



Paired removal of color and COD from textile dyeing wastewater by simultaneous anodic and indirect cathodic oxidation

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ABSTRACT

The anodic and indirect cathodic removals of color and COD from real dyeing wastewater were investigated simultaneously using a stacked Pt/Ti screen anode and a graphite packed-bed cathode in a divided flow-by electrochemical reactor. The anodically generated hypochlorite and cathodically generated hydrogen peroxide were the main species used to remove color and COD in the wastewater. Various experimental operating factors that can affect the removal efficiency were investigated, including the applied current density, the amount of NaCl added, the solution pH in alkaline ranges and the temperature. The color and COD removal efficiencies in the anodic chamber were much higher than those in the cathodic chamber. The overall (anodic plus cathodic) removal efficiencies increased with the applied current density, the amount of NaCl added and the temperature. In contrast, increasing the solution pH decreased the overall removal efficiency. The anodic and cathodic current efficiencies at 20 mA/cm² were 63.50% and 19.57%, respectively. In this work the total treatment cost for removing 1 g COD was US \$0.643 when an air cylinder was used.

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1. Introduction

Effluents released by the textile dyeing industry pose a serious threat to the environment. The treatment of spent dyeing wastewater is difficult because of its high color and COD content. Many methods have been developed to treat dyeing wastewater, either by physical, chemical, or biological processes [1]. Many textile dyeing plants in Taiwan still use a large amount of chemicals to precipitate or react with the pollutants in the wastewater. Unfortunately, the further treatment of the discharge is usually required because of the secondary pollution resulting from high chemical doses. While the removal of dyes using biological degradation has been extensively investigated in the past decades, only the treatment of dyeing effluent with a low dye concentration has been successful.

In recent years, electrochemical methods for the treatment of dyeing wastewater have been developed. The main advantages of adopting such techniques to treat pollutants are (1) the elimination of redox chemicals, thus avoiding the need to treat spent redox streams, (2) close control of the desired reactions using the applied potential or current, and (3) the increased possibility of on-site treatment [2]. In addition, an electrochemical reactor requires less space and can treat a variety of pollutants. Recently, anodic

oxidation, either direct or indirect, has been employed for removing the color or COD of dyestuffs in simple lab-made wastewater [3–10]. Rajkumar and Kim [6] found that the percentages of COD removal were 39.5–82.8% for different reactive dyes by anodic oxidation. In addition, Mohan and Balasubramanian [8] used three anode materials to treat acid violet 12 and concluded that the ruthenium oxide coated titanium anode had better oxidation efficiency. Panizza and Cerisola [11] found that complete color and COD removal of methyl red were only achieved using lead dioxide and boron-doped diamond (BDD). BDD was found to have good efficiency in treating wastewater because of its extremely high oxygen overvoltage [12–15]. However, a BDD anode is still very expensive, and thus the practical applications are currently very limited. Although anodic oxidation can be used to successfully treat simple lab-made dye-containing wastewater, few attempts have been made to treat real dyeing wastewater with complicated compositions [16–20]. Vlyssides et al. [16] used a Pt/Ti anode to treat real textile wastewater, and found that COD decreased by 86% and ADMI color units decreased by 100% at a very high chloride concentration. In addition, Parsa and Abbasi [17] anodically treated real wastewater and found that the decolorization kinetics followed a first order model. Finally, Malpass et al. [18] found that the energy required for removing color from real wastewater was considerably higher than that for removing color from a pure lab-made dye-containing solution due to the complex nature of real wastewater.

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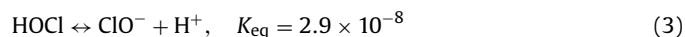
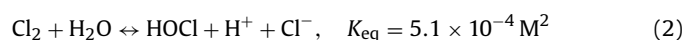
In addition to using the anodic oxidation of pollutants, methods that use hydrogen peroxide generated at the cathode have also been developed to treat pollutants. Do and Chen [21] studied the degradation of formaldehyde with electrogenerated hydrogen peroxide and found that the oxidation rate was second order in formaldehyde and first order in hydrogen peroxide. Moreover, Do and Yeh [22] investigated *in situ* paired electro-oxidative degradation of phenol using hypochlorite and hydrogen peroxide and reported that the overall (anodic plus cathodic) removal of phenol increased to 178.1%. Recently, electro-Fenton technology which combines Fe^{2+} ions with cathodically generated hydrogen peroxide has received an increasing amount of attention [23–30], although it is only applicable to acid solutions, usually less than pH 4. For example, Wang et al. [28] investigated the removal of acid red 14 by electro-Fenton technology and found that 70% of TOC was removed after 360 min electrolysis. In our previous study [30], the removal efficiency of color using the electro-Fenton method reached 70.6% after a 150 min treatment of real textile wastewater.

