



Article

Optimization of Operating Conditions for Electrochemical Decolorization of Methylene Blue with Ti/ α -PbO₂/ β -PbO₂ Composite Electrode

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Abstract: α -PbO₂ was introduced into the intermediate layer of an electrode to prevent the separation of the electrodeposited layer and maintain oxidizing power. The resulting Ti/ α -PbO₂/ β -PbO₂ composite electrode was applied to the electrochemical decolorization of methylene blue (MB) and the operating conditions for MB decolorization with the Ti/ α -PbO₂/ β -PbO₂ electrode were optimized. The morphology, structure, composition, and electrochemical performance of Ti/ α -PbO₂ and Ti/ α -PbO₂/ β -PbO₂ anode were evaluated using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The optimum operating parameters for the electrochemical decolorization of MB at Ti/ α -PbO₂/ β -PbO₂ composites were as follows: Na₂SO₄ electrolyte 0.05 g L⁻¹, initial concentration of MB 9 mg L⁻¹, cell voltage 20 V, current density 0.05–0.10 A cm⁻², and pH 6.0. MB dye could be completely decolorized with Ti/ α -PbO₂/ β -PbO₂ for the treatment time of less than one hour, and the dye decolorization efficiency with Ti/ α -PbO₂/ β -PbO₂ was about 5 times better, compared with those obtained with Ti/ α -PbO₂.

Keywords: electrochemical decolorization; methylene blue; PbO₂ electrode; composite; purification



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1. Introduction

Recently water pollution by dyes in rivers and oceans has become a very serious global environmental problem, since about 20–50% of the applied dyes in textile industry remain in the aqueous phase [1,2]. To solve this problem, we need to treat dyes contained in domestic wastewater and industrial waste. In particular, synthetic dyes contain substances that are toxic and carcinogenic to the human body and can be harmful if taken into the body [1,2].

Various advanced oxidation processes (AOPs) for decomposing or utilizing wastewater containing synthetic dyes have been reported, such as ozonolytic oxidation [3,4], Fenton/electro-Fenton processes [5,6], photocatalysis [7,8], electrocoagulation [9], and electrochemical oxidation [10,11]. Among them electrochemical oxidation has features such as easy operability, low environmental load, safety, and high energy efficiency, it is regarded as one of the technologies of advanced oxidation treatment of wastewater containing toxic organic pollutants [10,11].

Ti-based PbO₂ and boron-doped diamond (BDD) electrodes have a large oxygen generation overvoltage [12–16]. The Ti-based PbO₂ is one of the promising electrode materials, because it can anodize harmful organic substances in wastewater and decompose them efficiently and has the merits of low cost. Methylene blue (MB), which is intensively used

in textile industries, is a non-biodegradable, synthetic, and hazardous organic compound. It is also used as a medicine to treat methemoglobinemia. Common side effects include headache, vomiting, confusion, shortness of breath, hypertension, and so on [17–19]. Firstly, we have tried to modify the Ti-based PbO₂ electrodes for the electrochemical remediation of MB wastewater [20]. However, there is little information on the optimum operating conditions for the electrochemical decolorization of MB with Ti-based β -PbO₂ electrode. Therefore, the present work has mainly dealt with the optimization of operating conditions for the electrochemical degradation of MB at Ti/ α -PbO₂/ β -PbO₂ electrode. Moreover, the morphology, structure, composition, and electrochemical performance of Ti/ α -PbO₂/ β -PbO₂ were evaluated by using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

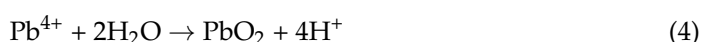
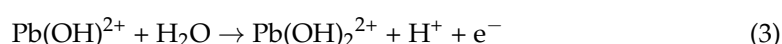
2. Materials and Methods

2.1. Chemicals and Materials

Titanium, copper, and platinum plates (purity: 99.9%, thickness: 1.0 mm) were purchased from Nilaco Co, Ltd. (Tokyo, Japan). Acetone (99.5%), HNO₃ (70%), and NaOH (97%) were obtained from Nacalai Tesque Co, Ltd. (Kyoto, Japan). PbO (99.5%), Pb(NO₃)₂ (99.5%), Cu(NO₃)₂ (99.9%), Na₂SO₄ (99%), and methylene blue (C₁₆H₁₈ClN₃S, 98.5%) were obtained from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). All of other chemicals were analytic grade. All of the solutions were prepared with pure deionized water.

2.2. Preparation of Electrodes

Before the coating, titanium plates (30 × 10 mm, 0.10 mm thickness, 99.5%) were pretreated by sandblasting and ultrasonic cleaning in acetone and ultrapure water [21]. We used an H-type cell for the electrodeposition. The α -PbO₂ layer was electrochemically deposited on the titanium plate in an anolyte (50 mL) consisting of 0.1 mol L^{−1} PbO₂ and 3.5 mol L^{−1} NaOH with a catholyte (50 mL) of 3.5 mol L^{−1} NaOH at 5 mA cm^{−2} for 2 h [22]. Finally, the electro-deposition of the β -PbO₂ layer was performed on the α -PbO₂ layer in 0.3 mol L^{−1} Pb(NO₃)₂ anolyte (50 mL) with 0.3 mol L^{−1} Cu(NO₃)₂ catholyte (50 mL) at 10 mA cm^{−2} for 2 h [23–26]. The PbO₂ formation process is shown as follows (Equations (1)–(4)):



2.3. Characterization

The surface morphology of each layer of the electrodes was investigated with Hitachi S-4000 scanning electron microscopy (SEM). XRD was performed using X-ray diffraction (XRD, Ultima IV, horizontal sample type, RIGAKU Corp., Tokyo, Japan) to analyze the crystal structure that makes up each electrode. The chemical composition and state of the active layer of electrodes were investigated using a Quantera SXM X-ray photoelectron spectrometer (XPS, ULVAC-PHI, Chanhassen, MN, USA) using Al K α radiation. All of the electrochemical measurements, including the electrochemical impedance spectroscopy (EIS), were performed in an electrochemical workstation equipped with a three-electrode cell system (VersaSTAT 3F; AMETEK Scientific Instruments, Berwyn, PA, USA). The working electrode was the prepared PbO₂ electrode. A platinum plate and a silver-silver chloride electrode (Ag/AgCl sat. KCl) were used as the counter and reference electrodes, respectively.

