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Removal of organic dye pollutants from wastewater by electrochemical oxidation

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The removal of chemical oxygen demand (COD) and color from simulated dye wastewater containing organic dyes, direct yellow 4, $C_{26}H_{20}N_4O_8S_2Na_2$ and acid yellow 17, $C_{16}H_{10}O_7N_4S_2Cl_2Na_2$ experimentally investigated using an electrochemical undivided cell reactor with Pt as anode and steel as cathode. Particular attention was paid to probe the effect of supporting electrolyte (NH_4Cl), cell voltage, pH, and treatment time on the electrochemical treatment efficiency. Experiments were also carried out using 0.2 M NH_4Cl as supporting electrolyte under the condition of free pH. The experimental results showed that the process could efficiently remove the color and COD from simulated dye waste water. The overall COD removal reached at 69.9% by using supporting electrolyte and increasing voltage. The process can be described by pseudo first-order kinetics for the removal of COD.

Keywords: Electrooxidation; Wastewater; Platinum anode; Dye; Direct yellow 4; Acid yellow 17

1. Introduction

Wastewater from dyeing and finishing factories is a significant source of environmental pollution [1]. The wastewater is typically characterized by high levels of chemical oxygen demand (COD) and color. Furthermore, commercial dyes are intentionally designed to resist biodegradation [2]. Due to the characteristics of dyeing wastewater, their treatment is rather difficult [3].

Various physical, chemical, and biological techniques have been employed to clean dyeing wastewater, however most of these are becoming inadequate due to the enforcement of new and/or tighter regulations concerning the discharge of wastewater in many countries [4,5]. Over recent years there has been a growing interest in the development of electrochemical methods for the destruction of toxic organic contaminants of wastewater [6,7]. Such methods have been successfully tested to deal with various industrial wastewater including dye pollutants [3,4]. However for some

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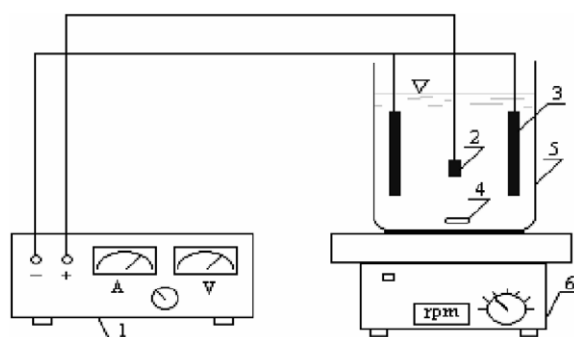


Figure 1. Schematic view of the experimental set up (1, DC power source; 2, anode; 3, cathode; 4, stirring bar; 5, electrochemical cell; 6, magnetic mixer).

dyes which have high water solubility and low molecular weight, traditional electrochemical methods do not work efficiently [3]. Of particular interest in this study is to improve the efficiency of removal of COD by using Pt and steel electrodes at different conditions for the supporting electrolyte. Soluble dyes direct yellow 4, $C_{26}H_{20}N_4O_8S_2Na_2$ and acid yellow 17, $C_{16}H_{10}O_7N_4S_2Cl_2Na_2$ were selected as model dyeing pollutant in this investigation. These types of dye compounds are among the target group of colorants used in various industries and are stable with respect to biochemical oxidation.

2. Experimental section

2.1. Electrochemical cell

The experiments were carried out in a 400 mL batch electrolytic cell. A laboratory DC power supply (ADAK-PS-450, Iran) with current voltage monitor was employed to provide the electric power during electrolysis.

The cell was equipped with a magnetic stirrer in order to keep the electrolyte well mixed with an electrolysis platinum plate (Pt) $2 \times 2 \text{ cm}^2$ and two steel plates (AISI 304) $2 \times 8 \text{ cm}^2$ were used respectively as anode and cathode. Both electrodes were placed vertically and parallel to each other in the electrolytic cell, with a Pt anode in the center of the cell (figure 1). All the experiments were carried out in laboratory conditions and potentiostatic state 5, 10 V and free pH.