This study was designed to investigate the removal efficiencies of color and COD in real wastewater using anodic and indirect cathodic oxidation in a divided reactor. A packed Pt/Ti anode and a graphite cathode were used in the flow-by three-dimensional electrochemical cell. The electrochemical reactor had a high surface-to-volume ratio, which is vital for scaling up for industrial applications. The anodic and cathodic compartments were separated by a cation permeable membrane to keep the anolyte and catholyte from mixing, and the removal efficiencies from the anodic and cathodic reactions could thus be separately investigated. Several operating factors that can affect the removal efficiencies of color and COD were studied in the present work, including the applied current densities, the amount of NaCl added, the pH in alkaline ranges, and the temperature.

2. Theoretical background

2.1. Anodic oxidation of pollutants

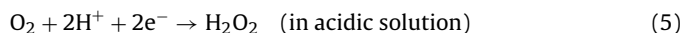
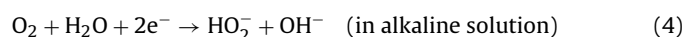
Pollutants in a solution can be destroyed by the following mechanisms in anodic oxidation. First, direct oxidation of the pollutants at the anode surface may occur. Second, the pollutants may be indirectly oxidized by the active hydroxyl radicals produced at the anode when an anode of high oxygen overvoltage is used [11,13]. Third, chlorine-based oxidants may be generated following a cycle of chloride–chlorine–hypochlorite (chlorate)–chloride when Cl^- exists in the solution [6,10]. Several studies have reported that the chlorine-based mechanism plays the main role in wastewater treatment. The reaction scheme for the production of such oxidants involves the following electrochemical and ordinary chemical reactions [7,16,31]:



The hypochlorous acid and hypochlorite are usually strong enough to destroy many species in the solution.

2.2. Indirect cathodic oxidation of pollutants by hydrogen peroxide

Hydrogen peroxide can be produced at the cathode through the two-electron reduction of dissolved oxygen in the solution by the following reactions [23–25]:



Hydrogen peroxide is a mildly strong oxidant, and therefore can be used to oxidize some pollutants in wastewater. However, the yield of hydrogen peroxide is usually low when a traditional two-dimensional plate-type electrode is used. Recently, gas diffusion cathodes and three-dimensional carbon-based cathodes with a high specific surface area have been used to obtain high yields of hydrogen peroxide [24,27,30]. Provided that the solution is acidic, usually pH < 4, adding Fe^{2+} ions to the solution produces hydroxyl free radicals with high oxidizing power according to Fenton's chemistry [25–29]. However, this technology is not suitable for alkaline wastewater unless the solution pH is adjusted.

3. Experimental

Fig. 1 schematically shows the electrochemical flow reactor used in this work. The electrochemical generation of hypochlorite and hydrogen peroxide was conducted in a divided flow-by cell. The cell was made of 0.2 cm thick acrylic material, and was 15 cm high, 5 cm long, and 5 cm wide. It was divided into anodic and cathodic chambers with a separator made of a plastic plate, 0.1 cm thick. The separator was cut with a hollow window at the center. A cation permeable membrane, 4.5 cm wide and 7 cm high, was used to keep the anolyte and catholyte from mixing. The cathodic chamber was packed randomly with 50 Rasching rings made of graphite for use as the cathode. The anode was made of 10 packed Pt/Ti plates, supplied by a local electroplating company. All of the chemicals used were of reagent grade. There were two current feeders made of titanium plates in the anodic and cathodic chamber, respectively. Small glass beads (0.3 cm in diameter) were packed at the bottom of the cathodic chamber and anodic chamber, respectively, to increase the uniformity of the flow velocity distribution.

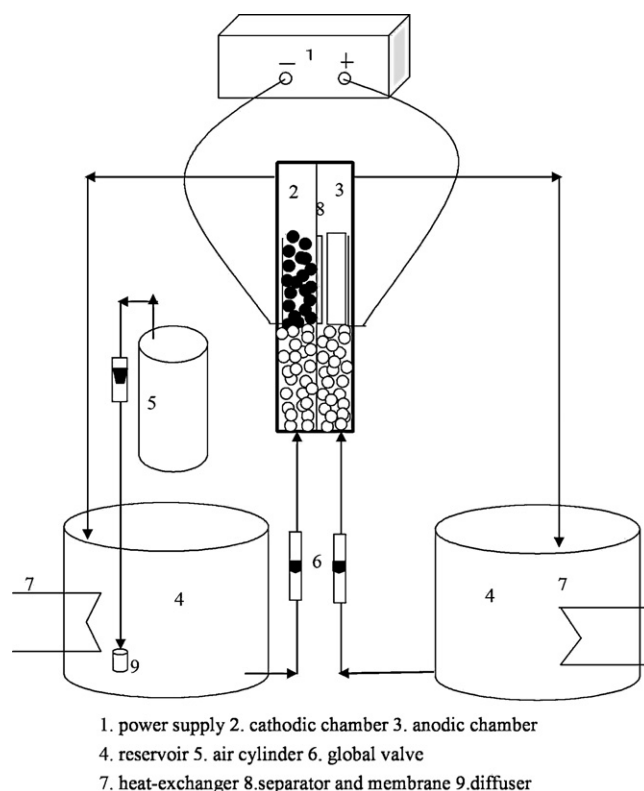


Fig. 1. The experimental setup in this study: (1) power supply, (2) cathodic chamber, (3) anodic chamber, (4) reservoir, (5) air cylinder, (6) global valve, (7) heat-exchanger, (8) separator and membrane, and (9) diffuser.

