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A comparison of electrolysis and Fenton reaction pretreatment methods for dye wastewater

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ABSTRACT

Electrochemical oxidation is an effective pretreatment method for dye wastewater. In this study, the pretreatment of actual dye wastewater by electrochemical oxidation using a Ti/PbO_2 anode and a Ti/RuO_2 anode were compared with the data obtained by the Fenton reaction. The optimum pH, Fe^{2+} dosage, and H_2O_2 dosage were 3.0, 400 mg/L, and 480 mg/L, respectively, for the Fenton process. The chemical oxygen demand (COD) was reduced by 26.5% by the Fenton reaction at the optimum conditions. Various densities (20–30 mA/cm^2) were applied in the electrolysis process and the appropriate current density was 20 mA/cm^2. The reduction in the COD and color removal increased with time, and pH fluctuations did not have a significant effect on the process. The electrolysis process was more efficient for decolorization than the Fenton process in the presence of chlorine. Among the three methods, electrocatalytic oxidation using a Ti/PbO_2 anode was the most efficient method for COD removal and decolorization. At 90 min, the COD decreased by 25% and color removal was 95% with a high current efficiency of 62%.The cost of this process was 0.308 USD per kilogram reduction in the COD.

Keywords: Fenton reaction; Electrolysis; Ti/RuO_2 electrode; Ti/PbO_2 electrode

1. Introduction

Due to large-scale production and extensive use of dyes, a large volume of wastewater is generated during dye production, and the color, pH, chemical oxygen demand (COD), salt content, and biodegradability of this wastewater can cause considerable problems in the environment [1–4]. The major pollutants are unreacted dyeing compounds, surfactant, salts, and organics washed out during dyeing process. Traditional wastewater treatment technologies can hardly meet the increasing standards for color of effluents [3,6,8]. Pretreatment of dye wastewater becomes essential. Consequently, the interest of dye wastewater treatment has increased in recent years [5–7,9–11].

Pretreatment of concentrated effluents would lead to decrease in organic load and color, and the biotreatability of the effluent could be also improved. Processes used for pretreatment of dye wastewater include chemical oxidation with different reagents such as hypochlorite, ozone, Fenton reagents, and some combined technologies [7,11–13,16]. Among

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them, Fenton reaction is one of the most widely used and efficient method. In recent years, there is a growing interest in investigating the application of electrochemical oxidation for removing dyes from wastewater [1–3,17–20]. Both ways were proved to be efficient to dye wastewater. But few researchers investigated the comparisons between Fenton reactions and electrochemical oxidation for dye wastewater treatment besides that Szpyrkowicz et al. [12] investigated a comparative study on pretreatment technologies of simulated dye wastewater and concluded that Fenton reagents was the most appropriate method for disperse dyes.

In the Fenton system, hydrogen peroxide reacts with ferrous ions, producing hydroxyl radicals that are powerful oxidants, and can degrade organic pollutants into water and carbon dioxide nonselectively [14–16]. Fenton's reagent is widely used in dye wastewater treatment, but the cost of the Fenton's reagent and disposal of the $Fe(OH)_3$ sludge that is generated make the Fenton reaction an expensive wastewater treatment method. Electrochemical oxidation, which takes place on the surface of an anode, degrades pollutants directly or indirectly without addition of any chemical reagents [19–21]. Therefore, it is regarded as an environment-friendly wastewater treatment technology. A catalytic electrode material with high activity is required to improve the energy efficiency of this treatment method. The Ti/RuO_2 electrode which has been widely used in the chlor-alkali industry and electrosynthesis is an effective chlorine evolution electrode and considerated as an active anode in wastewater treatment because chloride ion is quite common in effluents [22–23]. The Ti/PbO_2 electrode has attracted several scientific groups for its electrocatalytical activity as well as stability and its applications in dye wastewater treatment have been investigated. The results indicated that the Ti/PbO_2 was quite promising as an anode material [23–28]. Boron-doped diamond (BBD) electrode has been reported recently and has been proved more efficient in simulated dye wastewater [29–31]. But the high cost of BBD electrode has limited itself from industrial application.

The efficiency of Fenton reaction and electrochemical oxidation was affected by diverse parameters due to their different mechanism. In the present study, pretreatment of actual dye wastewater by electrochemical oxidation using a Ti/PbO_2 anode and a Ti/RuO_2 anode was compared with the Fenton reaction by analyzing the color and COD reduction in the effluent, and the effects of operating conditions such as current density, initial pH, and reaction time were investigated. The results could be used to guide engineering applications.

