Photoelectrocatalytic Decolorization of Reactive Brilliant Red X-3B

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The RuO$_2$/TiO$_2$ photo electrode and stainless steel net cathode were prepared by dip-coating method, respectively. The electricity assisted photocatalytic system was built up by using UV high pressure mercury lamp as the light source, RuO$_2$/TiO$_2$ electrode as photo anode, stainless steel net as counter electrode and reactive brilliant red X-3B(X-3B) as the synthetic wastewater. Various factors, such as different degradation methods, the chloride concentration, applied current and original pH value that influences the photoelectrocatalytic decomposition of X-3B dye, have been studied. The decolorization ability of photoelectrocatalytic degradation X-3B compared with the photocatalytic degradation and the electrochemical degradation. The results showed that photocatalytic and electrochemical oxidation has a synergistic effect on decolorization of X-3B. The possible roles of the electrolyte on the reactions and the probable mechanisms of effect were also discussed.

Key Words: Photocatalysis, Electricity assisted photocatalysis, Ruthenium-titanium anode, X-3B.

INTRODUCTION

Recently, with the development of dye industry, a lot of wastewater appeared which is high concentration, deep colour and complicated constitutions is ejected into the rivers and seas and the water conditions are polluted badly[1]. Among of dyes, the reactive brilliant red X-3B is one of the most representative substance of azo dyes. The X-3B dye has a high solubility in water (80 g/L) and is red in colour. Every year there have 1.6×10^9 m^3 of various dye wastewater in China drains into the river without satisfactory treatment and the decolorization is the first concern[2]. Thus, the study of degradation X-3B dye is always one of the hot-spots in environmental protection.

Photocatalysis is a promising advanced oxidation technology and has already been successfully applied for the disinfection and purification of dye wastewater by using the semiconductor photocatalyst, such as the TiO$_2$[3], ZnO[4], Cu$_2$O[5] and CdS[6], *etc*. The TiO$_2$ powder is generally used as one of the most popular photocatalysts in photocatalytic oxidation for wastewater treatment because of its high catalytic activity, good catalytic stability, non-toxicity and low price[7]. Although it has been proven that a great mumber of organic compounds can be effectively mineralized under UV-VIS irradiation, the recovery of TiO$_2$ powder from treated water is a still difficulty in widely extending its application in practice[8,9].

In order to improve the quantum efficiency, many measures were carried out by some material investigators. The TiO$_2$ was doped with a series of substance[10,11] and coated on the several carriers (Ti[12], ITO[13] and Ni[14], *etc*.), applied to degradation organic wastewater and obtained a good results. Recently, some researchers have started to investigate electrochemical oxidation assisted with photocatalytic reactions[15]. The photoelectrocatalytic (PEC) treatment process, which is a combination of electrochemical and photocatalytic treatment processes, was originally introduced in 1972 as a means to split water[16]. Later studies have demonstrated that by applying a biasing potential or current decreases the recombination rate of photogenerated electron and hole pairs, which improves the efficiency of oxidizing organic contaminants. All related studies have shown that the efficiency of TiO$_2$ in the PEC process was higher than in the TiO$_2$/UV process[17]. Some more recent developments have made it easier to separate electron and hole reactions in the photoelectrocatalytic system. This has provided an even greater advantage with respect to retarding the recombination of electrons and holes thereby improving the efficiency of TiO$_2$ as a photoelectro-catalyst[18].

In this work, the RuO$_2$ doped TiO$_2$ electrode was prepared by dip-coating method and applied to decolorization of X-3B using the electricity assisted photocatalytic technology. The effect parameters of the degrading reaction which include different degradation methods, electrolyte concentration, applied

current and initial pH were studied systematically. The mechanism of decolorization of X-3B has also been discussed.