Table 1
Some characteristics of the original wastewater.

Color (ADMI unit)	2175
COD (mg/dm ³)	1354
pH	8.84
Cl ⁻ concentration (mg/dm ³)	183.4
SS (mg/dm ³)	84.2
Conductivity (μs/cm)	1939

The graphite and Pt/Ti screens were pickled in alkaline (1 M NaOH) and acidic (1 M H₂SO₄) solutions alternatively for cleaning and then rinsed with deionized water before electrolysis was conducted. The flow of the solution was in a recirculating loop. 1.5 dm³ of the catholyte was introduced into the bottom of the cathodic chamber by a pump, which then flowed out from the top and was returned to the reservoir. The flow operation of the anolyte (1.5 dm³) was the same as that of the catholyte. The flow rates of the anolyte and catholyte were controlled and kept the same by a global valve, and measured using a rotameter. The air was sparged into the cathodic reservoir to increase the dissolved oxygen, which was reduced to hydrogen peroxide at the graphite cathode.

The mixed wastewater samples used in this study were taken from a textile dyeing plant located at Tainan County in Taiwan, and then stored in a dark environment. Before conducting the electrolysis, the suspended particles of colloidal ranges in the wastewater were removed by filtration with cellulose acetate filter papers (0.45 μm in pore diameter). Some characteristics of the wastewater were measured and these are given in Table 1. The pH of the wastewater was adjusted by adding 0.1 M NaOH_(aq) or 0.1 M H₂SO₄. The experiments were conducted in constant-current mode. The direct current used in this study was provided by a DC power supply (Instec, Model GPR-M/H-D Series). The electrolytic time was 240 min in all of the experimental runs.

Measurement of the ADMI color value (APHA-AWWA-WPCF, 1985) and the COD of the wastewater were conducted using a Hach spectrophotometer (DR5000). The pH of the solution was measured using a pH/ORP/conductivity meter (Myron L, ultrameter II). The temperature of the solution was controlled and kept constant in each reservoir during the electrolysis.

4. Results and discussion

4.1. Time-varying reduction in ADMI color and COD

In this study, the ADMI color and the COD removal efficiencies were calculated, respectively, using the following definitions:

$$\frac{\text{color}_{\text{original}} - \text{color}_{\text{treated}}}{\text{color}_{\text{original}}} \times 100\%$$

$$\frac{\text{COD}_{\text{original}} - \text{COD}_{\text{treated}}}{\text{COD}_{\text{original}}} \times 100\%$$

The anodic and cathodic removal efficiencies of color and COD were separately calculated, because the electrochemical reactor was of the divided type. Fig. 2 shows the typical anodic and cathodic removal efficiencies of color in the wastewater as a function of electrolysis time. The decrease in color and COD is attributed to the destruction of organic contaminants in wastewater when the electrolysis was performed. Both the anodic and cathodic color removal efficiencies increased with increasing time, continuing almost linearly up to 120 min. The anodic color removal efficiency reached 98.5% after 240 min electrolysis, while the cathodic efficiency only reached about 37.3%. Therefore, the anodic color removal efficiency

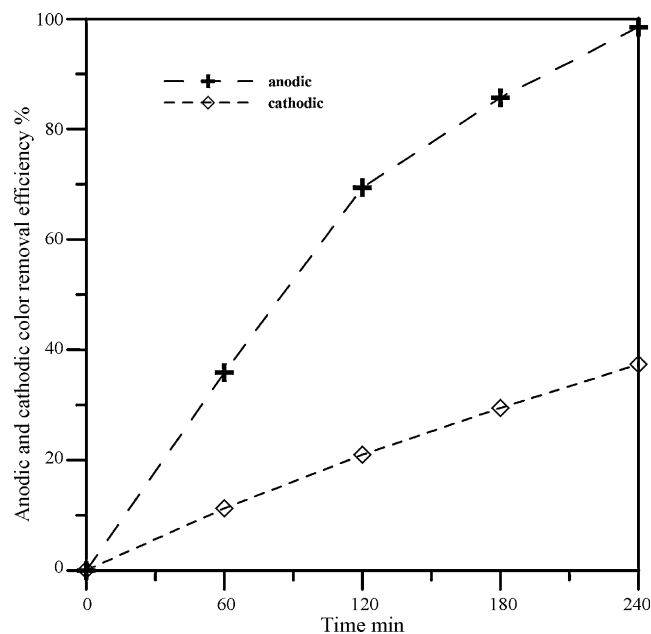


Fig. 2. The color removal efficiencies versus time; pH 8.0; current density 80 mA/cm²; NaCl addition 20.0 g/dm³; 40 °C.

