



Degradation of dye wastewater in a thin-film photoelectrocatalytic (PEC) reactor with slant-placed TiO₂/Ti anode

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ABSTRACT

A thin-film photoelectrocatalytic (PEC) reactor with slant-placed TiO₂/Ti anode was developed and successfully applied to degrade Rhodamine B (RhB) and textile effluent. Using a 5–150 mg L⁻¹ RhB solution as the model system, thin-film PEC removed total color and TOC by 99–28% and 78–15%, respectively, in 1 h, which is much higher than 82–7% and 60% to zero by conventional PEC. The enhanced treatment efficiency achieved by thin-film PEC process was attributed to the significantly reduced path length of irradiation light source. The wastewater was kept circulating during the experiments to timely refresh the aqueous film on the TiO₂/Ti anode and promote the mass transfer of the target pollutants and the degradation products in the bulk solution. The thin-film PEC reactor can degrade both simulated and real dye wastewater efficiently under UV light irradiation. Results suggested that thin-film PEC was particularly superior for treating a high concentration solution. The thin-film PEC reactor was also applied to treat RhB solution efficiently under solar light irradiation. The recycle experiments demonstrated excellent stability and reliability of the slant-placed TiO₂/Ti anode. This study proposed a simple and effective method to design PEC reactor applicable for industrial dye wastewater treatment.

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1. Introduction

TiO₂ is a cheap, non-toxic and stable semiconductor photocatalyst. TiO₂-based photoelectrocatalytic (PEC) oxidation has been proven to be an efficient method for degrading organic compounds [1–3]. Although this field has been an active area of scientific research, and many efforts have been made to improve the photocatalytic (PC) capability of the TiO₂ film electrode [4–6]; however, there are only a few literatures reporting PEC degradation of real wastewater [2] and development of PEC reactors applicable for real wastewater treatment has not yet been successfully achieved.

Since electron–hole pairs are produced by light irradiation, light intensity is a major factor in PEC reaction and the reaction rate is directly dependent on the irradiation intensity [7,8], the radiation path must be taken into account for PEC reactors design. That is to say, light absorption of target compounds and reactor's wall is an additional factor that has to be considered in the design of photoreactors. Unfortunately, the photoanode in conventional PEC reactor is completely immersed in solution; thus the radiation light has to pass through the wall of the reactor and sample solution before it reaches the photoanode surface [1,3,9], causing signifi-

cant loss of radiation power due to absorption, and consequent low treatment efficiency. High power light source has been employed by laboratorial researches [9,10]; however, the setup was complex (generally with a jacket to circulate cooling water), and considerable amount of light power was lost in the form of heat dissipation. Obviously, this method would not be applicable in industrial applications due to the high operating cost. Invalid light consumption is a well-known problem that restricts the practical application of TiO₂ PEC oxidation in real organic especially of colored wastewater treatment; however, only a few studies are available to address this problem [7].

In order to improve the light utilization efficiency of TiO₂ electrode, we proposed an original idea termed as thin-film PEC reactor with slant-placed TiO₂/Ti anode in this work, in which organic degradation happens on the surface of TiO₂/Ti anode, which is coated with an aqueous film. Based on Beer's law [11],

$$A = \varepsilon bc \quad (1)$$

where A is the absorbance, ε is the absorption coefficient, b is the path length, and c is the molarity of solution. The absorbance, or radiation power loss due to solution absorption in this study, can be significantly reduced with the decrease of path length.

We chose RhB solutions as the model system to evaluate the proposed thin-film PEC, and to compare with the conventional PEC. Industrial dye effluent was chosen as target compound to inves-

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tigate the feasibility of the thin-film PEC reactor because highly colored wastewaters are commonly discarded by the textile industry worldwide [12]. It is estimated that more than 15% of the world dye production, or ca. 400 tones a day [13], is released into the environment during synthesis, processing, and use. Most of the dyes disposed are of non-biodegradable nature and direct biological treatment of the colored effluents is not effective [14].

Photocatalytic materials have been widely studied in recent years. With the development of material sciences, more and more highly efficient and economic photocatalysts will be available for large-scale industrial applications. Free solar light is a good UV–visible radiation source to activate the modified or no-modified TiO_2 photocatalyst to treat wastewater. The significance of this research is to establish PEC procedures promising to be industrialized in the future for real wastewater treatment under solar light irradiation.

