

# Removal of Organics from the Wastewater of Dyebath by Electrooxidation

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**Abstract:** Residual dye in hydrolyzed form is the major organic constituent present in dyebath effluent resulting in the scarcity of water resources. The objective of this study is to remove organic pollutants by electrooxidation using graphite and  $\text{RuO}_2/\text{IrO}_2/\text{TaO}_2$  coated titanium (MMO) as electrodes. Among the two electrode materials used, graphite was found to be better in terms of COD removal, current efficiency and energy consumption. Nearly 85% of COD was removed using graphite whereas only 40% COD removal was achieved using MMO material as electrode. The influence of chloride ion and current density on the degradation of organics was studied. The results indicate that the electrooxidation is an effective technique for the treatment of dyebath effluent.

**Key words:** Electrooxidation, COD, current efficiency, graphite,  $\text{RuO}_2/\text{IrO}_2/\text{TaO}_2$  coated titanium.

## Introduction

The treatment of wastewater generated from textile industry is challenging due to variety of dyes that resist biodegradation. Particularly, the wastewater from dye-house is more complex and contains different classes of organic dyes and auxiliary chemicals. The residual dye concentration from reactive dye-baths will be as high as 25-40% because of their low fixation in hydrolyzed form (Chaudhuri and Sur, 2000). In view of stringent regulatory guidelines for the disposal of such effluents and to address the scarcity of water resources, it is essential to treat such water for reuse. The existing physico-chemical methods are inadequate for the effective removal of organics present in dye-house effluents. The biological treatment also is futile as 53% of 87 colours are non-biodegradable. The choice of the treatment process depends on the nature of the dye and its resistance to oxidation/reduction reactions (Hao et al., 2000).

The decolourization of simulated reactive dye-bath effluents using ozone/ $\text{H}_2\text{O}_2$ / $\text{TiO}_2$ /UV process was studied and found that the decolouration was effective (Alaton

et al., 2002; Perkowski and Kos, 2003). However, the advanced oxidation process was observed to be ineffective for the treatment of disperse and vat dyes (Namboodri et al., 1994). An enzymatic process (Graça et al., 2006), chemical oxidation using hypochlorite, ozone and Fenton's reagent, bisulfite catalyzed sodium borohydride reduction, GAC adsorption and anaerobic biodegradation technologies were tried for the treatment of textile wastewater (Ergas et al., 2006). Each technology was evaluated for its effectiveness in removing colour, COD and anticipated operating costs. Among the technologies evaluated, ozone, GAC absorption and electrooxidation were found to be efficient in producing high quality effluent suitable for reuse. The advanced oxidation technologies are inadequate to treat all the diverse pollutants present in textile wastewater.

In recent years, electrochemical oxidation is gaining importance for the treatment of industrial effluents due to its better efficiency. The COD of dyehouse wastewater could be removed to the extent of 89.8% by electrooxidation, membrane filtration and reverse osmosis (Xuejun et al., 2005). The effect of electrolytes

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such as NaCl and Na<sub>2</sub>SO<sub>4</sub> on electrooxidation of reactive dyebath effluent was also studied and concluded that better decolourization and removal of TOC could be accomplished in the presence of NaCl (Lopez and Gutierrez, 2006). The complete removal of colour and 98.7% COD were achieved by catalytic oxidation using modified kaolin and electrogenerated Fe(OH)<sub>3</sub> (Gutierrez et al., 2002). Since the zero discharge concepts are being implemented in India, various technological options are being studied to cope with the environmental regulations. The combination of electrooxidation, filtration and reverse osmosis are being tried on a priority basis to address the environmental issues of textile effluents. The efficacy of electrooxidation for the treatment of dyebath effluents using graphite and RuO<sub>2</sub>/IrO<sub>2</sub>/TaO<sub>2</sub> coated titanium is reported in the present study.

## Materials and Methods

The wastewater sample collected from a dyeing industry, situated in Tirupur, was analysed and its characteristics are incorporated in Table 1.

Graphite sheet, graphite rod, RuO<sub>2</sub>/IrO<sub>2</sub>/TaO<sub>2</sub> coated titanium (MMO) rods with effective anodic surface area of 200 cm<sup>2</sup>, 249.8 cm<sup>2</sup> and 413.8 cm<sup>2</sup> respectively were used as electrodes. The MMO rods were obtained from M/s Titanium and Tantalum Products Limited, Chennai and the graphite materials were procured from M/s. Carbone Lorraine.