2. Materials and methods

2.1. Electrolysis

Electrolysis was conducted in a rectangular reactor of 0.75 L volume equipped with a 10.0×10.0 cm plate anode (Ti/PbO_2 or Ti/RuO_2) and a 10.0×10.0 cm plate cathode (stainless steel) and the electrode spacing is 2.5 cm. A DC-stabilized power source was used to monitor and control the current. The preparations of Ti/PbO_2 electrode and Ti/RuO_2 electrode were reference to literature [32] and literature [33], respectively. A magnetic stirrer was used to assure the mass transfer rate of pollutants at the stirring rate of 100 rpm. The pH of the solution was adjusted with an appropriate volume of NaOH or H_2SO_4 solutions.

2.2. Fenton reaction

Fenton process consists of oxidation and coagulation. Firstly, hydrogen peroxide was added to the dye wastewater sample and the water was mixed rapidly for 10mins. Secondly, ferrous sulfate was added and the coagulation experiments proceeded with rapid mixing 10 min, slow mixing at 40 rpm for 20 min, and then standstill for 20 min.

2.3. Actual effluent

The sample of actual dye wastewater was provided by a company that produces dye intermediates in Zhejiang, China and it was used without any pretreatment in the experiment. The effluent containing dyeing compounds, surfactants, and salts was dark red, had a strong irritating odor, highly acidic, and nonbiodegradable. The results from water quality analysis of the sample are shown in Table 1.

2.4. Analytical methods

Color removal was monitored by measuring absorbance using a Hitachi U-2910 spectrophotometer. COD was determined by the dichromate method. The chloride ion is determined by ion chromatography with a Dionex TCS-2000. Current efficiency was

Table 1
Characteristics of the wastewater sample

Conductivity (ms/cm)	6.82
pH	1.2
TDS (mg/L)	3.42
COD (mg/L)	6,000–6,160
Cl^- (mg/L)	435

estimated from COD values, using the following relationship [2,3]:

$$CE\ \% = \left(\frac{COD_0 - COD_t}{8It}\right) FV \times 0.1 \tag{1}$$

COD_0 (mg/L) and COD_t refer to the initial COD and COD at reaction time, respectively. I is the current (A), F is the Faraday constant (96,487 C mol^{-1}), V is the electrolyte volume (L), and t is the reaction time (s).

3. Results and discussion

3.1. Fenton reagents doses and current density

A series of preliminary experiments were performed to optimize the doses for the Fenton reagents and current density for electrolysis processes. The best experiment conditions for Fenton process proved to be the following: pH = 3.0, H_2O_2 dose = 400 mg/L, and Fe^{2+} dose = 480 mg/L (only small improvement was associated with higher doses). Higher COD removal was obtained as the current density increased. The ideal current density was 20 mA/cm^2 for the actual effluent if the current efficiency (CE %) was taken into account. Higher current efficiency was obtained at lower current density as shown in Fig. 1.

As shown in Fig. 1, highest current efficiency was only obtained at lowest current density and shortest reaction time. More electrons were produced at higher current density leading to the increasing rate of pollutants consumption at the cost of undesirable side-reactions which lowered the current efficiency. The reaction rate was acceptable at the current density of 20 mA/cm^2. Thus, the optimal density for the actual dye wastewater was fixed at 20 mA/cm^2.

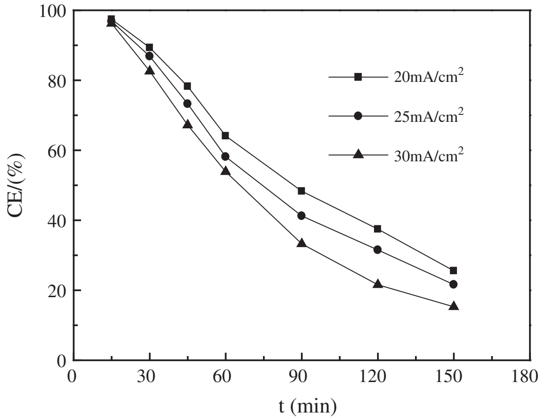

Fig. 1. Variation of current efficiency with current density (20–30 mA/cm^2) and interval time (15–150 min). T, 25 ℃; Use Ti/PbO_2 as anode.