2. Experimental

2.1. Materials and reagents

Titanium sheets (99.6% purity, length 10 cm, width 4.2 cm, thickness 1.5 mm, surface area 42 cm^2) were purchased from Shanghai Hongtai Metal Production Co., Ltd (Shanghai, China) and employed as the substrates for TiO_2 film coating. Tetrabutyl titanate (Sinopharm Chemical Reagent Co., Ltd, China) was used as a precursor for preparing TiO_2 colloidal suspensions. Textile effluent was collected from a textile factory (Shanghai, China). It referred to the original disposal from the textile furnishing and finishing process. The effluent sample was stored at 4°C and used without any further treatment. Its physicochemical properties are: $\text{pH} = 11.3$, conductivity = $208 \mu\text{S cm}^{-1}$ and $\text{TOC} = 277 \text{ mg L}^{-1}$. RhB (Shanghai Jiaying Chemical Co., Ltd, Shanghai, China) was of commercial grade and used as received. Na_2SO_4 (Shanghai Chemical Reagent Co., Ltd, Shanghai, China) was employed as the supporting electrolyte. All other chemicals were of reagent grade or better quality and used as received. All solutions were prepared in doubly distilled water.

2.2. Preparation of TiO_2/Ti electrode

The TiO_2/Ti anode used both in thin-film PEC reactor and conventional PEC reactor was prepared by sol–gel and dip-coating method. A detailed description of the preparation procedure can be found in our previous work [15]. The field emission scanning electron microscopy (FESEM) image and X-ray diffraction (XRD) pattern of the TiO_2/Ti anode demonstrate that the TiO_2 particulate was in size of about 46 nm and mainly was anatase [15].

2.3. TiO_2/Ti thin-film PEC reactor

The thin-film PEC reactor consisted of a Pyrex cell (length 65 mm, width 45 mm, maximum height 147 mm and minimum height 35 mm) using the TiO_2/Ti sheet as anode and Cu sheet (15 mm long, 10 mm wide and 1.5 mm thick) as cathode (Fig. 1a and b). The anode was placed at 60° slant angle. The minimum distance between the anode and cathode was about 1.0 cm. When the reactor was filled with sample solution, the TiO_2/Ti anode was arranged that 21 mm in length was immersed in the solution and the other part was exposed to the open air. This wastewater was circulated by a pump (BT00–100M, Longer Precision Pump Co., Ltd, Baoding, China) from the bulk solution to a reservoir. In order to evaluate the treatment effect of the proposed thin-film PEC and compare with the conventional PEC, a quartz cell (length 45 mm, width 10 mm, height 125 mm) was used in the experiment to carry out the conventional PEC oxidation, in which TiO_2/Ti anode was wholly immersed into the dye solution, distance between the anode

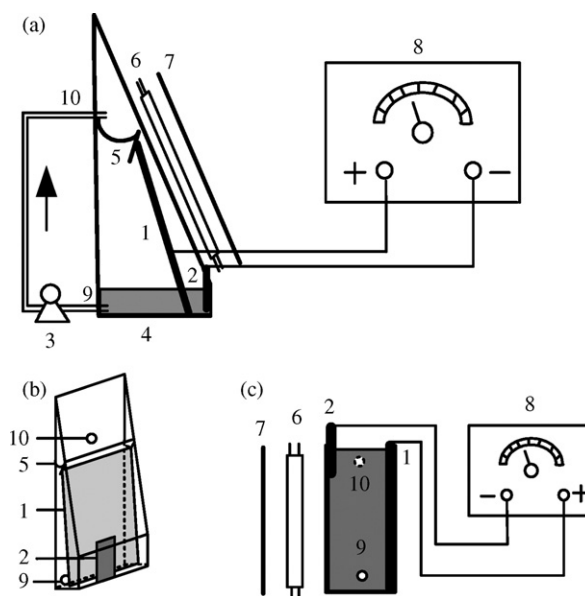


Fig. 1. (a) Schematic diagram of the side view of the thin-film PEC reactor. (b) The front view of the reaction cell. (c) Schematic diagram of the side view of the conventional PEC reactor. The figure is not to scale. 1: TiO_2/Ti anode; 2: cathode; 3: pump; 4: reaction cell; 5: reservoir; 6: UV lamp; 7: aluminum foil; 8: DC power supply; 9: water outlet; 10: water inlet.

and cathode was about 7 mm (Fig. 1c). In conventional PEC process, wastewater was circulated the same flux as the thin-film PEC process.