2.4. Electrochemical Decolorization

Electrochemical decolorization and oxidation of MB was performed in a home-made, divided H-type cell. A Nafion 117-type cation exchange membrane (0.18 mm thickness,

Sigma-Aldrich, St. Louis, MO, USA) was used as the diaphragm. The 9 mg L⁻¹ MB anolyte solution (50 mL) contained the 0.50 mol L⁻¹ Na₂SO₄ supporting electrolyte [1,2]. The catholyte was 0.50 mol L⁻¹ Na₂SO₄ solution. The prepared PbO₂ electrodes and Pt foil (30 × 10 mm, 0.10 mm thickness, 99.98%) were acted as the anode and cathode, respectively. The cell voltage between anode and cathode was 5~30 V. The decolorization of MB was measured by UV-Vis absorption spectrometry (UV-2450; Shimadzu, Kyoto, Japan).

3. Results and Discussion

3.1. Characterization of Electrodes

3.1.1. XRD Analysis

XRD was used to analyze and determine the crystal structure of Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂ composites. Figure 1 shows the XRD patterns of the prepared Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂ electrodes.

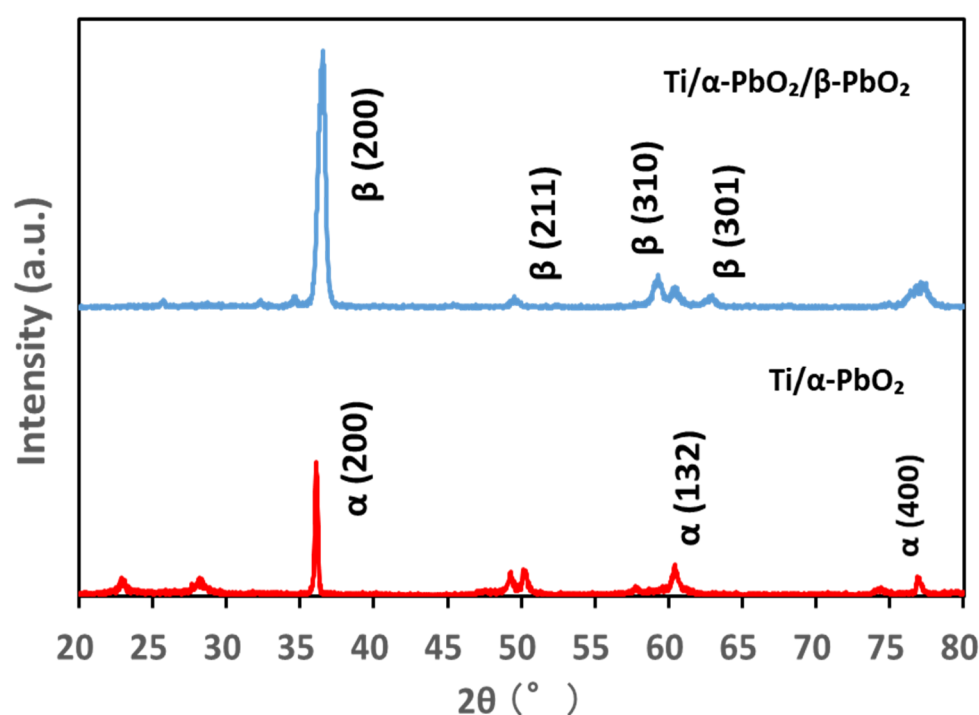


Figure 1. XRD spectra of Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂.

The characteristic diffraction peaks of α-PbO₂ at 36.06°, 60.38°, and 76.96° correspond to the lattice planes (200), (132), and (400) [14,27,28], whereas those of β-PbO₂ located at 36.52°, 49.4°, 59.3°, and 62.8° correspond to the lattice planes (200), (211), (310) and (311), respectively [27,29,30]. The main diffraction peaks of α-PbO₂ and β-PbO₂ both corresponded to the lattice plane (200). Since no unexpected diffraction peak was generated in each pattern, it can be considered that impurities were not generated during the electrode fabrication. The diffraction peaks indicate that the β-PbO₂ layer is electrochemically deposited on α-PbO₂ layer. The XRD peak of Ti/α-PbO₂/β-PbO₂ are sharper and stronger compared that with Ti/α-PbO₂, indicating it that the crystallinity of the electrode seems to be improved. Ti/β-PbO₂ were not be fabricated because β-PbO₂ could not be electrodeposited on the Ti.

The half-peak width of the strongest diffraction peaks (200) was employed to calculate the average particle sizes of PbO₂ crystals by the Debye-Scherrer formula (Equation (5)).

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (5)$$

where D is the average particle sizes (nm), K a constant (0.89), λ the wavelength of X-ray (0.15418 nm), β the half-height width of diffraction peak, and θ the diffraction angle. The average particle sizes of Ti/ α -PbO₂ and Ti/ α -PbO₂/β-PbO₂ electrodes were 0.85 nm and 0.30 nm, respectively. Thus, there was a distinct difference in average particle sizes as shown in the SEM images.

3.1.2. SEM Study

Figure 2 shows SEM images of Ti/ α -PbO₂ and Ti/ α -PbO₂/β-PbO₂ electrodes. The surface of the Ti/ α -PbO₂ electrode was coated with fragile cotton-like fine particles (Figure 2a). On the other hand, the surface of the Ti/ α -PbO₂/β-PbO₂ electrode was decorated with dense pyramidal fine particles (Figure 2c). Compared with Ti/ α -PbO₂ electrode, in Ti/ α -PbO₂/β-PbO₂ electrode the surface of the fine particles is smoother and denser, and strengthened chemically and physically [14,28,30].