EXPERIMENTAL

Reactive brilliant red X-3B (X-3B) (Fig. 1) (Tianjin Tianshun Chemical Company, China) was used without further purification. All other chemical reagents were analytical grade. Deionized and doubly distilled water was used throughout the study.
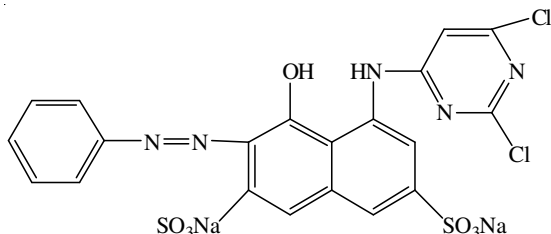

Fig. 1. Molecular structure of X-3B

Titanium mesh and stainless steel net (purity > 99.5 %) were obtained from Changsha Liyuan new material Co. Ltd. in China. D.C. stabilized power supply (Zaoxin electronic equipment Co. Ltd. Shenzhen of China), 300W high pressure mercury lamp (Wavelength about 365 nm), Model 7501 UV-VIS spectrophotometer (Tianmei Instrument Factory, Shanghai), Model PHS-3C precision pH-meter (Shanghai Leici instrument Inc., China).

Preparation of ruthenium titanium anode: The titanium mesh (34 cm × 34 cm), as the backing substrate, was immersed in 10 % of oxalic acid solution to remove the surface oxide film after 2 h boiling. Colloid solution was prepared by mixing the solution of titanium tetrachloride, ruthenium trichloride and concentrated hydrochloric acid (Ti, Ru atomic number ratio of 7:3). Then, distribute the mixing solution evenly over the pretreated titanium mesh. Finally, repeat the above steps six times, the ruthenium titanium mesh anode was obtained by sintering 40 min in 450 ℃ muffle furnace after natural drying[19].

Preparation of stainless steel net cathode: Cut a piece of stainless steel net (34 cm × 34 cm), were polished to the smooth surface and soaked with diluted hydrochloric acid for 10 min. The best treatment measure of stainless steel mesh cathode was: firstly, with rust removal, then wash it in clean water and finally soaked in acetone for 15 min to remove oil and pollution, drain and set aside.

The hybrid emulsion of MWCNTs and PTFE (the mass ratio of 1:1) were coated on the stainless steel net surface after the cathode got dry and put into an oven for 20 min under 120 ℃, then, the stainless steel mesh electrode was crushed on the flat vulcanizing machine under the pressure of 100 kg/cm^{2} and heated in the muffle furnace under 450 ℃ for 10 min. Repeating the process, until the thickness of coating was l mm. The stainless steel mesh cathode was obtained after natural cooling.

Experimental device and analytical method: The experimental device is shown in Fig. 2. The photoelectrocatalytic equipment includes the anode chamber and cathode chamber which consist of the organic glass, both chamber volume of
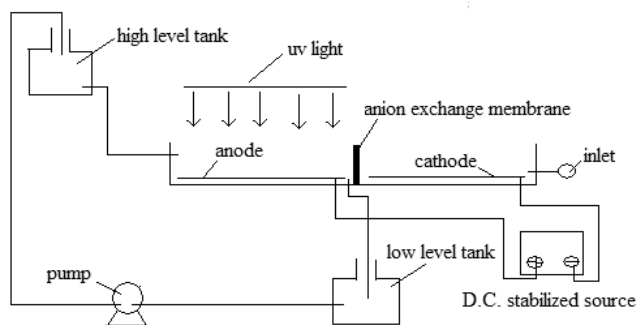

Fig. 2. Schematic diagram of photoelectrocatalytic apparatus

4.5 L. The photoelectrochemical oxidation of X-3B was carried out potentiostatically in a parallel two-compartment see-through quartz cell separated by anion exchange membrane using RuO_2/TiO_2 as the anode, stainless steel mesh as the cathode and the high pressure mercury lamp as the light source, respectively. The constant current and voltage were supplied by D.C. stabilized source and the reaction was carried out at room temperature.

The 20 L 200 mg/L X-3B solution was placed the high level tank and the cathodic solution were stirred by the air. The pH of the solution was adjusted using dilute hydrochloric acid or aqueous sodium hydroxide solution. At regular time intervals, 5 mL sample of the anode chamber was taken and centrifuged. A supernatant was used to analyze the concentration of X-3B. The dye X-3B was analyzed on a UV-VIS 7501 spectrophotometer, the determination wavelength was 536 nm which is the maximum absorption wavelength of X-3B. The determined absorbance was converted to concentration through the standard curve method of X-3B. The decolorization rate of X-3B was calculated by the following equation[20]:

Decolorization rate

$$= \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where C_0 and C_t were the concentration of X-3B when reaction time was 0 and t, respectively. A_0 and A_t were the absorbance of X-3B when reaction time was 0 and t, respectively.