PEC experiments under artificial UV light were carried out as below:

An 11 W mercury lamp (Philips, 254 nm) was placed about 3 cm away from and parallel to the TiO_2/Ti anode. In order to maximize the use of the light energy, the mercury lamp was backed by a piece of aluminum foil placed behind the lamp and opposite to the reactor, so that light could be reflected and used to irradiate the TiO_2/Ti electrode. The radiation power was 15 mW cm^{-2} measured by a power meter (Spectra Physics, model 407A, USA) at the position where the electrode was placed. However, we have to point out that, when the electrode was immersed in the solution, the effective light intensity reaching the electrode surface declined, depending upon the composition and concentration of the sample solution. The cell and lamp were placed in a box, and the electrodes were connected to a DC power supply.

PEC experiments under solar light were carried out on sunny days of November 19th and 21st 2007 between 10:00 a.m. and 3:00 p.m. The reaction cell was adjusted timely so that the TiO_2/Ti anode faced the sun. Solar light intensity was measured for every 30 min and the average light intensity over the duration of each experiment was calculated. The average intensity of solar light measured by the power meter above was 6.3 and 6.7 mW cm^{-2} on November 19th and 21st, respectively.

2.4. Degradation experiments

Four sets of blank experiments were performed to verify the feasibility of the thin-film PEC process. The sample was $55 \text{ mL } 20 \text{ mg L}^{-1}$ RhB solution containing 1.0 g L^{-1} Na_2SO_4 electrolyte. The wastewater circulating speed was 7.7 L h^{-1} if not specifically mentioned. The first set of experiments was to circulate the solution without providing irradiation and bias potential to evaluate the physical adsorption removal of RhB by TiO_2/Ti electrode. The second set of experiments was to evaluate the photo-degradation of RhB, in which the solution was circulating and irradiated with UV

light but Ti instead of TiO_2/Ti electrode was used. The third set of experiments was to circulate the solution with UV illumination but without bias potential to evaluate the photocatalytic (PC) degradation effect of TiO_2/Ti electrode. The fourth set of experiments used the TiO_2/Ti electrode as anode (bias +0.8 V) in darkness to perform normal electrolysis (EC) degradation.

The PEC experiments were carried out at two modes, i.e. thin-film and conventional mode to treat 55 mL RhB solution at different concentration levels (containing $1.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$), and thin-film PEC was applied to treat real textile effluent. The bias potential applied to the TiO_2/Ti electrode was optimized and +0.8 V was employed for RhB solution and +1.0 V for textile effluent if not specially mentioned. Initial pH value of the RhB solution was adjusted to 2.50 with $1 \text{ mol L}^{-1} \text{ NaOH}$ or H_2SO_4 before PEC treatment if not specially mentioned (optimum efficiency was obtained at this pH value). Samples were taken from the cell at desired intervals and filtered through a Millipore filter (pore size $0.45 \mu\text{m}$) before chemical analyses.

2.5. Chemical analysis

Concentrations of dye in the solutions were determined by measuring absorbance using a Unico UV-vis spectrophotometer (UV-2102 PCS, UNICO, Shanghai). The absorbance was measured in 1 cm quartz cell at 563 nm for RhB solution and 514 nm for textile effluents because they have maximum absorbance at these wavelengths, respectively. Sample from initial RhB concentration higher than 20 mg L^{-1} solution was diluted suitable times to measure absorbance and calculate decolorization efficiency. TOC concentration represents the mineralization extent of organic substances. It was measured using a TOC/TN analyzer (Jena 3000, Germany). pH value was measured with a PHS-3C pH meter (Shanghai Leici Apparatus Manufactory, Shanghai, China), and solution conductivity was obtained with a DDS-307 conductivity analyzer (Shanghai Leici Apparatus Manufactory, Shanghai, China).