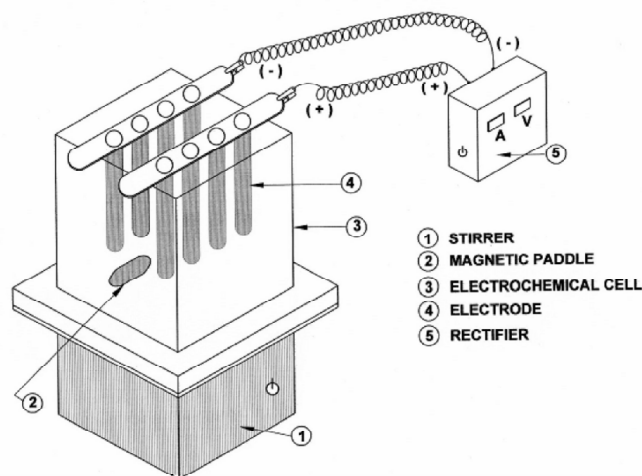
Four graphite rods connected to a common aluminum strip forms an anode assembly and equal number of rods were used for cathode assembly. In the case of MMO, nine rods were used for each assembly. The gap between anode and cathode assemblies was maintained at 1 cm.

**Table 1: Physico-chemical characteristics of dye bath effluent before and after electrooxidation**

Parameter	Raw effluent	After electro-oxidation*
Colour	Dark Blue	Colourless
pH	9.9	10.02
Total Dissolved Solids (mg L <sup>-1</sup> )	27690	25540
Total Suspended Solids (mg L <sup>-1</sup> )	90	5.0
COD (mg L <sup>-1</sup> )	370	74
BOD (mg L <sup>-1</sup> )	5	N.A
TKN (mg L <sup>-1</sup> )	3	nil
Chloride (mg L <sup>-1</sup> )	15775.3	14711.8

\*Using graphite sheet at 25 mA cm<sup>-2</sup> for 210 min

The schematic diagram of the electrode assembly and the experimental set-up is shown in Figure 1.



**Figure 1: Schematic diagram of experimental set-up.**

For each experiment, two litres of sample was used and the bulk electrolysis was performed in undivided electrochemical cell under galvanostatic condition. Magnetic stirrer was used to avoid the concentration gradient. Samples were collected at regular time intervals and analyzed for COD, BOD, Suspended Solids (SS), Total Dissolved Solids (TDS), chloride and nitrogen according to the standard methods (Lenore et al., 1992). UV-visible spectrum of the sample was recorded using UV-visible spectrophotometer (Model: Shimadzu UV-VIS 160 A).

## Result and Discussions

The dye-bath wastewater was subjected to electro-oxidation using two different anode materials viz. graphite and MMO. The changes in the absorbance characteristics of the wastewater during electrooxidation were recorded. It was observed that the effluent was totally decolourized within five minutes of electro-oxidation at an applied current density of 25 mA/cm<sup>2</sup> using graphite sheet. This clearly indicates that the chromophoric groups of organic molecules are destroyed fully within a short duration of electrooxidation.

### Effect of Anode Materials

The oxidation efficiency depends on the anode material. Electrodes with high over-potential is preferred for better oxygen evolution (Chen, 2004). The influence of anode materials on COD reduction was studied at a constant current of 5 A and the results are shown in Figure 2. It

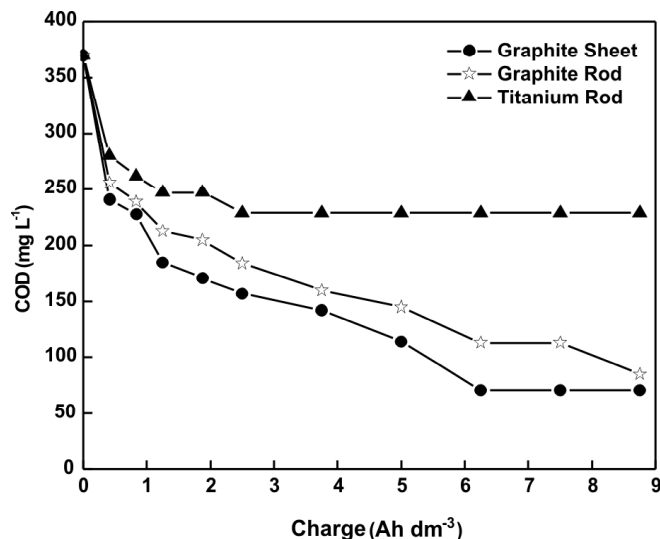
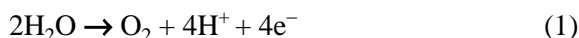
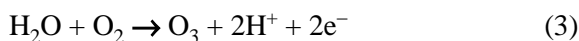
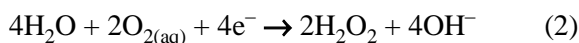