was much higher than the cathodic one in this work. Fig. 3 shows the time-varying removal efficiencies of COD using anodic oxidation and indirect cathodic oxidation. It was observed that the anodic COD removal efficiency reached about 51.5% after 240 min electrolysis, while the cathodic efficiency reached only about 13%. The reasons for the low cathodic removal efficiency compared to the anodic one are probably that (1) the yield of hydrogen peroxide was lower because Eq. (4) is comparatively sluggish [21] and (2) the oxidizing power of hydrogen peroxide may not be high enough to destroy some of the pollutants in real wastewater. Compared to the removal efficiencies of color and COD for both anodic oxidation and indirect cathodic oxidation, the removal efficiencies of COD were much lower. The residue of destroyed dye species, although colorless, probably still made some contributions to the COD. The above results suggest that color was easier to remove than COD in the

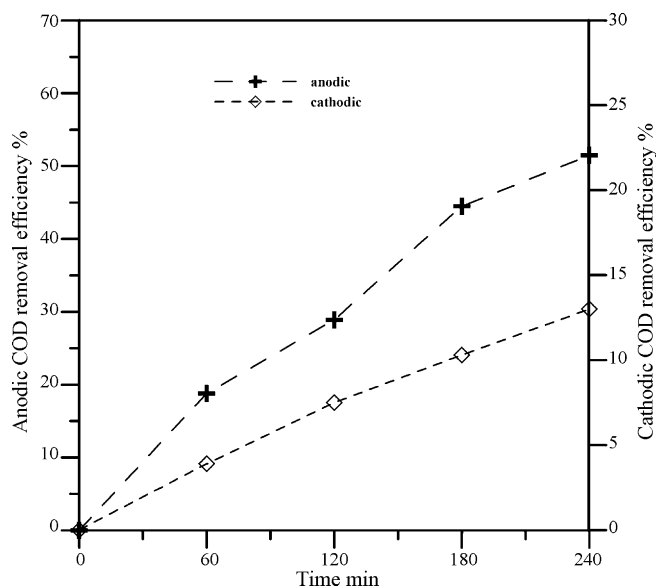


Fig. 3. The COD removal efficiencies versus time; pH 8.0; current density 80 mA/cm²; NaCl addition 20.0 g/dm³; 40 °C.

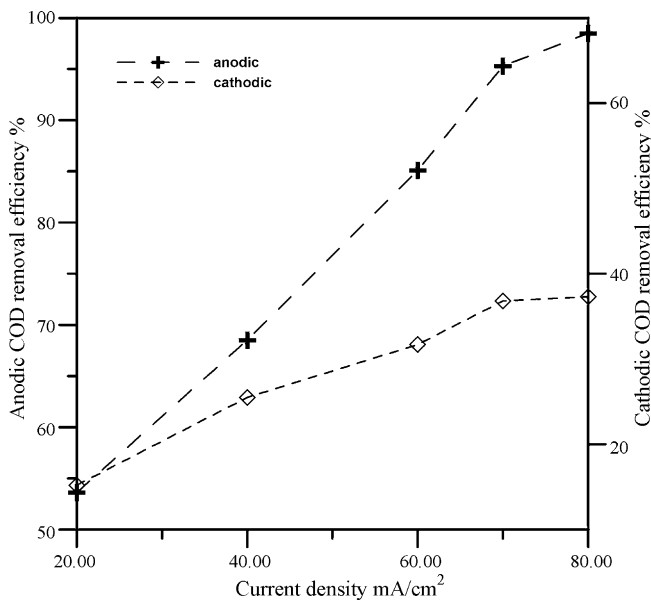


Fig. 4. The color removal efficiencies at different current densities; pH 8.0; NaCl addition 20.0 g/dm³; 40 °C.

wastewater, and this supports the results of several other studies on treating synthetic dye-containing wastewaters [5,8,9].