3. Results and discussion

3.1. Calculation of aqueous film thickness

The thickness of the aqueous film on TiO_2/Ti anode can be roughly determined using following equations [16]:

$$Q = SV = W\delta V \quad (2)$$

$$V = 0.5gt \sin \alpha \quad (3)$$

$$L = 0.5gt^2 \sin \alpha \quad (4)$$

where S is the section area that the wastewater flows through, V is the volume of wastewater flowing through the section area S per time, i.e. it is the wastewater average velocity on the anode surface on conditions of neglecting resistance and effect of wastewater flux, δ is the aqueous film average thickness, Q is the wastewater flux and it can be measured, W is the width of the anode, L is the length of the anode, g is the acceleration of gravity, t is the time for wastewater flowing through the anode surface, α is the slant angle of anode, and 0.5 is coefficient of average between maximum and minimum velocity.

3.2. Selection of circulating flux

The effect of circulating flux on decolorization efficiency for thin-film PEC oxidation is shown in Fig. 2. The results demonstrate that degradation efficiency is stable as circulating flux is low, and decreases with the increase of circulating flux as it is $>7.7 \text{ L h}^{-1}$. This can be explained mainly because circulating flux can affect the

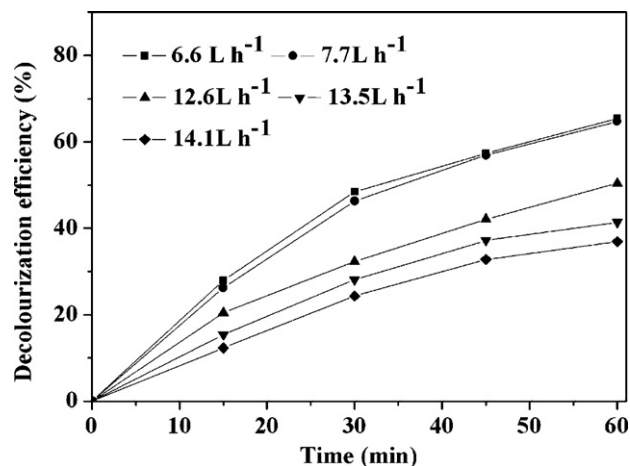


Fig. 2. Effect of circulating flux on decolorization efficiency ($C_{\text{RhB}} = 50 \text{ mg L}^{-1}$, bias potential 0.8 V, pH 2.50, $1.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$, UV lamp).

aqueous film thickness. At a flux of 6.6, 7.7, 12.6, 13.5 and 14.1 L h^{-1} , the average film thickness calculated using Eqs. (2) and (3) was about 67, 78, 128, 137 and $143 \mu\text{m}$, respectively.

Aqueous film thickness can affect degradation in two aspects: on the one hand, it can affect reaction chance of TiO_2 photocatalyst and RhB molecule in the aqueous film, and the chance increases with the increase of film thickness; on the other hand, it can affect the light intensity on the anode surface, and the light intensity decreases with the increase of the film thickness due to solution absorption based on Beer's law. Moreover, circulating flux can affect the residence time of wastewater on the anode surface and thus affect the degradation degree of RhB molecule. Considering these aspects, there is an optimal circulating flux and 7.7 L h^{-1} is selected in this work.

3.3. Selection of bias potential

The bias potential is an important parameter in the process of PEC degradation of organics. Bias potentials ranged between +0.4 and +1.2 V were monitored over 1 h of thin-film PEC treatment. Results are shown in Fig. 3. The results demonstrate that the decolorization efficiency increases as a function of applied potential up to +0.8 V for RhB and +1.0 V for real effluent. Further increases in

