed by the azo bond under the strong influence of the electron-donating dimethylamino group, and the band at 270 nm is ascribed to the $\pi\text{-}\pi^*$ transition related to aromatic rings (Fan *et al.* 2009). It can be observed in Fig. 10 that the intensity of both bands decreases with the same ratios during the electrolysis. This fact indicates that the discoloration occurs simultaneously with oxidation of aromatic rings. From Fig. 10a, we can find that $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes give faster color removal rate than PbO_2 electrodes. For $\text{PbO}_2\text{-TiO}_2$ nanocomposite electrodes, the absorption peak at 465 nm become weaker with the increase of reaction time and nearly disappears after 240 min (Fig. 10a), and no new absorbing band could be found, which indicates that the reaction intermediates have no conjugated π system and no new chromophore forms during the

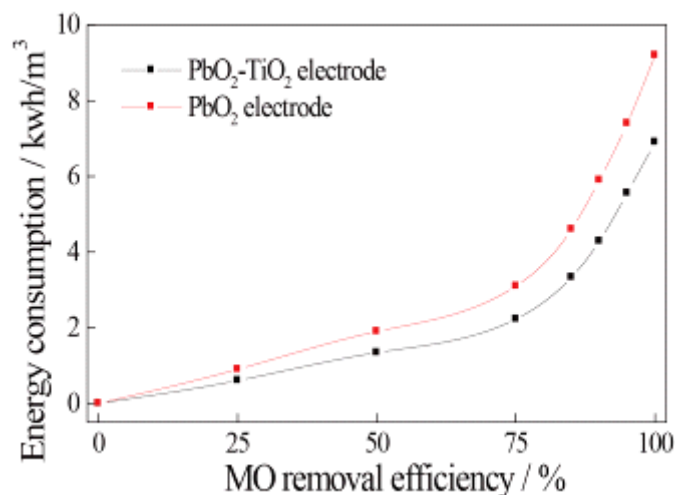


Fig. 9. Evolution of the energy consumption against MO removal efficiency on $\text{PbO}_2\text{-TiO}_2$ and PbO_2 electrodes

CONCLUSION

PbO₂-TiO₂ nanocomposite electrodes were successfully prepared by the anodic electrodeposition, which is finer and more compact than PbO₂ electrodes. Electrochemical measurements show that PbO₂-TiO₂ nanocomposite electrodes possess higher oxygen evolution overpotential and the electrocatalytic degradation of MO on the electrodes is direct oxidation process. The MO and COD removal efficiency in 0.1 mol/L Na₂SO₄ solution containing 30 mg/L MO could achieve 95.5% and 77.2%, respectively, with an current density 30 mA/cm² and pH values 3 after 240 min. In essence, PbO₂-TiO₂ nanocomposite electrodes are effective anodic materials for MO degradation and promising for the electrooxidation of other organic pollutants in wastewater.

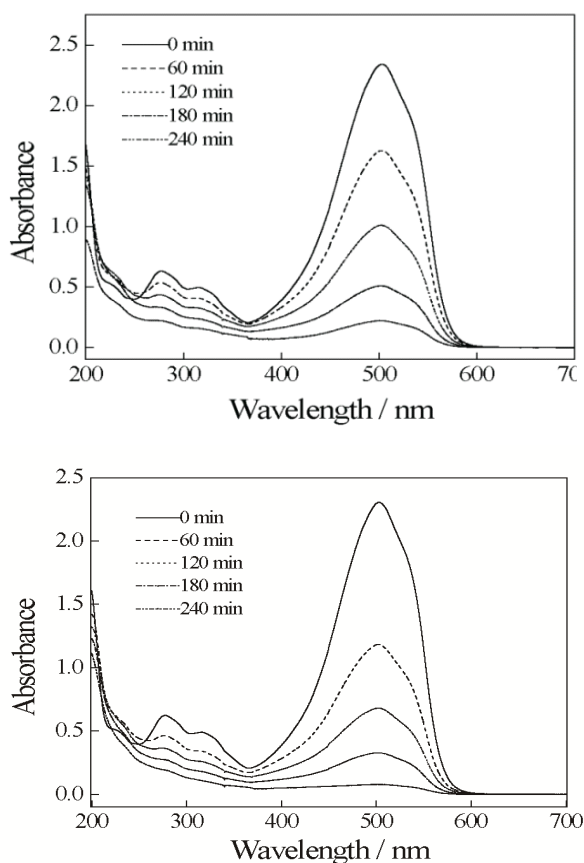


Fig. 10. Changes in the UV-vis spectra with time during electrolysis of MO on (a) PbO₂ electrodes and (b) PbO₂-TiO₂ nanocomposite electrodes

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