Figure 2: Effect of anode material on COD removal at constant current (5A).

may be noted that the decrease in COD is 141 mg/L in the presence of MMO electrodes and 300 mg/L in the presence of graphite. The rate of COD reduction was observed to be relatively high at the initial stages and gradually decreased with time. The decrease in the rate of COD removal at latter stages suggests that the oxidation is controlled by diffusion process. In electrooxidation process, the pollutants are oxidized directly at the electrode surface and also indirectly by the oxidizing agents generated electrochemically into the bulk solution away from the electrodes (Comninellis and Pulgarin, 1991). The oxygen evolution is the primary reaction at the anode. The anodic evolution of oxygen could be represented as



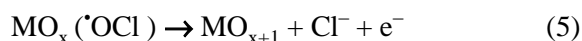
The molecular oxygen can be converted to active oxygen according to the following equations.



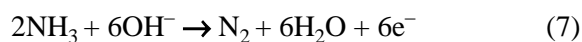
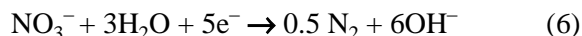
Szpyrkowicz et al. (2005) have suggested the generation of various oxidants such as nascent oxygen, ozone, hydrogen peroxide and oxy chlorides in the presence of chloride. Simultaneous chloride ion measurements (Figure 3) revealed that the  $\text{Cl}^-$  concentration was decreased to the extent of 2000 mg/L from its original concentration of 15775 mg/L in the presence of graphite electrode. This implies the generation of active chlorine during electrolysis. The electrochemical discharge of chlorine at the anode as secondary electrochemical reaction can be represented as



At 25°C and normal atmospheric pressure, the chlorine gas thus liberated from anode can dissolve in water to the extent of 6.413 g/L. Depending on the pH of the aqueous solution, hypochlorous acid and hypochlorite ion will be formed. Since the solubility of oxygen and ozone in water is very less and the experiments were conducted around pH 10.0, oxidation of organics might have occurred mainly due to oxy chloride and  $\text{OH}^\bullet$ . Serikawa et al. (2000) have observed strong catalytic effect in the conversion of organic pollutants to innocuous  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the presence of chloride ion. Raghu et al. (2007) have suggested that the oxidation of organics in the presence of chloride ion proceeds via adsorption of  $^\bullet\text{OCl}$  on metal oxide and possible transition of oxygen atom to metal oxide forming higher metal oxide.



The initial Kjeldhal nitrogen present in the sample to the extent of 3 mg/L was found to be totally eliminated during electrooxidation. The electrochemical reduction of nitrate and removal of  $\text{NH}_3$  to nitrogen can be represented as follows:

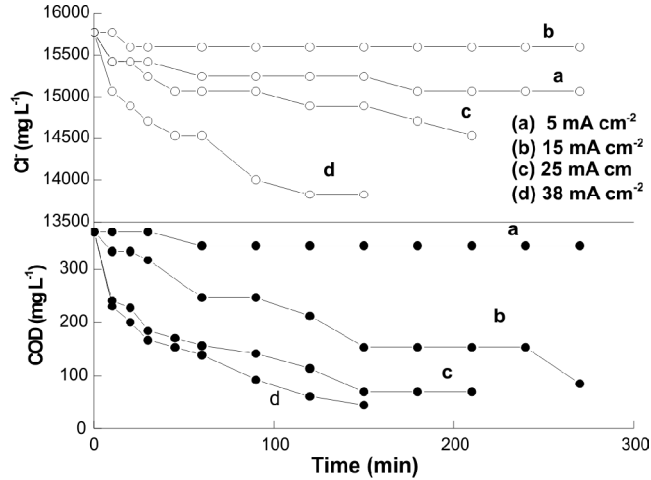


Thus the organic molecules can be disintegrated to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  by electrochemical process.