4.2. Effect of applied current density

Current density is a very important variable in electrochemical engineering. The effects of applied current density on color and COD removal are shown in Figs. 4 and 5. The current density in this work was defined as the applied current divided by the projected area (30 cm²) of the ion-exchanging membrane between the anodic and cathodic compartments. As can be seen, the anodic removal efficiencies significantly increased from 53.6% to 98.5% for color and from 22.4% to 51.5% for COD when the applied current density was increased from 20 mA/cm² to 80 mA/cm². According to the possible reaction mechanisms at the Pt/Ti anode, the direct

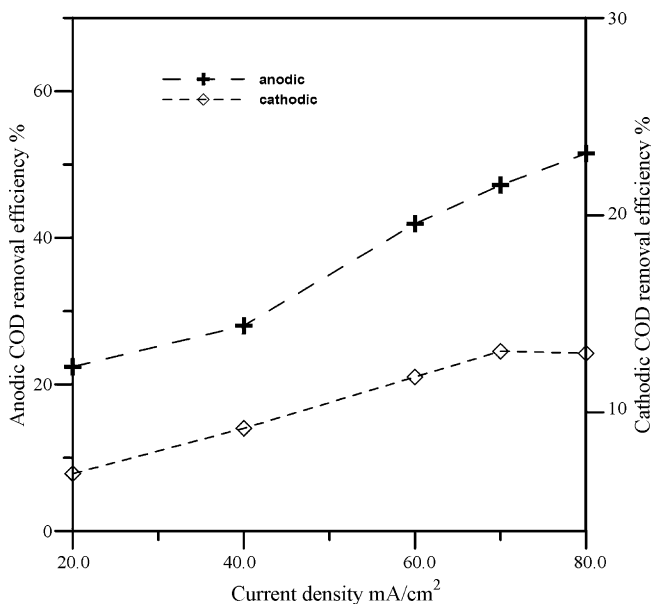


Fig. 5. The COD removal efficiencies at different current densities; pH 8.0; NaCl addition 20.0 g/dm³; 40 °C.

anodic oxidation rate will increase with increasing current density if the pollutants can transport efficiently to the anode surface. In addition, electrodes such as Pt/Ti employed in the present investigation work very well as catalytic anodes to liberate chlorine from NaCl-containing solution. Therefore, in this work the oxidants may be generated following a cycle of chloride–chlorine–hypochlorite (chlorate)–chloride, according to Eqs. (1)–(3). The concentrations of HOCl and OCl⁻ are sensitive to the solution pH. When pH > 10, all of HOCl will convert into OCl⁻. The amount of hypochlorite, produced increased with increasing applied current density [4,6,10]. The more hypochlorite that was produced, the more color and COD were removed by the reaction of pollutants and hypochlorite. For indirect cathodic oxidation, the cathodic removal efficiency also increased with increasing applied current density, but not by as much as in the case of anodic oxidation. The cathodic removal efficiencies increased from 15.2% to 37.3% for color and from 6.9% to 13.0% for COD when the applied current density was increased from 20 mA/cm² to 80 mA/cm², because the amount of hydrogen peroxide generated at the cathode increases with increasing current density [21]. However, the cathodic COD removal efficiency slightly leveled out when the current density exceeded 70 mA/cm². This probably occurred because peroxide can accept two electrons, and can thus be reduced to hydroxide at the cathode by the following reaction [24]:



Compared to the anodic oxidation, there was a smaller the influence of current density on indirect cathodic oxidation.

4.3. Effect of NaCl addition

NaCl is usually added to wastewater when indirect anodic oxidation is performed [4–10]. Intentionally adding NaCl to the wastewater increases the solution conductivity, decreases the energy consumption, and promotes indirect anodic oxidation by producing hypochlorite at the anode. Figs. 6 and 7 show the effect of the amount of NaCl added on the color and COD removal efficiencies, respectively. It was found that intentionally adding up to 15.0 g NaCl to the wastewater significantly increased the removal efficiency of color, while the limiting value was obtained when the NaCl added exceeded 15.0 g. On the other hand, no limiting

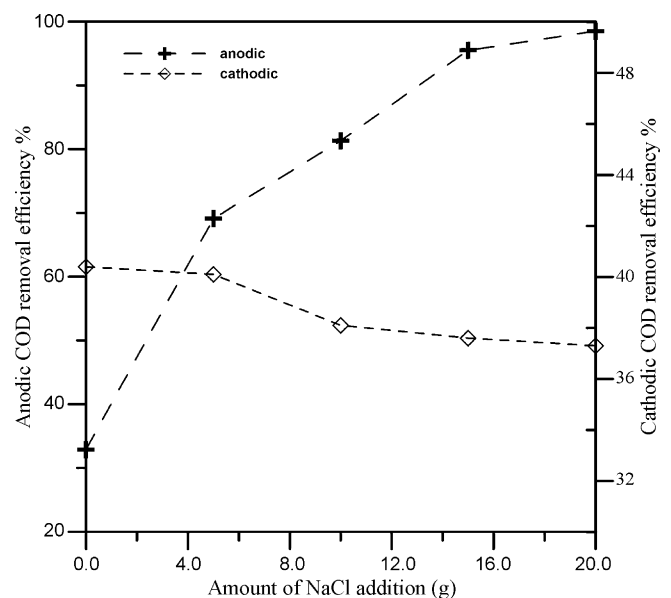


Fig. 6. The color removal efficiency at different amounts of NaCl addition; pH 8.0; current density 80 mA/cm²; 40 °C.

