Electrochemical Treatment of Textile Dye Wastewater by Mild Steel Anode

J. G. BHAVYA*, H.B. REKHA*+ AND USHA N. MURTHY*

This paper presents the results of the treatment of textile dye wastewater generated from a textile processing industry by electrochemical method. Experiments were conducted at current densities of 12, 24 and 48 A/m^2 using mild steel as anode and cathode. During the various stages of electrolysis, parameters such as COD, color and BOD_5 were determined in order to know the feasibility of electrochemical treatment. It was observed that increasing the electrolysis time and increased current density bring down the concentration of pollutants. Also COD removal rate and energy consumption during the electrolysis were calculated and presented in this paper. The present study proves the effectiveness of electrochemical treatment using MS as anode for TDW oxidation.

Key words: *Electrochemical oxidation, COD, color, mild steel anode, textile dye*

Introduction

The textile industry is one of many industries that utilize large volumes of water in the manufacturing process. This water, used in the dyeing and finishing processes, ends up as wastewater, which needs to be treated before its final discharge. Frequent changes of the dye stuff employed in the process cause considerable variation in the wastewater characteristics, such as intense color, high chemical oxygen demand (COD), dissolved solids values, temperature and highly fluctuating pH[7] and low biodegradability especially the effluent from the dyeing stages of the dyeing and finishing process[11].

Color is one of the most important water quality parameter. During the dying process, about 5-20% of the dye is lost due to its partial adsorption on the fibers. Dyes are manufactured to have high chemical resistance because they are normally chemical species that are very difficult to degrade (aromatic dyes) [3]. It damages both aquatic flora and fauna. Furthermore, colored effluents may contain considerable amounts of toxic compounds, especially azo dyes that are known to be highly carcinogenic [5].

The removal of dyes is therefore a challenge to both the textile industry and the wastewater treatment facilities. Dyeing wastewater is usually treated by conventional methods such as biological oxidation and adsorption. Because of the large variability of the composition of textile wastewater, most of these traditional methods are becoming inadequate [11].

Recently there has been growing interest towards electrochemical techniques for the treatment of wastewater containing organic pollutants. Two important features of the electrochemical process are converting non-biocompatible organics into biocompatible compounds and oxidation of organics into carbon dioxide and water [8].

Electrochemical oxidation of wastewaters

Electrochemical oxidation of pollutants can take place through two different oxidation mechanisms as shown in **Fig.1.** (a) direct anodic oxidation, where the pollutants are destroyed at the anode surface and (b) indirect oxidation where, a mediator (HClO, $H_2S_2O_8$ and others) is electrochemically generated to carry out the oxidation. It has to be kept in mind that during electro-oxidation of aqueous effluents, both oxidation mechanisms may coexist. Hence in the present study MS electrode used for anode (direct oxidation) and sodium chloride present in the effluent (Indirect oxidation) used as supporting electrolyte.
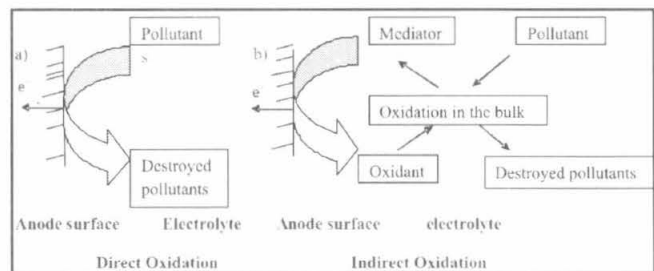

Fig. 1: (a) direct and (b) indirect electrolytic treatment of pollutants

* Department of Civil Engineering, University Visvesvaraya College of Engineering (UVCE), Bengaluru University, Bengaluru-560 056, Karnataka (India).