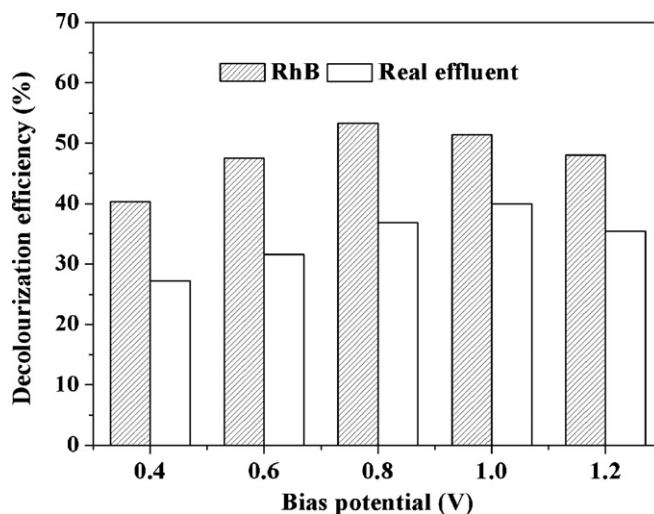


Fig. 3. Effect of bias potential on decolorization efficiency for RhB ($C_{\text{RhB}} = 50 \text{ mg L}^{-1}$, circulating flux 7.7 L h^{-1} , pH 5.56, $1.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$, UV lamp) and real effluent (circulating flux 7.7 L h^{-1} , UV lamp).

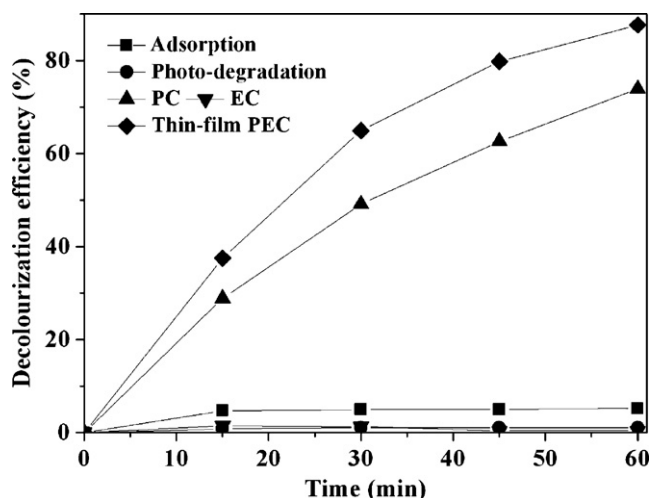


Fig. 4. Decolorization of 20 mg L⁻¹ RhB solution using different processes (potential 0.8 V, pH 2.50, circulating flux 7.7 L h⁻¹, 1.0 g L⁻¹ Na₂SO₄, UV lamp).

potential lead to a slight reduction in degradation. This can be explained by more water oxidized by photogenerated holes [17]. Bias potentials +0.8 and +1.0 V were selected as optimal bias potential, respectively, for RhB solution and real effluent.

3.4. Treatment of the RhB solution by different processes

In a TiO₂/Ti PEC process, RhB may be degraded or removed under various pathways including TiO₂ adsorption, photo-degradation, photocatalysis (PC), electrolysis (EC), and photoelectrocatalysis (PEC). The degradation of RhB evaluated by color removal under the aforementioned conditions is shown in Fig. 4. Almost no RhB was removed by photo-degraded directly and electrolysis (EC) using +0.8 V bias. Around 5% of RhB was removed by TiO₂ adsorption and 74% by PC in 60 min. However, the thin-film PEC exhibited superior performance, achieving 88% color removal within the same time frame.

The overall PEC reaction is affected by light intensity and mass transfer [18,19]. The excellent performance of the thin-film PEC with slant-placed TiO₂/Ti anode was attributed to the following reasons: (1) the utilization efficiency of UV radiation was significantly improved for the upper part of the TiO₂/Ti electrode because of the negligible light loss associated with the thin aqueous film; (2) the degradation products were removed and new RhB molecules were adsorbed in a timely manner on the electrode surface through circulating solution by the pump. This was a dynamic system always with a maximum pollutant load on the thin-film PEC part at a given time, kinetically favoring the degradation; (3) the lower part of the anode worked as a conventional PEC reactor to further degrade the dyes in the solution, even though the efficiency was lower due to the loss of radiation power when light passed through the bulk solution; and