3.2. Effect of initial pH

The wastewater was treated by electrolysis processes at initial pH values of 0, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0, and 9.0 and by the Fenton at initial pH values of 1.0, 2.0, 3.0, 4.0, and 5.0. Changes in the COD and color are shown in Fig. 2.

The initial pH had a significant impact on the Fenton reaction (Fig. 2(A)). The COD was reduced by about 26.5% at initial pH values between 1.0 and 3.0. By comparison, at pH values of 4.0, the COD only decreased by 13.5%. At the pH equal to 5.0, the COD was apparently increased, even exceeded the initial value. This phenomenon induced that Fenton reaction was suppressed at the pH of 5.0 or above and unreacted hydrogen peroxide was calculated in the COD values. The initial pH had a minimal effect on the electrolysis processes with the Ti/PbO_2 and Ti/RuO_2 anodes. The reduction in the COD was stable at all pH values at about 24% with the Ti/PbO_2 electrode and 15% with the Ti/RuO_2 electrode, and the Ti/PbO_2 electrode seemed to have more surface activity than the Ti/RuO_2 anodes. The Fenton reaction failed to decolorize the wastewater and even intensified the wastewater color (Fig. 2(B)). This induced that Fenton reaction has a priority to consume other organics rather than dyes in the actual effluent. By contrast, the electrolysis process was effective for decolorization. The color removal by electrolysis was not dependent on the pH, and the color decreased by about 90% with Ti/PbO_2 and 30% with Ti/RuO_2. The electrolysis process was better for decolorization than the Fenton reaction because of the presence of chloride ions in the wastewater (Table 1). Chlorine plays an important role in indirect electrochemical oxidation and the decolorization efficiency would increase by electrolysis as the following reactions take place [1,18,20]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{4}$$

Hypochlorous acid, HOCl, is a strong decolorant that is generated on the anode surface and oxidizes the pollutants. The chloride ion concentration decreased from 435 to 387 mg/L at 90 min. And the fact that color removal occurred greater than COD reduction implies that dyes were converted into many intermediates which are quite resistant to electro-oxidation. Decolorization occurs more significantly than

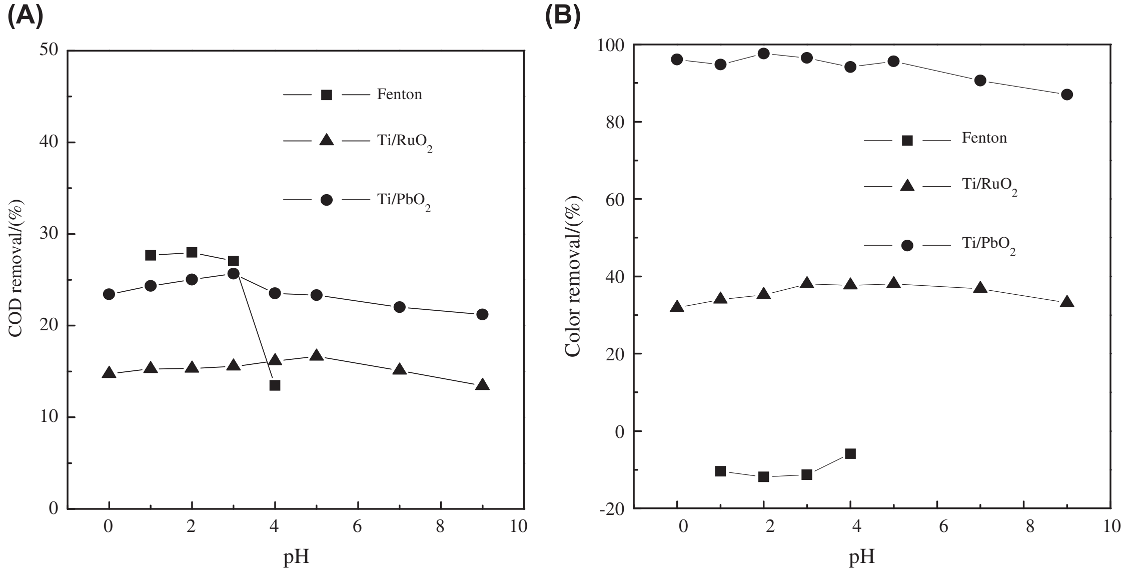

Fig. 2. Changes in reduction of the COD and color of the wastewater with increasing initial pH (0–9.0). Electrolysis conditions: current density, 20 mA/cm^2; reaction time, 90 min; T, 25℃. Fenton reaction conditions: Fe^{2+} dosage, 400 mg/L; H_2O_2 dosage, 480 mg/L; reaction time, 40 min; T: 25℃.