+ Corresponding author: Assistant Professor, Department of Civil Engineering, UVCE, Bangalore University, Bengaluru (India)-560 056. Mob. : +91 9483546644; Ph. : +91 80 22961662,1920, email: rekhahb@gmail.com

Direct oxidation

Direct oxidation of pollutants takes place in two steps: (i) diffusion of pollutants from the bulk solution to the anode surface and (ii) oxidation of pollutants at the anode surface. Consequently, the efficiency of the electrochemical process depends on the relationship between mass transfer of the substrate and electron transfer at the electrode surface. The rate of electron transfer is determined by the electrode activity and current density. During anodic oxidation of organic pollutants two different pathways can be followed:

• Electrochemical conversion: Organic compounds are only partially oxidized (eq(1)). Therefore, a subsequent treatment may be required.

$$R \longrightarrow RO + e^- \qquad \text{.......(1)}$$

• Electrochemical combustion: Organic compounds are transformed into water, carbon dioxide and other inorganic components:

$$R \longrightarrow CO_2 + H_2O + Salts + e^- \qquad \text{.........(2)}$$
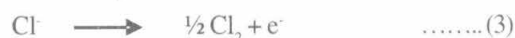
Indirect oxidation

During indirect electrochemical oxidation, a strong oxidizing agent is electro-generated at the anode surface and then destroys the pollutants in the bulk solution. The most common electrochemical oxidant is probably chlorine which is formed by the oxidation of chloride at the anode. Although the role of active chlorine in the oxidation of organic pollutants is not clear, ammonia oxidation is usually acknowledged to take place through this mechanism. The extensive use of active chlorine is due to the ubiquitous presence of chloride in waste waters and to its quite effective action. Other common oxidants that can be electrochemically produced are hydrogen peroxide, peroxodisulfuric acid ($H_2S_2O_8$) and ozone.

Operating conditions

Among the variables that are usually modified in electrochemical oxidation processes, the current density (intensity per unit area of electrode) may be the term most frequently referred to because it controls the reaction rate. The effect of current density on the treatment efficiency depends on the characteristics of the effluent to be treated. The physico-chemical characteristics of the wastewater (nature and concentration of electrolyte, pH value and concentration of target pollutants) also affect the electrochemical oxidation process. The pH value and temperature, affects mostly indirect oxidation processes. In chloride mediated reaction, the pH value may affect the oxidation rate because it determines the primary active chloro species that is present in the effluent. During indirect oxidation, chlorine evolution occurs at the anode [1];

$$Cl^- \longrightarrow \tfrac{1}{2} Cl_2 + e^- \qquad \text{........(3)}$$

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \qquad \text{........(4)}$$

$$HOCl \longrightarrow OCl^- + H^+ \qquad \text{........(5)}$$

The overall desired reaction is [9],

$$Dye + OCl^- \longrightarrow intermediates \longrightarrow CO_2 + Cl^- + H_2O \qquad \text{.......(6)}$$
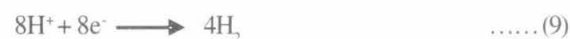
The electrochemical process can be a viable alternative. It consists of a cell in which the sacrificial electrodes, made of iron are the site where Fe ions regenerated due to a given applied potential. This stage is known as the anodic stage, in which the metallic or iron is oxidized. Once formed, these cations immediately undergo further spontaneous reactions to produce the corresponding hydroxides/polyhydroxides. These compounds have a strong affinity for dispersed/dissolved substances, as well as counter-ions to cause coagulation/adsorption phenomena. The electrochemical process with steel as anode in aqueous system is quite complex. It is generally believed that there are three possible mechanisms involved in the process, namely electrocoagulation, electrofloatation and electrooxidation. Oxidation and reduction of the electrochemical process occur, respectively, at anode and cathode of iron electrodes. The mechanism of removal of pollutants with iron electrodes is shown below [3].

Anode:

$$4\,Fe \longrightarrow 4Fe^{2+} + 8e^- \qquad \text{......(7)}$$

$$4Fe^{2+} + 10H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 8\,H^+ \qquad \text{......(8)}$$

Cathode:

$$8H^+ + 8e^- \longrightarrow 4H_2 \qquad \text{......(9)}$$

Overall:

$$4Fe^{2+} + 10H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 4H_2 \qquad \text{......(10)}$$

The aim of the present work was to study the technical viability of the electrochemical oxidation process for the removal of COD and color from an effluent generated by a textile processor of fabric manufacture.