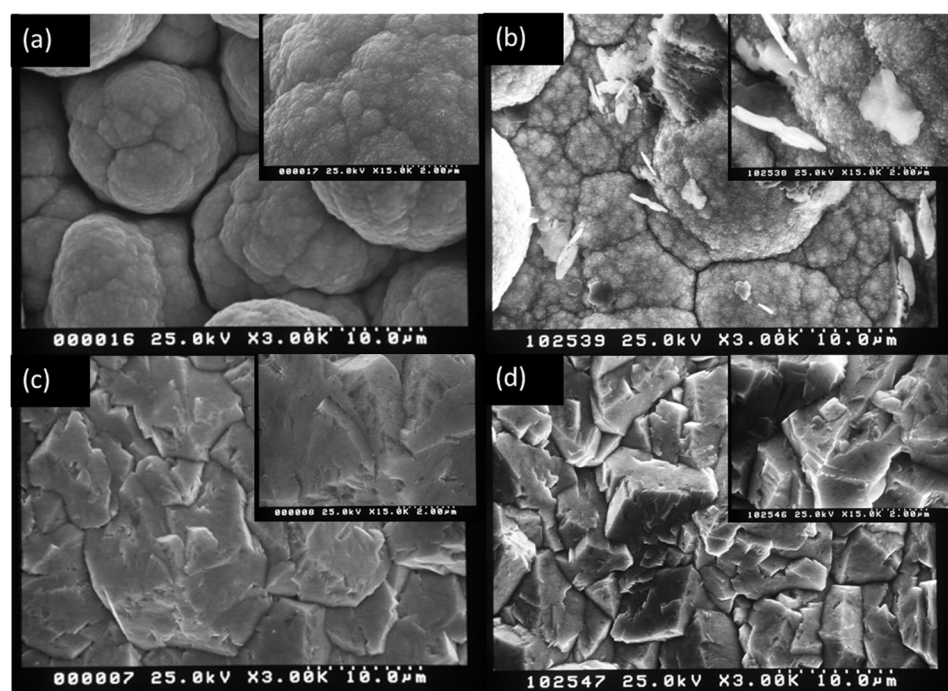


Figure 2. SEM images of (a) Ti/ α -PbO₂; (b) Ti/ α -PbO₂ used for 5 h; (c) Ti/ α -PbO₂/β-PbO₂; (d) Ti/ α -PbO₂/β-PbO₂ used for 5 h.

These electrodes were applied to 5 h of electrochemical decolorization, and then the surface shape was examined. In the case of the Ti/ α -PbO₂ electrode, aggregates of organic impurities were observed on the coating surface, and disintegration of fine particles was also observed to some extent (Figure 2a,b). On the other hand, for the used Ti/ α -PbO₂/β-PbO₂ electrode, it was observed that the fine particles on the coating surface maintained a perfect pyramidal shape and the electrode surface was not changed during the electrolysis (Figure 2c,d). The results indicate it that Ti/ α -PbO₂/β-PbO₂ composite electrode has better stability, durability, and recyclability.

3.1.3. XPS Analysis

We obtained information on the chemical states of the elements in Ti/ α -PbO₂ and Ti/ α -PbO₂/β-PbO₂ electrodes by XPS analysis. The results of the XPS survey show very sharp characteristic peaks of Pb and O in both samples, confirming the successful preparation of the PbO₂ anode on the titanium plate (Figure 3a). In addition, clear peak shifts of Pb_{4f} and O_{1s} were observed at the Ti/ α -PbO₂/β-PbO₂ electrode, compared to the Ti/ α -PbO₂ electrode (Figure 3b,c). The shift can be attributed to the existence of a strong interaction between α -PbO₂ and β-PbO₂. The XPS spectra of Pb_{4f} are shown in Figure 3b. α -PbO₂ has

two peaks centered on 138.4 and 143.3 eV, which correspond to $4f_{7/2}$ and $4f_{5/2}$ of Pb^{4+} , and the difference in binding energy was calculated to be about 4.9 eV, whereas β - PbO_2 has peaks centered on 137.5 and 142.4 eV, both $4f_{7/2}$ and $4f_{5/2}$, had a negative side shift to the 0.9 eV, compared to the peak of α - PbO_2 , respectively [14,27,30]. The XPS spectra of O_{1s} are shown in Figure 3c.

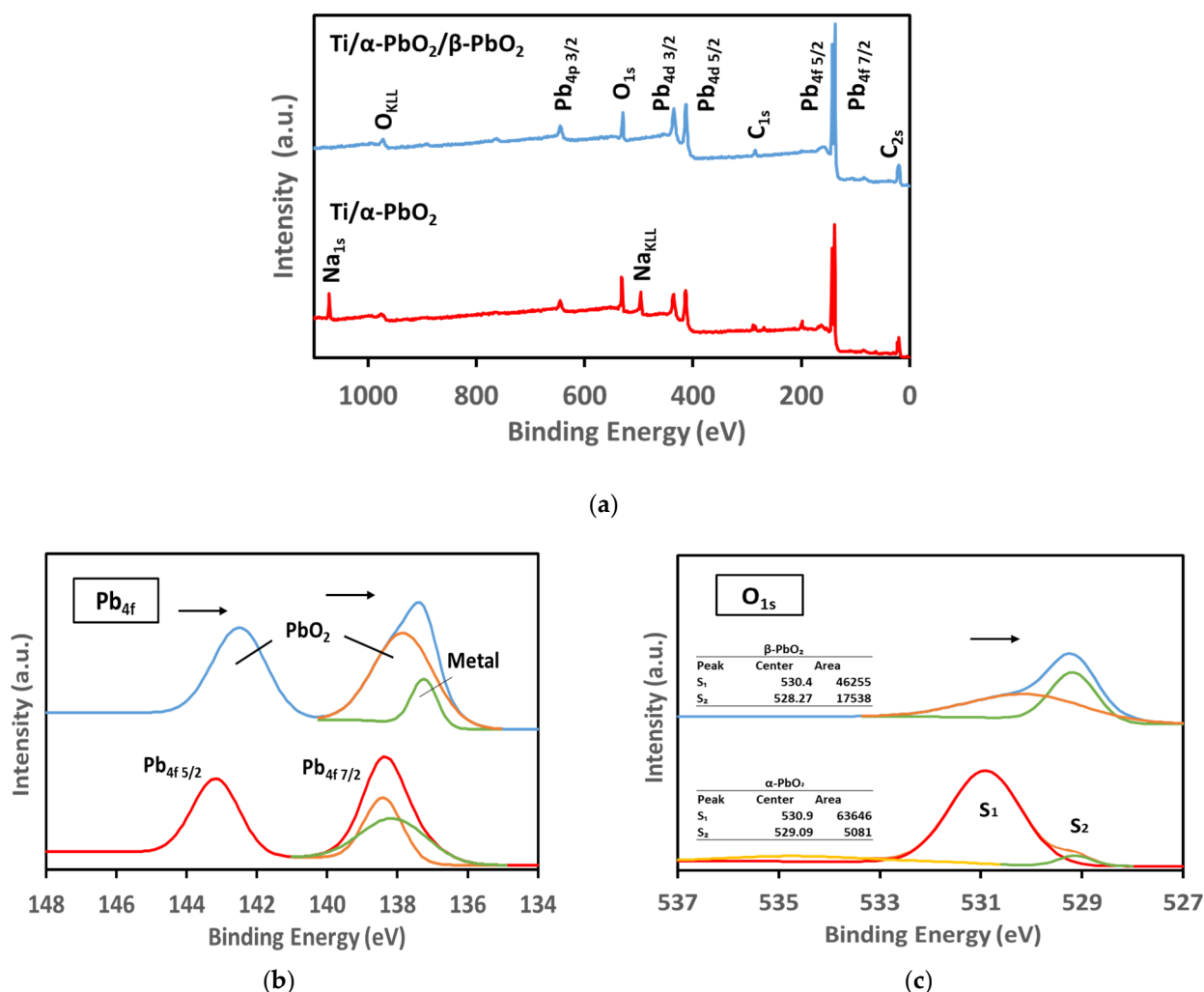


Figure 3. (a) XPS analysis of Ti/ α - PbO_2 /β- PbO_2 and Ti/ α - PbO_2 ; (b) Pb_{4f} spectra of Ti/ α - PbO_2 /β- PbO_2 and Ti/ α - PbO_2 ; (c) O_{1s} spectra of Ti/ α - PbO_2 /β- PbO_2 and Ti/ α - PbO_2 .