2.2. Materials

The synthetic wastewaters investigated in this study were prepared in the laboratory using Aldrich chemicals including direct yellow 4, acid yellow 17 and distilled water. For the supporting electrolyte, NH_4Cl (Merck) was used. The synthetic wastewaters were prepared with different initial COD between 138 and 736 ppm as shown in tables 1 and 2. All the BOD/COD ratios of the synthetic wastewaters are below 0.2, indicating that the organics are poorly biodegradable.

Table 1. The COD removal efficiencies for direct yellow 4.

Time (min)	COD removal (%)	pH	Time (min)	COD removal (%)	pH
5 V	Initial COD 210 ppm	BOD/COD 0.09	10 V	Initial COD 221 ppm	BOD/COD 0.10
Direct yellow 4					
0	0	7.15	0	0	7.15
30	0.09	7.14	30	0.45	7.13
60	0.19	7.13	60	0.90	7.12
90	0.19	7.13	90	1.07	7.12
5 V	Initial COD 268 ppm	BOD/COD 0.14	10 V	Initial COD 292 ppm	BOD/COD 0.16
Direct yellow 4 (0.2 M NH ₄ Cl)					
0	0	6.50	0	0	6.50
30	17.5	3.77	30	38.4	1.90
60	28.4	2.94	60	61.5	1.70
90	33.6	2.54	90	69.9	1.64

Table 2. The COD removal efficiencies for acid yellow 17.

Time (min)	COD removal (%)	pH	Time (min)	COD removal (%)	pH
$V = 5$ V	Initial COD 138 ppm	BOD/COD 0.08	$V = 10$ V	Initial COD 138 ppm	BOD/COD 0.09
Acid yellow 17					
0	0	6.57	0	0	6.57
30	0.58	6.58	30	1.45	6.60
60	0.72	6.59	60	2.17	6.61
90	0.72	6.61	90	2.89	6.63
$V = 5$ V	Initial COD 736 ppm	BOD/COD 0.11	$V = 10$ V	Initial COD 640 ppm	BOD/COD 0.15
Acid yellow 17 (0.2 M NH ₄ Cl)					
0	0	5.70	0	0	5.70
30	10.2	3.42	30	20.5	2.37
60	29.3	2.90	60	40.6	1.86
90	38.3	2.66	90	52.2	1.85

2.3. Procedures

The electrochemical oxidation of wastewater was conducted with and without the supporting electrolyte, the operating voltage being selected to find out the influences of operating parameters. The electrolysis was carried out under free current for 90 min, for all samples and COD measurement was carried out based on open reflux standard method after each 30-min time interval.

3. Results and discussion

In this work, the influence of voltage is studied under the condition of free pH as shown in tables 1 and 2. Two voltages 5 and 10 V were run during each electrolysis, the anode was constant. The results are shown in figures 2 and 3.

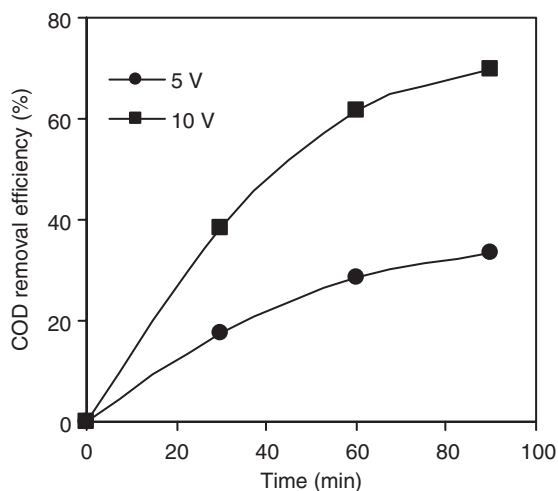


Figure 2. Electrolysis results of direct yellow 4 by using Na_4Cl 0.2 M.