Materials and methods

Effluent samples from a textile processor located in the city of Bangalore (India), were collected from the dye bath unit, containing a mixture of waste dye solution, whose main characteristics are shown in **Table 1**. The experimental set-up (**Fig. 2**) consisted of a glass beaker with 1 lit capacity, in which two electrodes having an inter-electrode gap of 40 mm were

placed vertical and parallel to each other. Commercially available Mild Steel (MS) of dimension 5 cm x 5 cm was used as anode and cathode. The effective area of electrode was 25 cm^2 (0.0025 m^2). The experiments were carried out with the raw effluent at room temperature and with constant agitation. The electrodes were connected to a DC power supply (Textronix 35D, 0-15V, 0-10A). The electrolysis was carried out under galvanostatic conditions covering a wide range of operating conditions. During the experiment, samples were collected at regular intervals and analyzed for various parameters. After the experiment, the power was switched off and the electrodes were disconnected. The electrolytes (effluent solution) resulting from electrochemical treatment were analyzed for COD, color, BOD, pH according to the standard methods suggested by APHA[2].

The pH measurements were made on Elico Ion Analyser (LI 126). The chemical oxidation demand was estimated by closed reflux method, using COD digestion apparatus, Model ET 108, Lovibond. DO probe connected to Water Quality Analyzer, microprocessor based, Model PE138, Elico used to measure DO directly based on which BOD$_5$ was calculated. Determination of the color of the wastewater was carried out by measuring the absorbance at a wavelength of 508nm (λ_{max}). The absorption spectra of the samples were recorded on Elico Scanning Mini Spectrophotometer (SL 177), recording the spectra over 340nm to 1000nm range. The percentage of color removal was calculated as follows;

Color removal (%) = $[(\lambda_{max} - \lambda_t)/ \lambda_{max}]$ *100

Where,

λ_{max} = Absorbance of the raw sample at 508nm.

λ_t = Absorbance of the samples collected at regular time intervals, t at a fixed wavelength of
        508nm.

The results are expressed in terms of current density i.e. current per area of electrode which determines the rate of a process [6]. The removal rate for COD has been calculated in terms of COD removed/hr/A/m^2. The energy consumption for the removal of 1 kg of COD was calculated and expressed in Watt hour (Wh). The cell voltage during the electrolysis was taken for calculating the energy consumption.

Results and discussion

The characteristics of the TDW are given in **Table 1**. It is known from the literature that initial pH does not have significant effect in the degradation of organic pollutants by indirect electrochemical oxidation. The amount of sodium chloride in TDW was found to be 1200 mg/L. In the present study sodium chloride present itself was used as a supporting

Table 1: Characteristics of textile dye wastewater

Parameter	Range of values
pH	9.2-9.3
Total Solids (mg/L)	1244-5772
Total Dissolved Solids(mg/L)	541-2260
Total Suspended Solids(mg/L)	28-1675
Total Volatile Solids (mg/L)	660-2428
Alkalinity (mg/L)	440-1300
Chlorides (mg/L)	1000-1200
BOD (mg/L)	177-307
COD (mg/L)	2016-3162
BOD$_5$/COD	0.09-0.1

electrolyte and additional electrolyte was not added. The oxidation of organic compounds present in the effluent is mainly due to the generation of hypochlorite and free chlorine.

During the present investigation the operating parameters such as current, electrolysis time were varied to explore the effect on COD and color removal. Results showed that higher COD and color reduction occurred at higher charge input and electrolysis time.