The low binding energy component of the O_{1s} peak near 528.4–533.1 eV (S_1) is derived from the crystal lattice oxygen [14,27]. On the other hand, the high binding energy component of the O_{1s} peak near 527.2–529.4 eV (S_2) is attributed to the surface-adsorbed or chemisorbed OH^- groups and H_2O on the oxide. The hydroxyl groups generated on the electrode surface can be trapped in the induced holes to form hydroxyl radicals.

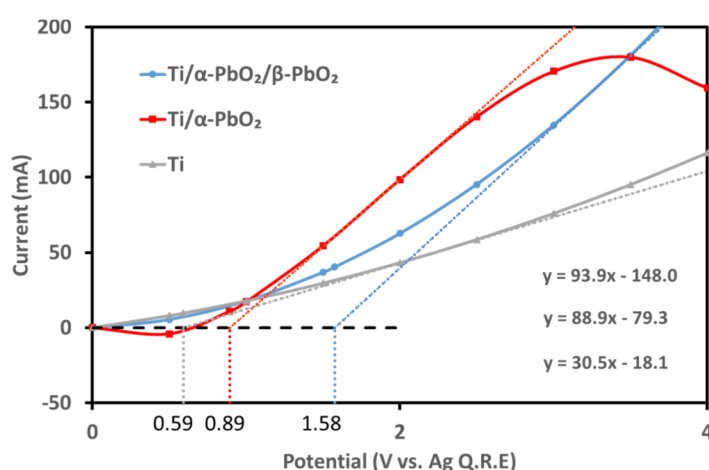
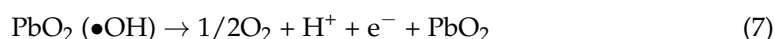
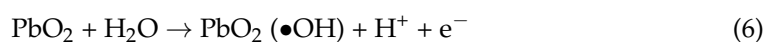
From the results, it is predicted that electron-hole recombination will be suppressed and electrode catalyst efficiency will be improved [14,26,30]. By comparing the number of hydroxyl groups (S_2) present on each electrode surface, β- PbO_2 (17,538) was larger than α- PbO_2 (5081). As shown in Table 1, the percentage ($\epsilon\%$) of the S_2 to the total oxygen ($S_1 + S_2$) for Ti/ α - PbO_2 /β- PbO_2 electrode was 27.5%. Obviously, $\epsilon\%$ increased, compared to Ti/ α - PbO_2 electrode (7.40%). Therefore, the Ti/ α - PbO_2 /β- PbO_2 electrode was favorable to generate more $\cdot OH$ radicals and has better electrode catalytic activity.

Table 1. Analysis of O_{1s} peaks from electrodes.

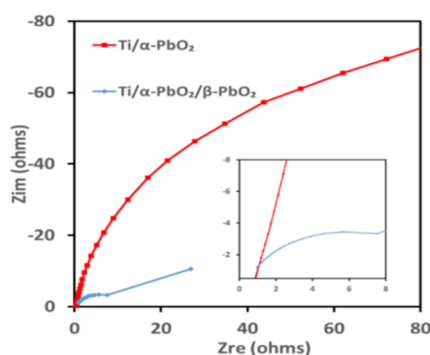
Electrode	Binding Energy (eV)		S ₁ Content %	S ₂ Content %
	S ₁	S ₂	S ₁ /(S ₁ + S ₂)	S ₂ /(S ₁ + S ₂)
Ti/α-PbO ₂	530.9	528.3	92.6	7.4
Ti/α-PbO ₂ /β-PbO ₂	530.4	529.1	72.5	27.5

3.1.4. Electrochemical Performance

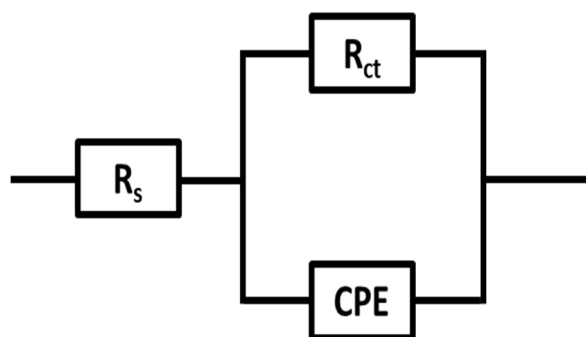
Figure 4a shows the polarization curves of Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂ electrodes in 0.50 mol L⁻¹ Na₂SO₄ solution (scan rate 2 mV s⁻¹). The oxygen evolution potentials (OEPs) of prepared electrodes are determined by the extrapolation of current density curve. The OEP at the Ti/α-PbO₂/β-PbO₂ electrode (1.58 V) is more positive than that at the Ti/α-PbO₂ electrode (0.89 V). High OEP inhibits the oxygen evolution reaction and is very effective for increasing the electrochemical oxidation efficiency of organic pollutants contained in wastewater [31–33]. Therefore, the Ti/α-PbO₂/β-PbO₂ electrode may be suitable for decolorizing methylene blue. The oxygen evolution reaction is shown as follows (Equations (6) and (7)):



(a)



(b)



(c)

Figure 4. (a) Polarization curves in 0.50 mol L⁻¹ Na₂SO₄ at scan rate of 2 mV s⁻¹. (b) Electrochemical impedance spectroscopy in 0.50 mol L⁻¹ Na₂SO₄ with frequency range of 10⁵–10⁻¹ Hz. (c) Randles equivalent circuit.