RESULTS AND DISCUSSION

Effect of different decolorization methods: In this study, the electricity assisted photocatalytic degradation method (PEC, UV, I = 1.0 A) is compared with the X-3B decolorization rate of the photocatalytic degradation method (PC, only UV) and the electrochemical degradation method (ED, only I = 1.0 A). It can be seen from the Fig. 3, the decolorization rate is only 10.2 % under the condition of electrochemical degradation and reaction 2 h. However, the colour removal efficiency of X-3B can be reached to 78.6 % and 89.5 %, under the conditions of photocatalytic degradation and photoelectrocalaytic degradation, respectively. The results indicated that the decolorization ability of photoelectrocalaytic degradation is stronger than that of electrochemical degradation and photocatalytic degradation. Under anode-cathode electrodes, electrochemical reaction will combine with photocatalytic reaction, which will lead to the electrochemically and catalytically degradation of X-3B organic molecules.
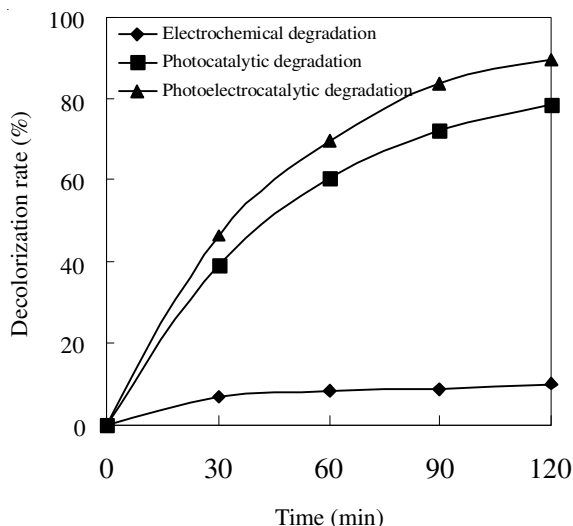
Fig. 3. Decolorization rate of X-3B in three different reaction systems

Effect of applied current: In the photoelectrocatalytic reaction system, the effect of different current on the decolourization rate of X-3B is shown in Fig. 4. The current applied were 0.5, 1.0, 2.0 and 5.0 A. From the Fig. 4, it can be seen that the colour removal efficiency of X-3B increases quickly in the initial 1 h and then reaches constant with the current increasing in the next 1 h. The colour removal rate of X-3B by photoelectrocatalytic method under the currents of 0.5, 1.0, 2.0 and 5.0 A could be 71.5 %, 90.3 %, 92.1 % and 98.2 %, respectively.
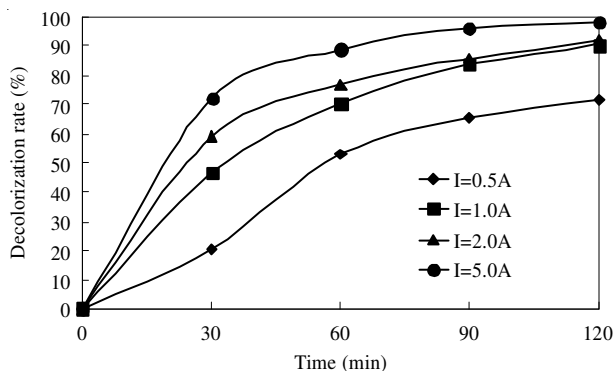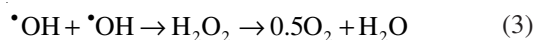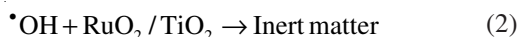