COD reduction for dye wastewater because of the unpleasant color which attracts much attention from the public. And several previous studies have shown color decreased faster than COD in dye-containing solutions in electrolysis processes [2,3,19]. These results indicate that the electrolysis process, especially with the Ti/PbO_2 anode, is more suitable than the Fenton reaction for treatment of dye wastewater.

3.3. Effect of reaction time

The wastewater was treated by the Fenton reaction and electrolysis for 15, 30, 45, 60, 90, 120, and 150 min (Fig. 3).

In the Fenton process, the reaction was almost complete with a maximum COD reduction of 26.5% at 30 min, but the color increased during this time because the Fenton reagents were consumed by other organics rather than the chromophores. In the electrolysis process, the COD and color decreased as the reaction time increased. After 120 min with the Ti/PbO_2 anode, the COD decreased by 26.5% and the color removal was 95%. The COD reduction was significantly more than that observed with the Fenton reaction, and higher COD and color removal could be obtained if the reaction prolonged but the COD reduction rate began to slow down. But as shown in Fig. 1, the current efficiency drastically decreased from 97% (15 min) to 40% (150 min). The current efficiency is a key indicator of electrochemical applications as electrochemical oxidation is widely known as a intensely energy consumption process. About 95% of color removal and 60% of current efficiency were obtained at 90 min which was considered as an appropriate reaction time. Current efficiency was also investigated in previous researchers [2,3,21,30]. In their work, usually only about 40% of current efficiency could be obtained. This can be explained that they all tried to treated the wastewater to standards for discharge and too long reaction time was needed which resulted in lower current efficiency. Thus, electro-oxidation is more appropriate as a pretreatment method. The Ti/PbO_2 showed better catalytic activity than the Ti/RuO_2 anode for reducing the COD and color (Fig. 3(A) and (B)). These results indicate Ti/PbO_2 would be more suitable than Ti/RuO_2 for treatment of dye wastewater. Although the Fenton process was fast, the electrolysis process provided more complete degradation of color. The electrolysis process with the Ti/PbO_2 anode was the best among the three treatment methods.

3.4. Cost comparison

The unit cost for treatment of pollutants is important for evaluation of the economic practicality of a technique. The cost per kilogram decrease in the COD was compared for the three methods, taking into consideration the reagent, electrode, and sludge disposal costs, and energy consumption (Table 2).

Costs for the Fenton reaction include consumption of ferrous sulfate and hydrogen peroxide, and disposal of sludge. The market prices of ferrous sulfate and 30% hydrogen peroxide are 45.16 and 241.95 USD/ton, respectively. The sludge from the