The charge transport behaviors of electrodes were investigated using electrochemical impedance spectroscopy (EIS). The interfacial behavior of Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂

PbO₂ electrodes was evaluated in 0.50 mol L⁻¹ Na₂SO₄ solution in the frequency range of 10⁵–10⁻¹ Hz. Figure 4b shows the Nyquist plots acquired from the EIS measurement of the Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂. As shown in the plot, one-semicircle traces can be obtained for each electrode, which reveals single time constant behaviors for the relation of charge transfer resistance. Generally, the radius of the semicircle is related to the charge transfer resistance, and the smaller the arc radius, the faster the electron transfer at the interface [30–33]. The Randles equivalent circuit as displayed in Figure 4c is frequently employed to simulate the electrochemical characteristics on electrode surface/solution interface. There are mainly R_s, CPE, and R_{ct} in the equivalent circuit. R_s usually presents the resistance of electrolyte and active material, which is considered as the junction with the real axis at the high-frequency end; CPE (constant phase element) represents the capacitive behavior on electrode surface; R_{ct}, the diameter of the semicircle, represents charge transfer resistance at the PbO₂ film/solution interface. 1/2 R_{ct} of Ti/α-PbO₂/β-PbO₂ (5.51) is smaller than that of Ti/α-PbO₂ (91.7), indicating that the improved electrochemical performance of the Ti/α-PbO₂/β-PbO₂ [31–34].

3.2. Optimization of MB Decolorization Conditions

3.2.1. UV-Vis Spectra

Figure 5a shows the change in the UV-Vis spectra of MB during the electrochemical decolorization process using Ti/α-PbO₂/β-PbO₂ electrode. Strong absorption peaks were observed at 292 and 664 nm, which are derived from the absorbance of the major chromophore group of MB [17,19]. The absorbance peak (0.03 mg L⁻¹) decreased with the electrochemical decolorization treatment time and disappeared completely after 30 min. The facts indicate it that the MB chromophore group has been completely removed [10,11]. Besides, a blue shift in absorbance was observed during the electrochemical decolorization process. This is universal in other bleaching approaches and means the appearance of by-products in the MB chromophore group [33–35]. It was confirmed that the Ti/α-PbO₂/β-PbO₂ electrode functioned as a good catalyst for electrical decolorization. In the present work, a sharp absorbance peak at 664 nm was used to show the degree of decolorization. Figure 5b compares the decolorization efficiency of MB using Ti/α-PbO₂ and Ti/α-PbO₂/β-PbO₂ electrodes as anodes by electrochemical method in 0.05 mol L⁻¹ Na₂SO₄ solution containing 3 mg L⁻¹ MB with the voltage at 20 V, current density 8–12 mA cm⁻², and initial pH value 6.0.

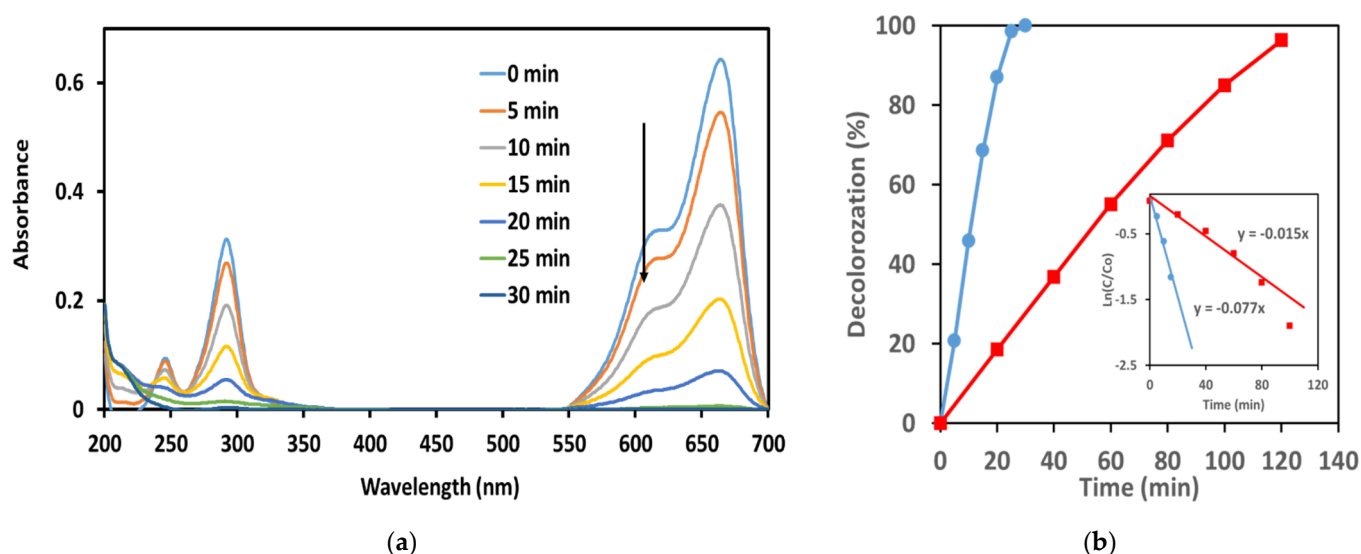


Figure 5. (a) UV-Vis spectra of MB during the electrochemical oxidation process with Ti/α-PbO₂/β-PbO₂. (b) Decolorization efficiency of MB with Ti/α-PbO₂/β-PbO₂ (blue) and Ti/α-PbO₂ (red). Na₂SO₄ electrolyte: 0.05 mol L⁻¹; reaction time: 2 h; electrode distance: 3 cm; initial pH: 6.0; reaction temperature: 25 °C; MB: 3 mg L⁻¹; and cell voltage: 20 V.

The methylene blue decolorization efficiency was obtained as follows (Equation (8)). Also, the semi-log graphs of MB decolorization fit the pseudo-first-order model, as described in Equation (9):

$$\text{MB decolorization efficiency (\%)} = (C_0 - C_t)/C_0 \times 100 \quad (8)$$

$$\ln(C_t/C_0) = -kt \quad (9)$$

where C_0 and C_t are absorbance values in 664 nm of the MB solution at the initial and the given time t , respectively, and k is the pseudo-first-order rate constant (min^{-1}). The result shows it that MB can be completely removed on $\text{Ti}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2$ electrodes after 30 min, whereas, on $\text{Ti}/\alpha\text{-PbO}_2$ electrodes it required 120 min under the same conditions. The decolorization processes for both electrodes followed the pseudo-first-order model [36,37], and the kinetics curves are shown in the inset. The rate constant of MB by $\text{Ti}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2$ electrode was 0.077 min^{-1} , which was about 5 times that of $\text{Ti}/\alpha\text{-PbO}_2$ electrode (0.015 min^{-1}) [38,39].