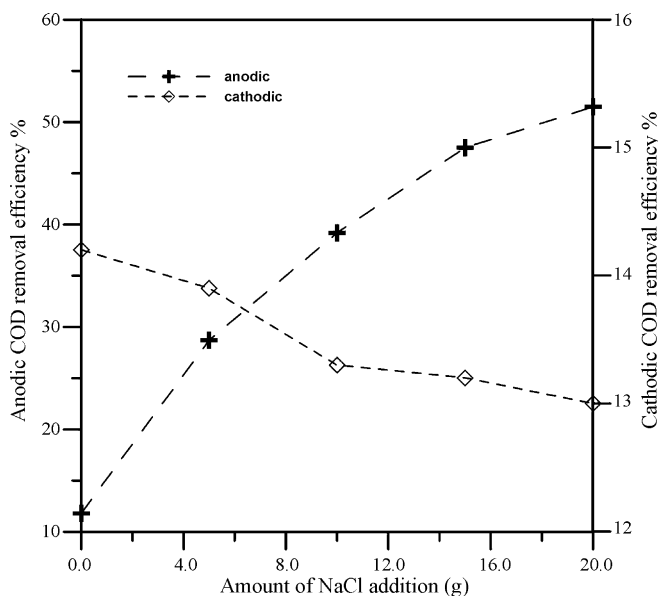


Fig. 7. The COD removal efficiency at different amounts of NaCl addition; pH 8.0; current density 80 mA/cm²; 40 °C.

value was observed for the removal efficiency of COD in the tested range of 0–20 g NaCl addition. The anodic removal efficiencies of color and COD significantly increased from 32.9% for color and 11.8% for COD with the original wastewater to 98.5% and 51.5% with the addition of 20.0 g NaCl, respectively. These significant increases in removal efficiencies were mainly due to the indirect anodic oxidation rate of the pollutants being proportional to the hypochlorite production rate, which increased with the increasing amount of Cl⁻. Eq. (1) was more competitive than the others at the anode when more Cl⁻ was added into the solution, and thus a higher hypochlorite concentration was obtained. In contrast, the addition of NaCl to the solution only had a small influence on the cathodic removal efficiencies, which slightly decreased as increasing amounts of NaCl were added. The removal efficiency of COD was 14.2% without NaCl addition, and 13.1% with the addition of 20.0 g NaCl.

4.4. Effect of pH

Because the pH of the original wastewater in our study was 8.84, only the pH effect in alkaline ranges was investigated in this work. For this reason, no Fenton chemistry was involved in the experiments. Figs. 8 and 9 show how the pH of the solution affected the removal efficiencies of color and COD, respectively. It can be seen that the pH had the opposite effects on the removal efficiencies of anodic oxidation and indirect cathodic oxidation. For anodic oxidation, the removal efficiencies decreased with increasing pH and this was possibly because an increase in the OH⁻ concentration increased the tendency for oxygen evolution at the anode according to the following reaction:



Consequently, the hypochlorite production rate was decreased because Eq. (7) is more competitive with increasing solution pH. Therefore, the removal efficiencies of color and COD in the wastewater were reduced by anodic oxidation. For instance, the removal efficiencies of color and COD significantly decreased from 98.5% for color and 51.5% for COD at pH 8–8.0.9 and 41.4% at pH 11 in the anodic chamber, respectively. Likewise, the effects of pH on the cathodic removal efficiencies of color and COD are also shown in Figs. 8 and 9. It was observed that the removal efficien-

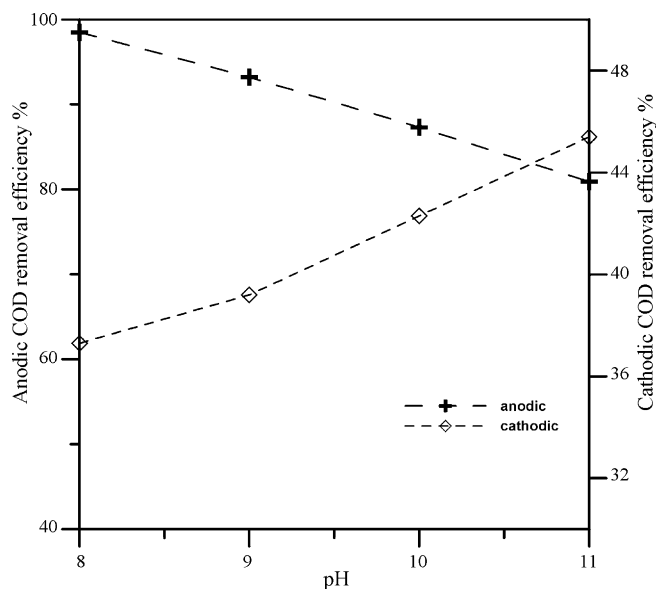


Fig. 8. The color removal efficiency at different pH; current density 80 mA/cm²; NaCl addition 20.0 g/dm³; 40 °C.

cies increased slightly with increasing solution pH in the cathodic chamber. When the solution pH rose from 8 to 11, the removal efficiencies of color and COD increased from 37.3% and 13.0% to 45.4% and 15.7%, respectively, after 240 min. This may be due to the electrochemical production of hydrogen peroxide being more efficient in a more alkaline solution [21,32].