### Effect of Current Density

Current density is an important operating variable in electrochemical oxidation process. It is defined as the ratio of current input to the electrolysis cell to the surface area of the electrode. Electrooxidation was carried out at different current densities of 5, 15, 25 and 38 mA/cm<sup>2</sup> using graphite as anode and the results are presented in Figure 3. It is apparent that COD was decreased from 370 mg/L to 270 mg/L at lower current density of 5 mA/cm<sup>2</sup>. By increasing the current density to 38 mA/cm<sup>2</sup>, the COD was reduced to 46 mg/L. It may be noted that as the current density is increased the concentration of oxy chloride in aqueous solution also increases and in turn the COD removal. The higher current density leads to higher power consumption and operating cost. The two important parameters i.e current efficiency (CE) and energy consumption (E) related to current density can be calculated using the following equations:

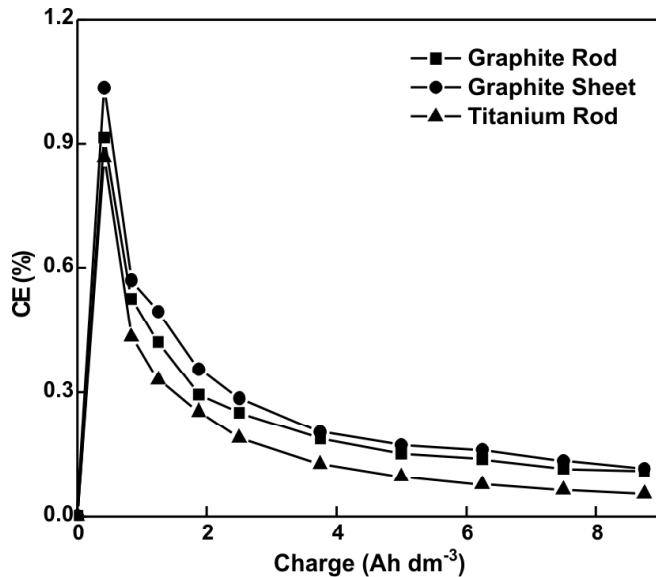
$$\text{CE (\%)} = \frac{(\text{COD}_o - \text{COD}_t) \times FV}{8It} \times 100 \quad (9)$$



**Figure 3: Effect of current density on COD removal and  $\text{Cl}^-$  concentration (Electrode: graphite sheet).**

$$\text{Energy consumption } (E) = IV_A t / \Delta \text{COD } V \quad (10)$$

where  $\text{COD}_0$  is initial COD value (g/L),  $\text{COD}_t$  is final COD value (g/L),  $I$  is the applied current (A),  $F$  is Faraday constant (96487 C/mole),  $V$  is volume of effluent (litre) and  $t$  is electro oxidation time (seconds).  $E$  is energy consumption (kWh/g) and  $V_A$  is applied voltage (V). CE as the function of charge ( $Q$ ) passed for different anode material at the constant current is shown in Figure 4. The results indicate that the graphite exhibit higher CE compared to MMO electrodes. The current efficiency below 1.0 is generally interpreted to the indirect oxidation. The operation of electrochemical reactor at



**Figure 4: Current Efficiency as a function of charge for different anode materials.**

an appropriate current density is essential to reduce the operating cost of the process. The power consumption and current efficiency calculated at different current densities and COD removals is shown in Table 2. The data clearly shows that better CE and power consumption could be realized at the current density of 25 mA/cm<sup>2</sup>.

**Table 2: Current efficiency and power consumption with respect to COD removal and current density**

COD Removal (%)	Parameters	Current Density (mA cm <sup>-2</sup> )		
		15	25	38
25	Time (min)	47	8	7
	Charge (Ah dm <sup>-3</sup> )	1.175	0.33	0.43
	CE (%)	26.4	92.9	70.8
	E (kWh g <sup>-1</sup> )	0.06	0.019	0.03
50	Time (min)	134	32	25
	Charge (Ah dm <sup>-3</sup> )	3.35	1.33	1.56
	CE (%)	18.5	46.5	39.7
	E (kWh g <sup>-1</sup> )	0.09	0.04	0.06
75	Time (min)	267	136	91
	Charge (Ah dm <sup>-3</sup> )	6.67	5.66	5.68
	CE (%)	13.9	16.4	16.4
	E (kWh g <sup>-1</sup> )	0.12	0.11	0.14

## Conclusions

The electro-oxidation of textile dye bath effluent was studied using graphite and MMO electrodes. The results show that the electrooxidation technique is very efficient in removing colour and COD of the dye bath wastewater. Though the colour removal was achieved within a short duration of five minutes, more time is required for COD removal. The COD removal of 85% was achieved by using graphite electrodes whereas MMO electrodes have yielded only 38%. In terms of current efficiency and power consumption, graphite material was found to be better than MMO electrodes. The current efficiency of graphite electrode was found to be around 90% during the initial stages and it gradually decreased to 16% at the final stages of electrooxidation.

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