3.2.2. Effect of Initial MB Concentration

Figure 6 shows the decolorization efficiencies of MB as a function of different initial MB concentrations. It can be observed that the MB decolorization rates decreased with the increase of initial MB concentration. The main reason could be ascribed to it that the treated MB amounts were almost the same even if the MB initial concentration increased and the competing between MB and its intermediates occurred for the active sites. Hence, we applied the kinetics constants of MB removal to express the competition for hydroxyl radicals between MB and its intermediates. When the MB concentration was high ($>15 \text{ mg L}^{-1}$), the reaction could not follow the first-order model, because the rate-determining step was mass transfer process (diffusion). From Fig inset, the k values were 0.098, 0.053, 0.036, 0.024, 0.016, and 0.020 min^{-1} for the initial MB concentration of 3, 6, 9, 12, 15, and 30 mg L^{-1} , respectively, which further proved the increased competition between MB and its intermediates for hydroxyl radicals with increasing initial concentration. When initial MB concentration increased from 3 to 15 mg L^{-1} , the decolorization efficiency k changed as the initial concentration increased. This can be explained by the rapid reaction of hydroxyl radicals with MB molecules at the electrode at the voltages without oxygen evolution. Thus, a relatively high concentration of MB (9 mg L^{-1}) was chosen as the optimum initial concentration [38,39].

3.2.3. Effect of Applied Cell Voltage

The applied current density is deeply involved in the control of hydroxyl radical generation, which is an important factor in the electrochemical decolorization of MB. Figure 7 shows the effect of applied current density on the electrochemical performance. From the results in Figure 7a, it can be found that when the applied voltages increased from 10 to 20 V, the MB removal efficiencies increased from 48.2% to 88.7%, as well as apparent rate constants increased from 0.011 to 0.027 min^{-1} , respectively. It can be deduced that increasing voltage had a positive influence on the decomposition of MB in the range 5–20 V. The enhanced decolorization and degradation of MB at larger current densities could have resulted in higher hydroxyl radical production. In Figure 7b, a current density after 10 min increased at the voltage of 30 V, however, only a slight increase occurred after 10 min when the voltage increased from 5 to 20 V. Thus, the increased oxygen evolution as the side reaction prevented the degradation of MB. The increase in the electrochemical decolorization efficiency with an increase in current density is a typical phenomenon for processes controlled by mass transfer. Therefore, the cell voltage of 20 V could be chosen for the optimum condition (corresponding to current density $0.05\text{--}0.10 \text{ A cm}^{-2}$), owing to the energy cost.

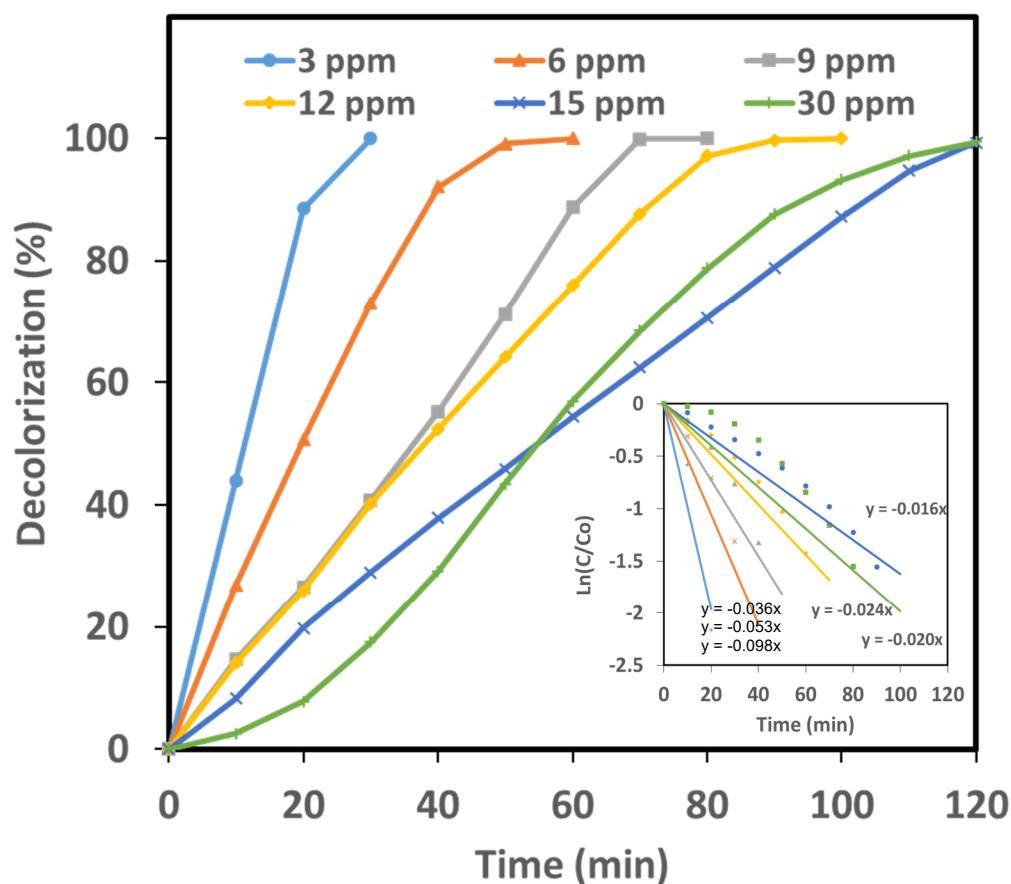


Figure 6. Effects of MB concentration on decolorization efficiency. Na_2SO_4 electrolyte: 0.05 mol L^{-1} ; reaction time: 2 h; electrode distance: 3 cm; initial pH: 6.0; reaction temperature: 25°C ; MB: $3\text{--}30 \text{ mg L}^{-1}$; cell voltage: 20 V.