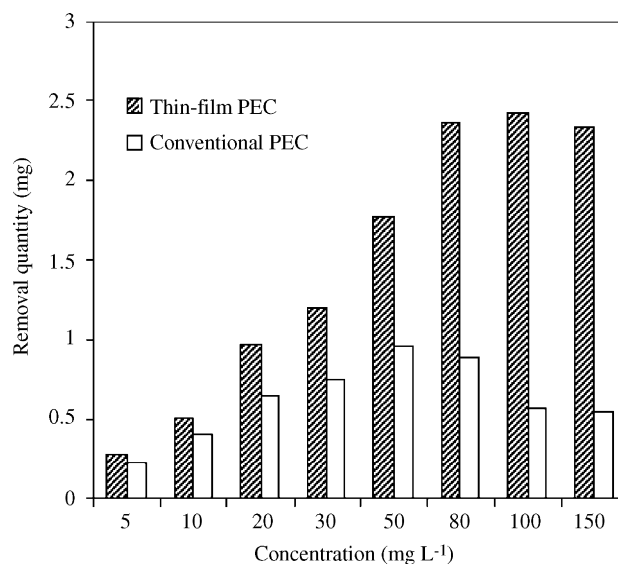


Fig. 5. Absolute quantity of RhB degraded for 1 h by thin-film PEC and conventional PEC procedure at different RhB concentration levels (bias potential 0.8 V, pH 2.50, circulating flux 7.7 L h⁻¹, 1.0 g L⁻¹ Na₂SO₄, UV lamp).

(4) the positive bias effectively prevented the recombination of the photon-induced electrons and holes, which extended the lifetime of the driven force for the degradation of organic pollutants [20].

3.5. Thin-film PEC vs conventional PEC

The thin-film PEC and conventional PEC were quantitatively evaluated and compared in the following experiments. Individual RhB solutions, with concentrations ranging from 5 to 150 mg L⁻¹, were treated by these two processes. Results of color and TOC removal are listed in Table 1. In the investigated concentration range, thin-film PEC demonstrated the removal of total color and TOC by 99–28% and 78–15%, respectively, in 1 h, which is much higher than 82–7% and 60% to zero by conventional PEC. It clearly shows that, using TiO₂/Ti photoelectrode with the same surface area and identical UV radiation source, thin-film PEC is superior to conventional PEC in overall performance.

A high concentration would limit the conventional PEC efficiency, which is a bottleneck problem preventing the technique from being industrialized. In contrast, one of the significant advantages of thin-film PEC is that its oxidation capacity increases with the increase of the solution concentration. Fig. 5 shows the absolute quantity of RhB removed by thin-film PEC and conventional PEC from RhB solution at different concentration levels in 60 min. With the increase of RhB concentration from 5 to 100 mg L⁻¹, the amount of RhB removed by thin-film PEC increased steadily and decreased a little at 150 mg L⁻¹. In contrast, the amount of RhB removed by the conventional PEC decreased after a maximum degradation was

Table 1

Thin-film PEC and conventional PEC degradation of RhB (1 h treatment, bias potential 0.8 V, pH 2.50, circulating flux 7.7 L h⁻¹, 1.0 g L⁻¹ Na₂SO₄, UV lamp).

C ₀ (mg L ⁻¹)	T _{254nm} (%) at C ₀	Thin-film PEC		Conventional PEC	
		% color removal	% TOC removal	% color removal	% TOC removal
5	37.8	99	78	82	60
10	30.3	94	75	74	44
20	16.9	88	65	59	32
30	6.90	73	53	45	26
50	0.23	64	44	35	18
80	0.00	54	38	20	10
100	0.00	44	29	10	3
150	0.00	28	15	7	Zero