4.5. Effect of temperature

Figs. 10 and 11 show the temperature effect on the removal efficiencies of color and COD. As can be seen, the opposite trends for anodic and cathodic removal efficiencies were observed in this work. For anodic removal, increasing temperature can enhance the removal efficiencies of color and COD from 87.9% for color and 42.4% for COD at 25 °C to 98.5% and 51.5% at 40 °C, respectively, since the production rate of hypochlorite and the chemical destruc-

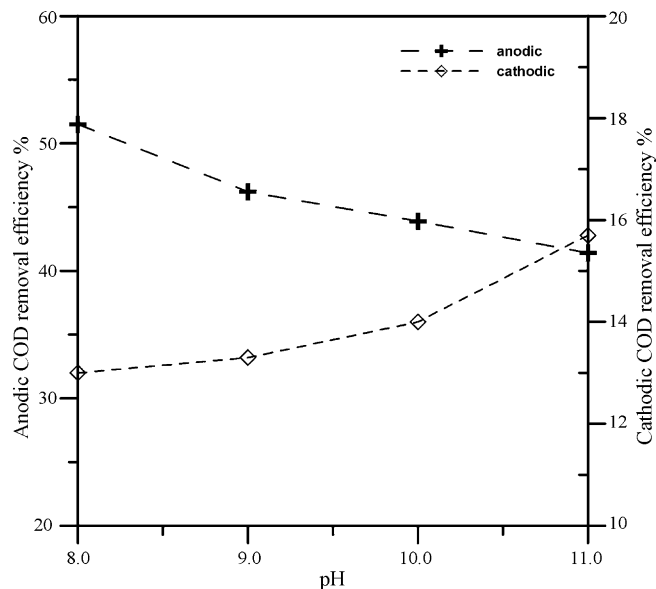


Fig. 9. The COD removal efficiency at different pH; current density 80 mA/cm²; NaCl addition 20.0 g/dm³; 40 °C.

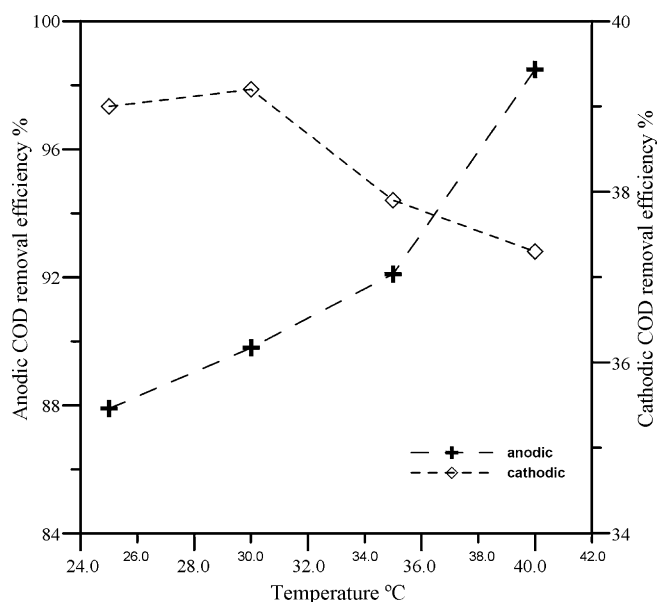


Fig. 10. The color removal efficiency at different temperatures; pH 8.0; current density 80 mA/cm²; NaCl addition 20 g/dm³.

tion of the pollutant increased as the temperature increased [22]. In contrast, temperature exerted a slightly negative effect on the generation of hydrogen peroxide and the subsequent color and COD removal efficiencies in the cathodic chamber. For instance, the color removal efficiency decreased from 39% to 37.3% when the temperature was increased from 25 °C to 40 °C. The negative temperature effect on the production of hydrogen peroxide at the graphite cathode may be due to the fact that increase in temperature may cause a decrease in the concentration of dissolved oxygen, which would be electrochemically converted to hydrogen peroxide [22,26]. In addition, the rate of self-decomposition of the hydrogen peroxide to water and oxygen increases as temperature rises [26,30]. A lower temperature was favored in the production and accumulation of hydrogen peroxide, and hence resulted in higher removal efficiencies of color and COD in the cathodic chamber.