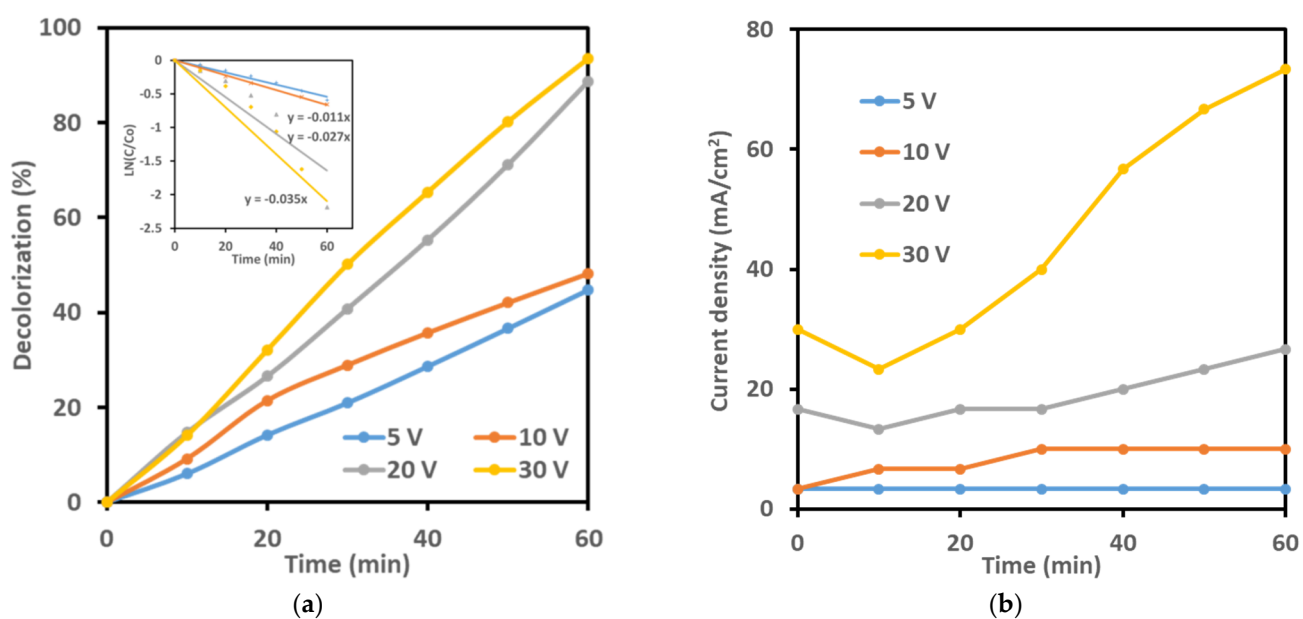


Figure 7. (a) Effects of cell voltage on decolorization efficiency. Na_2SO_4 electrolyte: 0.05 g L^{-1} ; reaction time: 1 h; electrode distance: 3 cm; initial pH: 6.0; reaction temperature: 25°C ; MB: 9 mg L^{-1} ; cell voltage: $5\text{--}30 \text{ V}$. (b) Current density change vs. treatment times.

3.2.4. Effect of Initial pH

The initial pH of the solution is a significant element of the electrochemical decolorization process. In Figure 8, the effect of initial pH on MB decolorization was investigated. The NaOH and H₂SO₄ solutions were used for pH adjustment to obtain a given pH value. It was found from Figure 8a that the decolorization efficiencies of MB under acid or alkaline conditions were better than those obtained under neutral conditions.

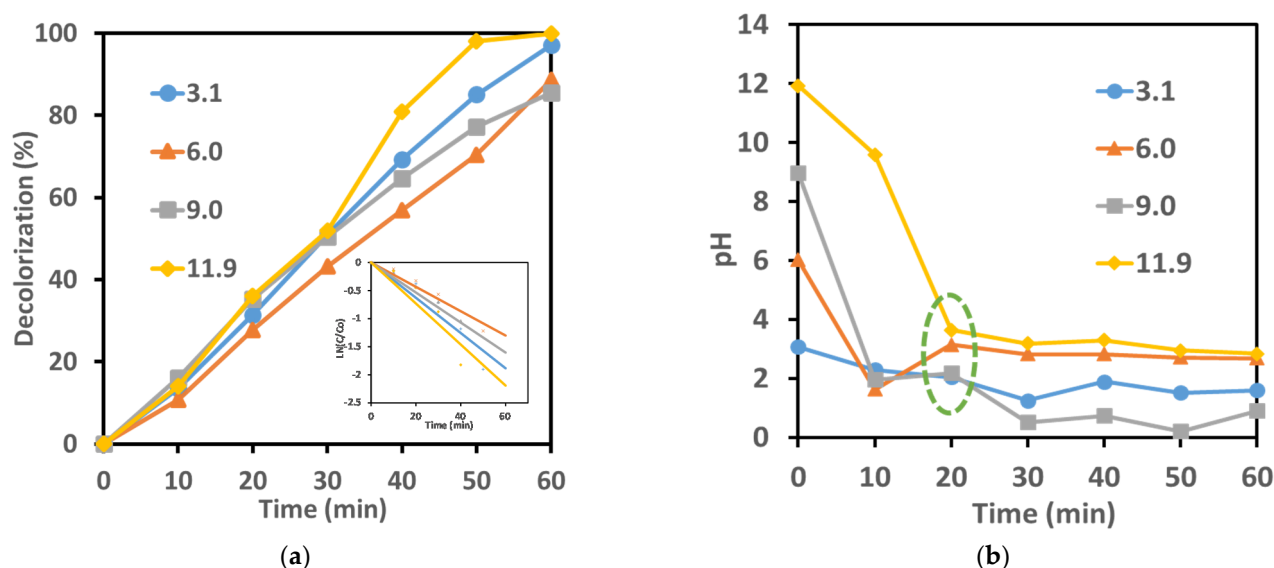


Figure 8. (a) Effects of pH on decolorization efficiency. Na₂SO₄ electrolyte: 0.05 mol L^{−1}; reaction time: 1 h; electrode distance: 3 cm; initial pH: 3.1–11.9; reaction temperature: 25 °C; MB: 9 mg L^{−1}; cell voltage: 20 V. (b) pH change vs. treatment times.

The *k* values of pH 11.9 and pH 3.1 were 0.015 and 0.009 min^{−1}, respectively, which were larger relative to those at pH 6.0. The results may be attributed to the oxygen evolution side reaction, electrostatic attraction, and the molecular MB structure. At lower pH (under acidic conditions), oxygen evolution is more strongly suppressed, leading to faster and more effective decolorization. At higher pH (under basic conditions), the electrostatic attraction is strong, because MB is present primarily in the form of anions, making it very difficult to adsorb to the electrode surface. In addition, the generation of hydroxyl radicals is effective in the presence of hydroxide ions. However, as shown in Figure 8b, the sample solution pHs changed to acidic conditions after 20 min. This change is derived from the generation of hydrogen ions during the electrochemical process. As a consequence, the difference in initial pH did not significantly affect the continuous decolorization, the initial pH 6.0 was the optimum pH value for considering the practicality and environment.