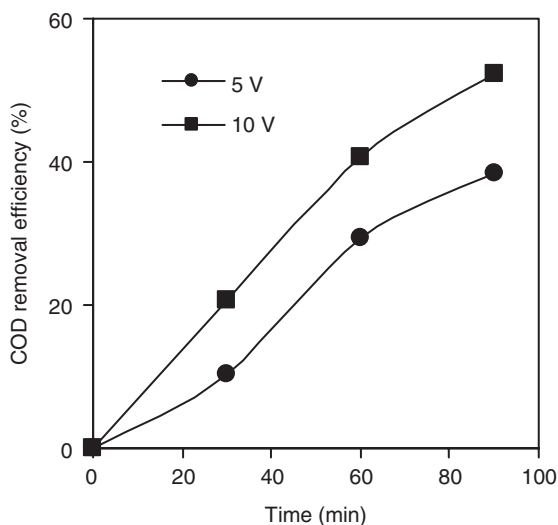


Figure 3. Electrolysis results of acid yellow 17 by using Na_4Cl 0.2 M.

The COD removal efficiencies of all the four compounds are increased as voltage and electrolysis time increased, the COD removal efficiency obtained with chloride is higher than those obtained without it. The effect of electrochemical treatment on color removal for direct yellow 4 is shown by UV-vis spectra (figure 4). The indirect oxidation effect of chlorine/hypochlorite is the main pathway for pollutants removal [8] therefore the superior effect of chloride in this study can also be due to the indirect oxidation effect of chlorine/hypochlorite.

In the electrochemical oxidation process, COD removal would be proportional to the pollutant concentration and also proportional to chlorine/hypochlorite concentration when chloride is used as supporting electrolyte, since pollutant removal

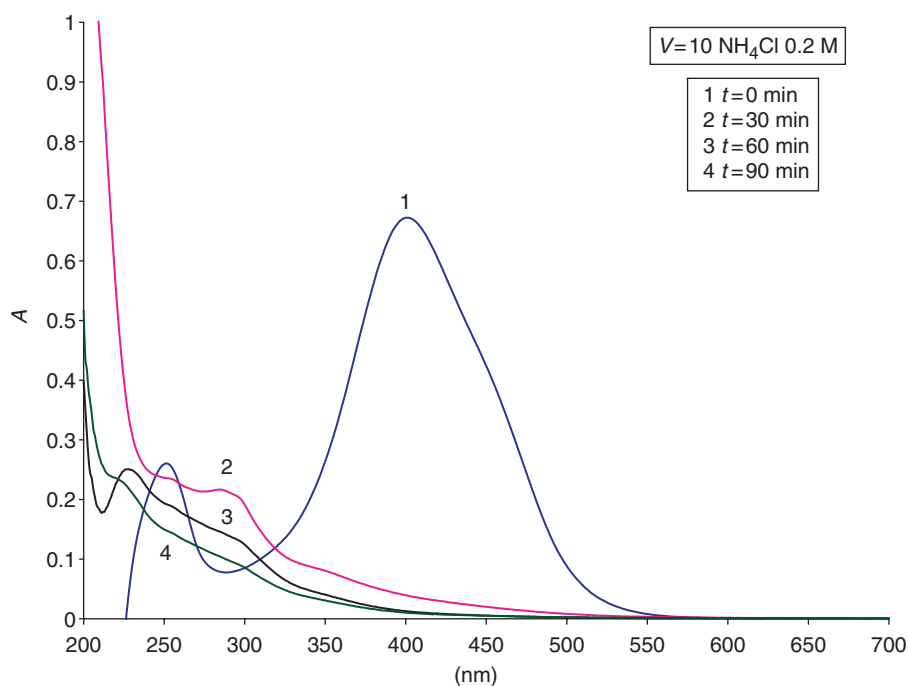


Figure 4. UV-vis spectra of direct yellow 4 shows the effect of treatment on color removal.

is due to the indirect oxidation effect of chlorine/hypochlorite. Therefore, the kinetics for COD removal in the indirect electrochemical oxidation process can be shown as follows:

$$-\frac{d[\text{COD}]}{dt} = \frac{k[\text{Cl}_2]}{[\text{COD}]} \quad (1)$$

During electrolysis, the chlorine/hypochlorite is produced by the anodic oxidation of chloride, and it would convert to chloride as the pollutants have been oxidized. Then the chloride would be anodically oxidized to form chlorine/hypochlorite, which oxidized the pollutants again. Accordingly the concentration of chlorine/hypochlorite during electrolysis can be assumed to be constant. Therefore the term of $[\text{Cl}_2]$ and kinetic constant (k) in equation (1) can be merged to simplify equation (2) to a pseudo first-order reaction kinetic and a new kinetic constant (k_{obs}) is formed as expressed by equation (2) and k_{obs} can be obtained by plotting a chart of $\ln([\text{COD}]_0/[\text{COD}]_t)$ versus time (figures 5 and 6):