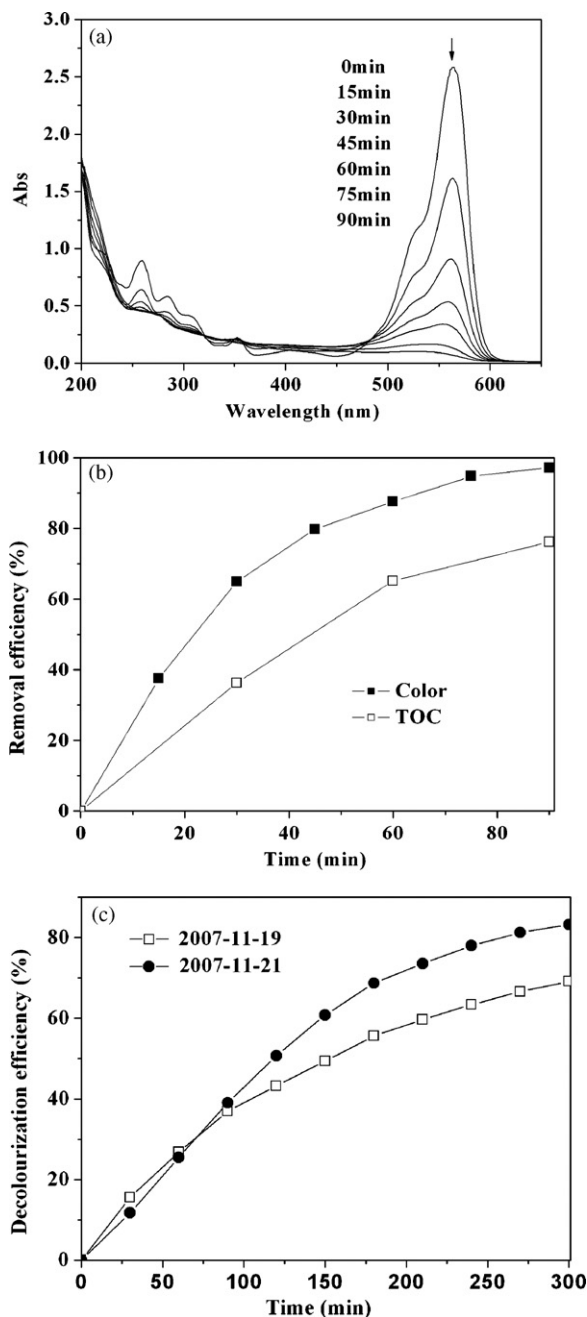


Fig. 6. (a) UV-vis spectra changes, (b) color and TOC removal by thin-film PEC as a function of time under artificial UV light irradiation and (c) color removal by thin-film PEC as a function of time under solar light irradiation (bias potential 0.8 V, pH 2.50, circulating flux 7.7 L h⁻¹, 1.0 g L⁻¹ Na₂SO₄).

obtained at 50 mg L⁻¹. We were not surprised because the transmittance of the 50 mg L⁻¹ solution was only 0.2%, and no transmittance was observed for the solution with RhB concentration of 80 mg L⁻¹ or higher (Table 1). In other words, the radiation power had been totally absorbed by the sample solution. Without light irradiation, the conventional PEC process actually became an electrolysis procedure.

3.6. Decolorization and mineralization of RhB treated by thin-film PEC

Fig. 6a shows absorbance spectra of a 20 mg L⁻¹ RhB solution at different time intervals of the thin-film PEC treatment under

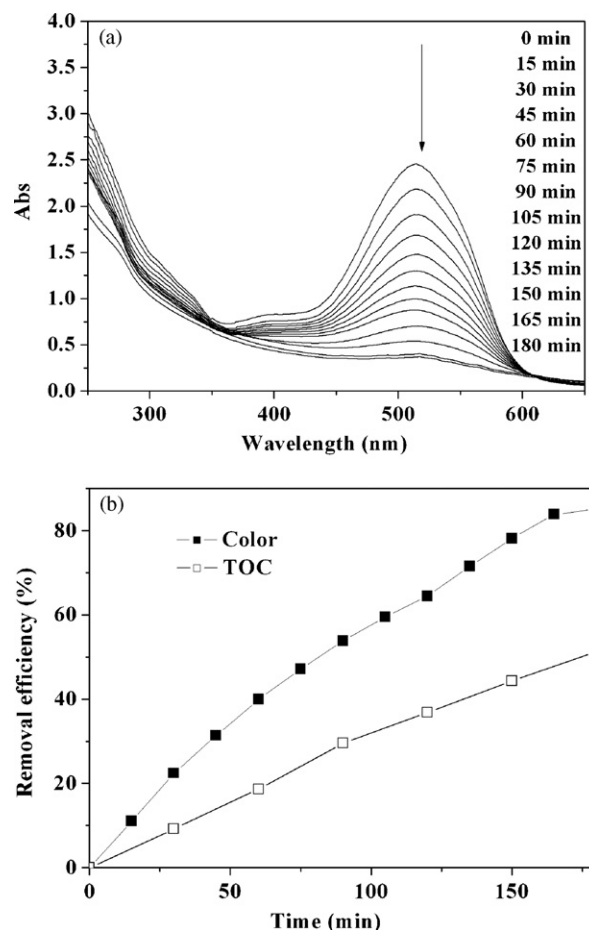


Fig. 7. (a) UV-vis spectra changes and (b) decolorization based on 514 nm and TOC depletion of textile effluent treated by thin-film PEC as a function of treatment time (bias potential 1.0 V, circulating flux 7.7 L h⁻¹, UV lamp).

artificial UV light irradiation. Absorbance rapidly reduced, indicating an effective treatment of the thin-film PEC for degradation of RhB. Decolorization and TOC removal significantly increased with time (Fig. 6b). By 1.5 h, 97% RhB disappeared while ~24% of TOC was still present in solution. Like other organic compounds, RhB requires a longer illumination time for total mineralization than its disappearance [2].