3.2.5. Effect of Initial Na₂SO₄ Concentration

Electrolyte concentration can be considered to be an important factor in the electrochemical decolorization process, since it greatly fluctuates the current density. Figure 9a shows the effect of electrolyte concentration on the decolorization efficiency of MB. The treatments were investigated with 0.01, 0.05, 0.07, 0.09, and 0.15 g L^{−1} Na₂SO₄ electrolyte. The results show it that an increase in electrolyte concentration significantly accelerates the decomposition of MB, and as the electrolyte concentration increases from 0.01 g L^{−1} to 0.15 g L^{−1}, the decolorization efficiency of MB increases proportionally (Figure 9a). Obviously, high electrolyte concentrations promoted the decolorization and decomposition of MB. Figure 9b shows almost constant current densities during treatment time. The Na₂SO₄ concentration had little effect on the fluctuation of current density.

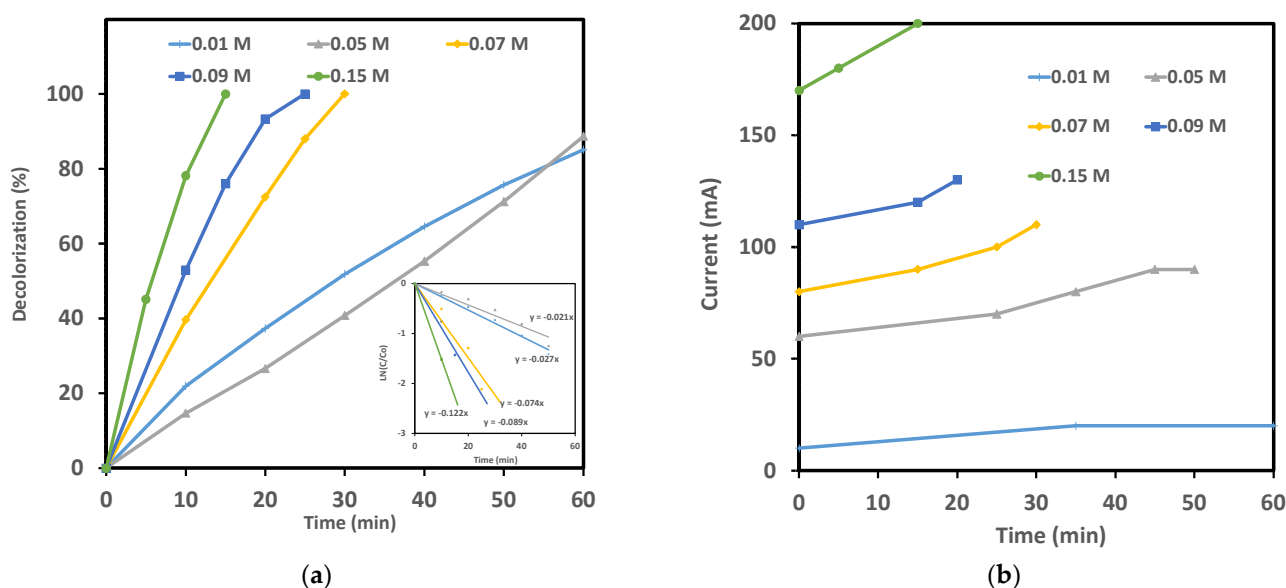


Figure 9. (a) Effects of concentration of Na₂SO₄ on decolorization efficiency. Na₂SO₄ electrolyte: 0.01~0.15 mol L⁻¹; reaction time: 1 h; electrode distance: 3 cm; initial pH: 6.0; reaction temperature: 25 °C; MB: 9 mg L⁻¹; and cell voltage: 20 V. (b) Current vs. treatment times.

3.3. Electrode Stability

The recyclability is a very significant parameter for assessing electrode stability, durability, and economic applicability. Therefore, the electrochemical stability of the Ti/ α -PbO₂/ β -PbO₂ electrode was estimated by conducting a recycling test for MB decolorization. Ti/ α -PbO₂/ β -PbO₂ electrode exhibited the similar decolorization efficiency for MB after five cycles to that of first treatment. Figure 10 shows that the XRD of Ti/ α -PbO₂/ β -PbO₂ electrode before and after repeated electrode. It was confirmed that the surface crystal structure could be retained, although the intensity of β -PbO₂ peaks reduced slightly. This result demonstrates it that the Ti/ α -PbO₂/ β -PbO₂ electrode can be repeatedly used as an excellent electrode.

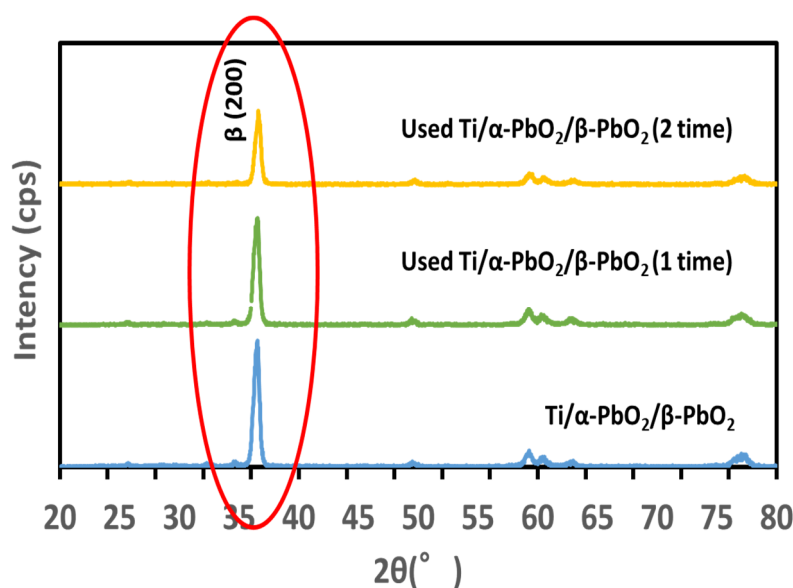


Figure 10. XRD of Ti/ α -PbO₂/ β -PbO₂ before and after five cycles. Na₂SO₄ electrolyte: 0.01 mol L⁻¹; reaction time: 1 h; electrode distance: 3 cm; initial pH: 6.0; reaction temperature: 25 °C; MB: 0.05 g L⁻¹; and cell voltage: 20 V.

4. Conclusions

The operating conditions for the electrochemical decolorization of MB with Ti/ α -PbO₂/β-PbO₂ were optimized. The optimum operating parameters for the electrochemical decolorization of MB at Ti/ α -PbO₂/β-PbO₂ composites were as follows: Na₂SO₄ electrolyte 0.05 g L⁻¹, initial concentration of MB 9 mg L⁻¹, cell voltage 20 V, current density 0.05–0.10 A cm⁻², and pH 6.0. The MB dye with 9 mg L⁻¹ concentration could be completely decolorized with Ti/ α -PbO₂/β-PbO₂ after a treatment time of less than one hour.

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