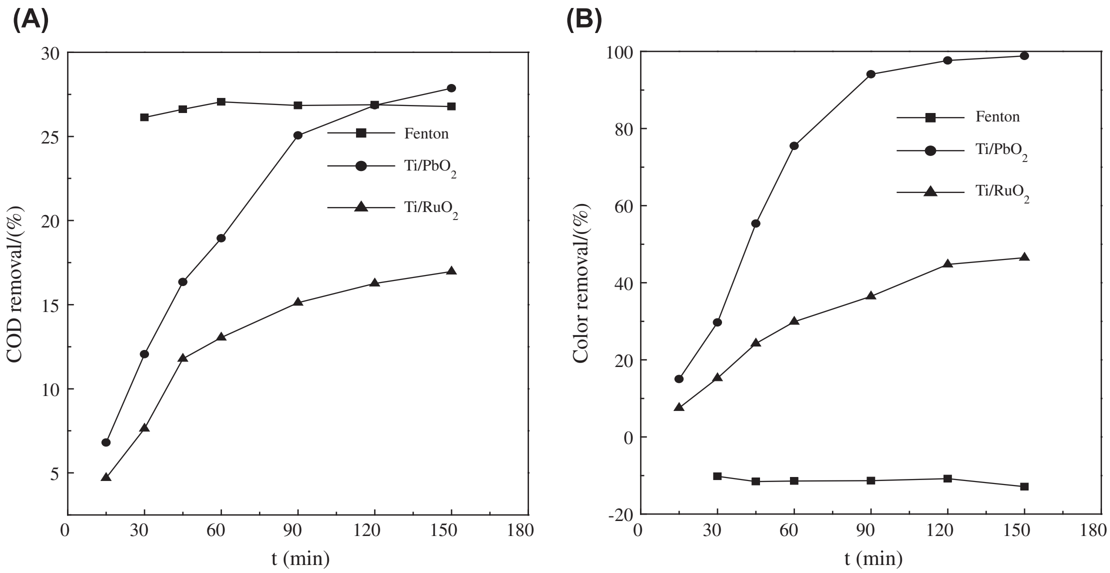

Fig. 3. Changes in the COD and color removal profiles with time (15–150 min). Electrolysis conditions: current density, 20 mA/cm^2; *T*, 25 ℃; pH, 1.2. Fenton conditions: Fe^{2+} dosage, 400 mg/L; H_2O_2 dosage, 480 mg/L; *T*, 25 ℃; pH, 3.0.

Table 2
Cost of per kg COD removed

Terms	Fenton reaction USD/kg COD	Ti/RuO$_2$ electrode USD/kg COD	Ti/PbO$_2$ electrode USD/kg COD
Reagent	0.121	/	/
Electrode	/	0.071	0.071
Energy	/	0.395	0.237
Sludge disposal	0.352	/	/
Total	0.473	0.466	0.308

Note: USD = US dollars.

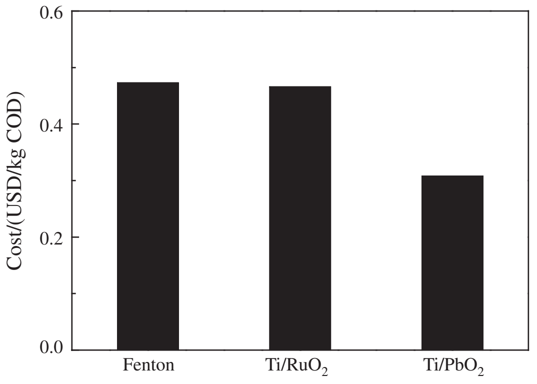

Fig. 4. Cost comparison of the three methods. Electrolysis conditions: current density, 20 mA/cm^2; reaction time, 90 min; initial pH, 1.2; *T*, 25 ℃. Fenton reaction conditions: Fe^{2+} dosage, 400 mg/L; H_2O_2 dosage, 480 mg/L; initial pH, 3.0; reaction time, 40 min; *T*: 25 ℃.

Fenton reaction is processed at specialized units for 241.95 USD/ton. The electrolysis process costs include the initial cost of the electrode and how often it needs to be replaced, and electricity consumption. Electrodes used for processing 100 m^3/d of wastewater cost about 4,839 USD with a depreciation rate of 20% each year. The electrolysis process used 5 kW h of electricity to treat every cubic meter of wastewater. The costs of three methods are compared in Fig. 4. The cost of electrolysis process using the Ti/PbO$_2$ anode was half that of the Fenton process and about 35% cheaper than the electrolysis process using Ti/RuO$_2$. Therefore, the electrolysis process using Ti/PbO$_2$ electrode as an anode is best for dye wastewater treatment.

4. Conclusion

The reduction in COD was similar for the electrolysis and Fenton processes, and both processes were short (<120 min). However, the electrolysis process was much cheaper than the Fenton process. In electrolysis, the rate of reduction in the COD and color decreased at reaction time >120 min. The COD reduction with the Ti/PbO$_2$ electrolysis process was higher than that of Fenton process after 120 min. Fenton reaction depends heavily on the pH of the wastewater while fluctuations in the pH had a minimal effect on the electrolysis reaction. Therefore, the electrolysis process is more suitable than the Fenton reaction for dye wastewater treatment, because of pH fluctuations and the complex composition of dye wastewater. Furthermore, the Fenton process had low efficiency for removal of color from the dye wastewater because of competitive responses in the actual dye wastewater. The electrolysis process was quite efficient for decolorization in the presence of chlorine and color decreased drastically than COD as dyes were converted into intermediate organics. The color removal was >95% for the process using Ti/PbO_2 as the anode at the current efficiency of 62%. In comparison to the Ti/RuO_2 anode, the Ti/PbO_2 anode performed better for reduction of the COD and color, and in cost-benefit analysis. Among the three methods, electrolysis with Ti/PbO_2 is the most suitable for actual dye wastewater pretreatment.

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