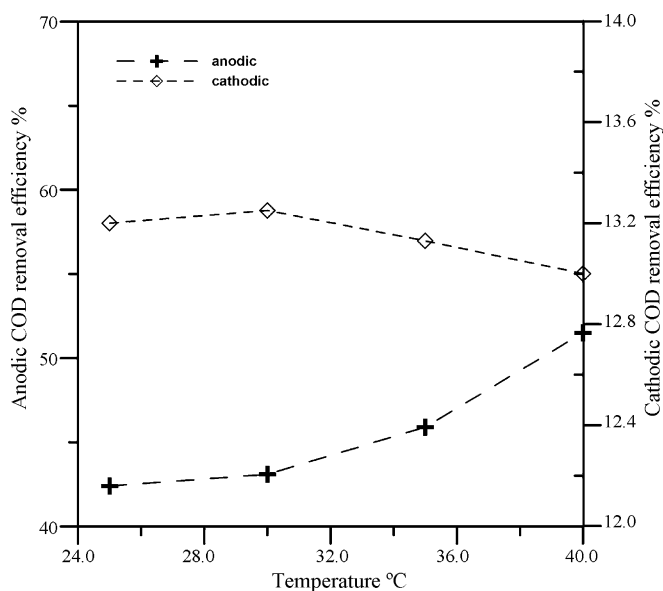


Fig. 11. The COD removal efficiency at different temperatures; pH 8.0; current density 80 mA/cm²; NaCl addition 20 g/dm³.

Table 2
Current efficiencies (CEs (%)) at various current densities.

	Current density (mA/cm ²)				
	20	40	60	70	80
Anodic	63.50%	39.70%	39.60%	38.24%	36.15%
Cathodic	19.57%	13.04%	11.15%	10.61%	9.22%
Overall	83.07%	52.74%	50.75%	48.85%	45.37%

4.6. Current efficiency

The current efficiency (CE) for the electrochemical treatment of pollutants can be calculated using the following equation [11]:

$$CE(\%) = \frac{COD_t - COD_{t+\Delta t}}{I \times \Delta t \times 8000} \times F \times V \times 100 \quad (8)$$

where COD_t and $COD_{t+\Delta t}$ are the COD values (mg/dm³) at time t and $t + \Delta t$, respectively; Δt (s) is the electrolysis time; I (A) is the applied current; F is Faraday's constant; V (dm³) is the solution volume. Table 2 shows the current efficiencies for anodic and cathodic removal for COD at various current densities. The current efficiency decreased with increasing current density for both anodic oxidation and indirect cathodic oxidation. The anodic and cathodic current efficiencies decreased from 63.5% and 19.57% to 36.15% and 9.22%, respectively, when the current density increased from 20 mA/cm² to 80 mA/cm². This is probably due to more input charge being wasted for producing side reactions at higher current density. The highest current efficiencies for anodic and cathodic removal of COD were 63.5%, and 19.57%, respectively.

4.7. Estimation of the operational cost

Electrochemical treatments generally have lower temperature requirement than those of other equivalent non-electrochemical processes, and there is almost no need for additional chemicals. The required equipment and operations are generally simple, easily automated and can effectively save labor cost. Typically, the investment cost is relatively high when a membrane is used in a divided electrochemical reactor because of the high cost of the membrane. However, this cost can be reduced by substituting a ceramic frit for the ion permeable membrane in practical applications. This can partly solve the problem of the high cost of membranes. However, the problem of increasing power cost still remains.

An economic evaluation of the treatment cost can be undertaken to ascertain the economic feasibility of the electrochemical treatment. In this study, the operational cost includes the cost of items such as electricity, sparging air and chemicals. According to the results obtained in this work and the economic data from Taiwanese market in 2008, the estimated total treatment cost for removing 1 g COD was US \$0.643 (electricity: 0.033, chemicals: 0.09, and sparging air: 0.52) when an air cylinder was used. However, if the air was supplied from the atmosphere, the cost was drastically reduced to \$0.123. Therefore, it is recommended to use the air from the atmosphere in future research.

5. Conclusions

The paired anodic and cathodic removals of color and COD from real dyeing wastewater were investigated in a divided flow-by packed electrochemical reactor, equipped with Pt/Ti screens as the anode and graphite rings as the cathode. It was found that the removal of COD in the wastewater was much more difficult than the removal of color. In this work, the main removal mechanisms of color and COD in the wastewater were found to be indirect anodic oxidation in the anodic chamber and indirect cathodic oxidation from the peroxide generated in the cathodic chamber. The exper-

imental results showed that the removal efficiencies of color and COD in the anodic chamber were much higher than those in the cathodic chamber. Considering the overall removal efficiencies of color and COD, both increased with increasing current density, amount of NaCl added, and solution temperature, and decreasing solution pH. The anodic and cathodic current efficiencies at 20 mA/cm² were 63.50% and 19.57%, respectively. The total treatment cost for removing 1 g COD in this work was \$0.643 when an air cylinder was used.

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