Fig. 6c shows the decolorization of RhB solution under solar light irradiation, decolorization efficiency reaches 69% and 83% after 5 h thin-film PEC treatment on different day. The result demonstrates that RhB wastewater can be decolorized efficiently utilizing free light source (solar light) as the irradiation source. Here, we have to point out that the experiments under solar light were carried out in winter in this work. When the experiments were carried out in summer, the decolorization efficiency must be improved since the light intensity in summer is higher than that in winter.

3.7. Application of thin-film PEC to treat textile effluent

TiO₂/Ti thin-film PEC was applied to treat textile effluent. The absorption spectra of effluent were obtained in the range of 250–650 nm (Fig. 7a). Fig. 7b shows the color removal and TOC depletion at 15 min intervals during the entire experiment. The solution absorbance at 514 nm rapidly decreased. For a treatment time of 180 min, color and TOC removal efficiency reached 85% and 51%, respectively. The results demonstrate that the thin-film PEC reactor can degrade practical dye wastewater efficiently.

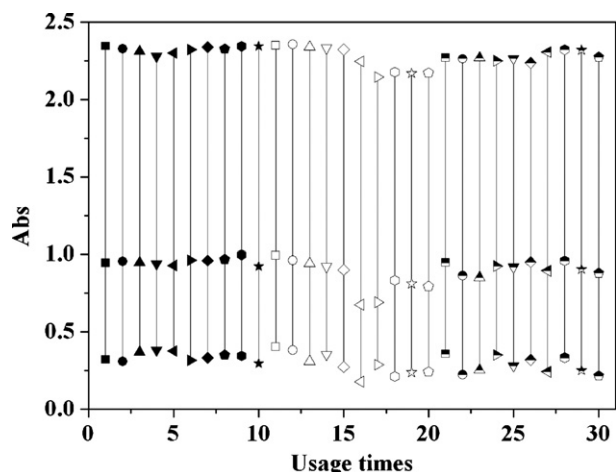


Fig. 8. Repeated decolorization of 20 mg L⁻¹ RhB solution by thin-film PEC process with the identical TiO₂/Ti electrode determined by decrease of absorbance of each solution at 0, 30, 60 min as shown from top to bottom (bias potential 0.8 V, pH 2.50, circulating flux 7.7 L h⁻¹, 1.0 g L⁻¹ Na₂SO₄, UV lamp).

3.8. Stability of TiO₂/Ti electrode

Stability of the TiO₂/Ti electrode is an important factor to take into consideration in real industrial application. Thirty runs of thin-film PEC process were repeated on a TiO₂/Ti electrode to treat 20 mg L⁻¹ RhB solution. Each run was operated for 1 h and 3 samples were collected at a time interval of 30 min. The average color removal for thirty runs was 86.8 ± 5.3% for RhB solution. Similar absorbance at the same time interval during the repeated process demonstrated excellent stability and reliability of the TiO₂/Ti anode (Fig. 8), which might result from quick degradation of organic compounds in the thin aqueous film and timely refreshment of the electrode surface. The result was similar to our previous work [15].

4. Conclusions

A TiO₂/Ti thin-film PEC reactor was successfully developed to enhance PEC degradation of Rhodamine B (RhB) and textile effluent. The high treatment efficiency achieved by the proposed thin-film PEC process was attributed to the enhanced light utilization resulting from the significantly reduced path length (down to average approximately 78 μm level). Results demonstrated that thin-film PEC reactor is superior to conventional PEC reactor in treating high concentration dye wastewater. It can degrade RhB solution efficiently under either artificial UV light irradiation or solar light irradiation. It also can degrade practical dye wastewater efficiently. Its application prospects are very promising and the industrialization of this technique is a goal worth pursuing.

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