Chemical oxygen demand

The variation of COD with electrolysis time for different current densities is presented in **Fig. 2**. It can be ascertained from **Fig. 2** that COD decreases with increasing
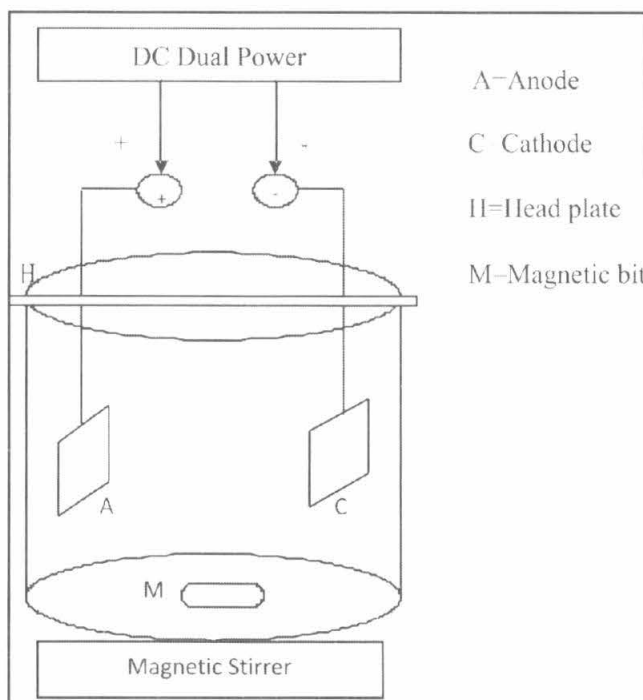

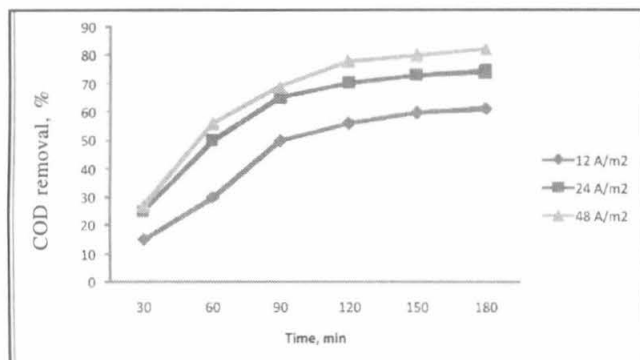Fig. 2 : A schematic diagram of an electrochemical cell

Fig. 2: COD removal at different current densities

electrolysis time. The trend of COD reduction with electrolysis time remains same for all the current densities adopted in the present investigation. Also rate of COD reduction increases with increasing current density. Mohan et.al, (2001)[9], reported COD reduction for different current densities varying from 1 to 5 A/m^2, COD reduction increased for a max current density of 5 A/m^2. When the current density is high, significant decrease in the current efficiency is expected from the production of oxygen (Current efficiency CE, the ratio of current consumed in producing a target product to that of total consumption) [6].

Color

The color removal is of great interest because color is considered the most important persisting polluting parameter of TDW. **Fig. 3** shows the color removal in percentage under various experimental conditions. It can be observed from the figure that at a current density of 48 A/m^2, 78% of color removal has been achieved with an electrolysis time of 90 min, later it was gradually increased. As the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore there is an increase in the floc production in the solution and hence the improvement in the efficiency of color removal[4].
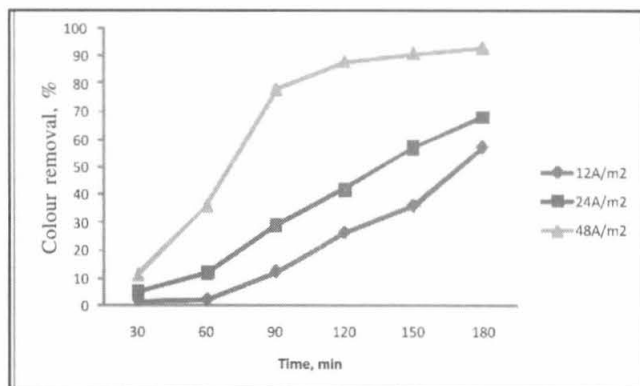

Fig. 3: Reduction of color at different current densities

Biochemical oxygen demand (BOD$_5$)