$$-\frac{d[\text{COD}]}{dt} = k_{\text{obs}}[\text{COD}] \quad (2)$$

The effect of voltage on k_{obs} is tabulated in table 3. It can be seen that all k_{obs} values are increased as the voltage increased. This means that the chlorine/hypochlorite production rate is improved by increasing the voltage during electrolysis of saline wastewaters.

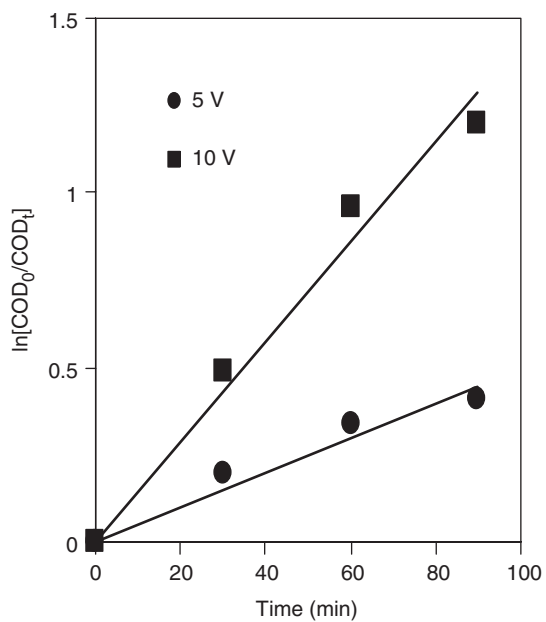
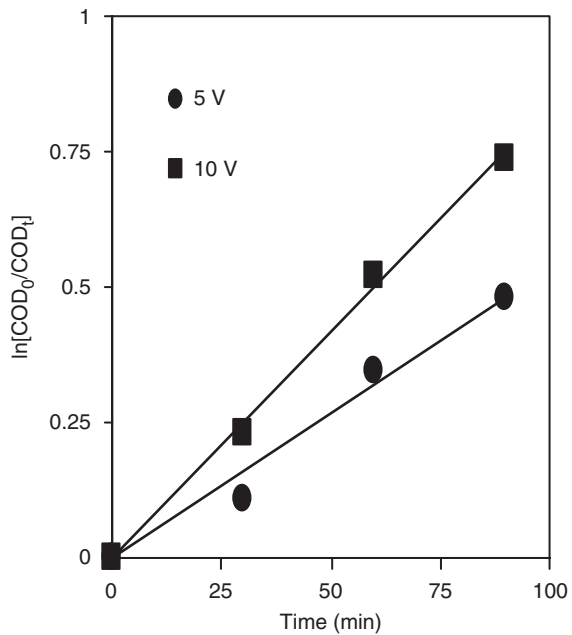
Figure 5. Plot of $\ln[\text{COD}_0/\text{COD}_t]$ vs. time for direct yellow 4.Figure 6. Plot of $\ln[\text{COD}_0/\text{COD}_t]$ vs. time for acid yellow 17.

Table 3. k_{obs} and R^2 by using supporting electrolyte NaCl 0.2 M.

Dye pollutant	$V = 5 \text{ V}$		$V = 10 \text{ V}$	
	$k_{\text{obs}} (\text{min}^{-1})$	R^2	$k_{\text{obs}} (\text{min}^{-1})$	R^2
Direct yellow 4	0.0050	0.9525	0.0143	0.9755
Acid yellow 17	0.0054	0.9759	0.0083	0.9967

4. Conclusion

In this study, the electrochemical oxidation process presents a good efficacy for destruction of organic dye pollutants. The COD can be readily removed; it was also found that chloride was a good supporting electrolyte because it can promote the progress of indirect oxidation effect of chlorine/hypochlorite.

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