Fig. 4. Effect of applied current on the decolorization rate of X-3B

The reason can be attributed to the two aspects *i.e.*, on the one hand, in the electricity assisted photocatalytic process, the separation of photo-generated electrons and holes is enhanced, but the enhancement effect has a saturation value. When the electric field gets enough power with the increasing current, the recombine rate decreases to the threshold value and the separation rate of photo-generated electrons and holes will not be enhanced further even the current applied continues to increase. Consequently, the quantum yield also reaches the maximum value. On the other hand, the new substance which resulting from the electrochemical reaction on the RuO$_2$/TiO$_2$ anode react with $^{\bullet}$OH competing with X-3B. The side reaction can reduce the $^{\bullet}$OH, then the reaction rate has been declined. The reactions can be explained reasonably by the following equations[21]:

$$^{\bullet}OH + RuO_2 / TiO_2 \rightarrow \text{Inert matter} \qquad (2)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \rightarrow 0.5O_2 + H_2O \qquad (3)$$

Furthermore, when the applied current is larger than 2.0 A, water splitting by electrolysis may occur and the resulting O$_2$ evolution will interfere with the effect of the electric field on photocatalysis. To improve degradation rate and energy efficiency, the optimal current value is 2.0 A in this experiment.

Effect of chloride ions: Fig. 5 shows that the NaCl electrolyte plays an important role during the decolorization behaviors of X-3B. When the chloride ion concentration of photoelectrocatalytic reaction system of 0.05, 0.10 and 0.20 mol/L, the colour removal efficiency can be up to 89.5 %, 90.9 % and 92.1 %, respectively, after reaction 2 h. The reason may be come from that the chloride ions discharged on the anode and Cl$_2$ emitted from the solution. Both Cl$_2$ and its hydrolytic products HClO has stronger oxidation[22]. The reaction equations are as follows:

$$Cl_2 - 2e^- \rightarrow Cl_2 \qquad (4)$$

$$Cl_2 + H_2O \rightarrow HCl + HClO \qquad (5)$$

$$HClO \rightarrow HCl + [O] \qquad (6)$$
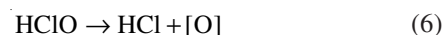
Active groups (Cl$_2$, HClO and [O]) are strong oxidants that have been observed being able to degrade organic pollutants effectively and they can also attack the azonic group of X-3B. The groups can oxidize the X-3B effectively, meanwhile and also brings aside reaction. The $^{\bullet}$OH may be consumed to produce active chlorine according to the reactions (7) instead of being reacted directly with X-3B[23].

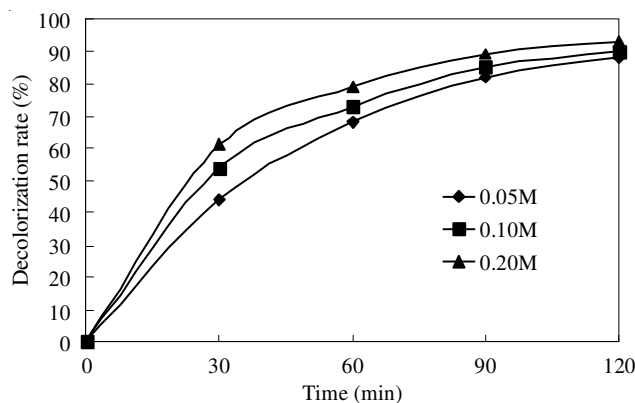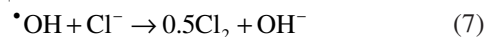$$^{\bullet}OH + Cl^- \rightarrow 0.5Cl_2 + OH^- \qquad (7)$$

Fig. 5. Effect of chloride concentration on the decolorization rate of X-3B

Effect of initial pH: The influence of pH (1, 2, 3, 5, 10 and 14) on the decolorization rate of X-3B dye (200 mg/L) in NaCl (0.10 mol/L) was investigated by the RuO$_2$/TiO$_2$ electrode. Fig. 6 shows the discoloration ratio of X-3B as a function of the reaction time when the aqueous solution pH is varied. The experimental results indicated that the colour removal rate of acidic condition is higher than that of basic condition, the decolorization rate is up to 93.3 % when the optimal pH of 3.0. From the Fig. 6, along with the pH from 10 to 14, the decoloration rate will go up but rarely change.

In the photoelectrocatalytic process, electrons in the conduction band and holes in the valance band are created by the
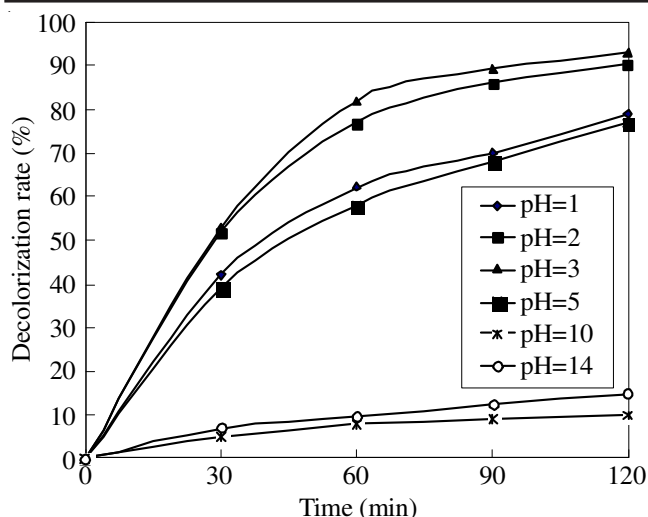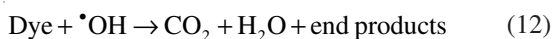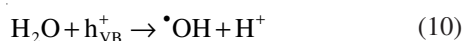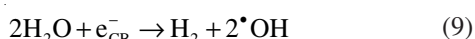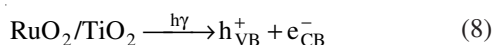
Fig. 6. Effect of initial pH value on the decolorization rate of X-3B

photo-excitation of electrons in the bulk of the RuO_2/TiO_2 electrode (eqn. 8). Conversely, during photoelectrocatalysis, electrons are driven toward the cathode by the action of the applied potential or current leaving behind a number of positive holes. Photogenerated electrons and holes take part in water splitting reactions that are generally explained by eqns. 9 and 10, respectively.

X-3B is a weak acid dye, the ionization equilibrium formula is shown in eqn. 11. The isoelectric potential of TiO_2 is 5.9[24], When pH < 5.9 the surface of RuO_2/TiO_2 electrode is positively charged and this condition attracts negatively charged ions. When pH is higher than the 5.9 of TiO_2, the surface of TiO_2 is negatively charged causing electrostatic repulsion between the negative ions and TiO_2 surface. At last, the decolorization product of X-3B is CO_2, H_2O and end-products by photoelectrocatalytic oxidation (eqn. 12).

$$RuO_2/TiO_2 \xrightarrow{h\gamma} h_{VB}^+ + e_{CB}^- \qquad (8)$$

$$2H_2O + e_{CB}^- \rightarrow H_2 + 2^\bullet OH \qquad (9)$$

$$H_2O + h_{VB}^+ \rightarrow {}^\bullet OH + H^+ \qquad (10)$$

$$Dye \rightarrow Dye^- + H^+ \qquad (11)$$

$$Dye + {}^\bullet OH \rightarrow CO_2 + H_2O + end\ products \qquad (12)$$

The result is in agreement with the homogeneous and heterogeneous photoelectrocatalytic process that has been observed for the decolouration of several organic compounds.

Conclusion

In this study, the electricity assisted photocatalytic degradation X-3B was carried out under the conditions of 200 mg/ L X-3B, applied current of 2.0 A, the NaCl concentration of 0.20 mol/L and initial pH of 3. The ability of photoelectrocatalytic decolorization X-3B is higher than that of photo-catalytic effect and electrochemcial oxidation. The photoelectrocatalytic effect has a synergistic action. The greater the applied current, the higher decolorization rate. The chloride plays a significant role in photoelectrocatalyltic degradation rate of X-3B. Under acidic conditions, the decolorization rate of X-3B is higher than alkaline conditions. At pH = 3, the decolor efficiency could reach 93.29 % after 2 h.

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