It is observed that BOD$_5$ has increased during the course of reaction as shown in **Fig 4**. The increase in BOD$_5$ concentration is attributed to the fact that some of the organics may have broken down into smaller fragments, which are more biodegradable than the parent compounds which in turn increase the BOD$_5$/COD ratio. The results indicate that the electrochemical oxidation improves the biodegradability of TDW and could be used for effective TDW oxidation or as a feasible pretreatment stage for biological post treatment.
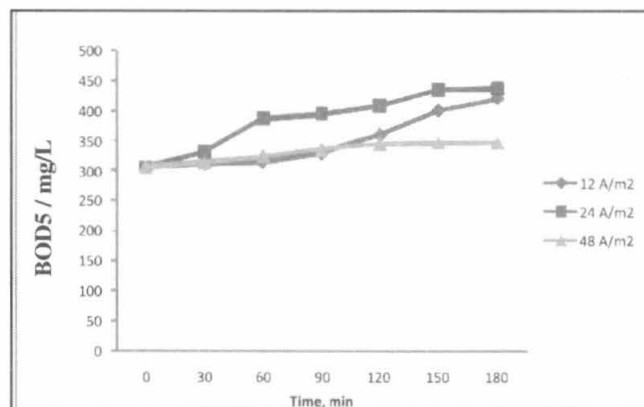

Fig. 4: Variation of BOD$_5$ at different current densities

Energy consumption and anode efficiency

The efficiency of MS as anode and energy consumption at various current densities is presented in **Table 2.** The anode efficiency has been calculated in kg of COD removed per hour ampere and per square meter (kg COD/h/A/m^2). The energy consumption per kg COD removal at the lowest current density is about 107.3 and 680.74 Wh, for higher current density. Application of higher current densities actually decreases the anode efficiency and increases the energy consumed per kg of COD removed. N N Rao et al. (2001)[10] reported that an increase in current density increases energy consumption related to Ti/Pt, Ti/PbO$_2$ and Ti/MnO$_2$. This may be due to the competing water electrolysis reaction that becomes dominant at higher current densities. The energy supplied to an electrochemical reactor plays an important role in any electrochemical process. Due to various reactions occurring at anode and cathode the organic species are finally converted into CO$_2$ [9]. As in any electrochemical process the reactions occur at the electrode/electrolyte interface so it is essential for the reactive species to be available at sufficient concentration at this interface in order to have good reaction efficiency. **Table 3** shows the quantitative analysis of MS electrode before and after electrolysis. It can be concluded that increased current density, increased the anode oxidation.

Table 2: COD removal rate and energy consumption.

Current Applied, A	Current Density A/m^2	Initial pH	COD, mg/L		Voltage	COD Removal Rate kg COD/h/A/m^2	Energy Consumption Wh/kg of COD
			Initial	Final			
0.03	12	9.2	3162	1233	2.30	8.57	107.30
0.06	24	9.2	3162	822	2.99	5.20	230.00
0.12	48	9.2	3162	576	4.89	2.87	680.74

Table 3: Quantitative analysis of MS electrodes before and after electrolysis

Current Density, A/m^2	Anode			Cathode		
	Initial weight, g	Final weight , g	Difference in weight, g	Initial Weight, g	Final weight , g	Difference in weight, g
12	30.4974	30.4032	0.0942	30.3071	30.3037	0.0034
24	30.8847	30.7095	0.1752	31.0816	31.0807	0.0009
48	30.2462	29.8912	0.3550	31.1737	31.1694	0.0043

Operating at lower current density always consumes less energy but, at the same time, increases the duration of electrolysis. Therefore, it is necessary to choose a current density that is suitable for real industrial application by way of maximum degradation, shorter reaction time, and less energy consumption. In the present study a current density of 48 A/m^2 was found to be optimum with respect to COD and color removal at an ideal time of 120 min in which about 78% of COD amd 88% of color removal has been achieved.

Conclusions

The results showed that the reduction of COD increased with the increase in electrolysis time. At a current density of 48 A/m^2, maximum color removal of 93%, COD reduction of 82% and increase in BOD$_5$/COD ratio from 0.1 to 0.61 was achieved. The energy consumption per kg of COD removal at the lowest current density was about 107.3 and 680.74 Wh for higher current density. The results illustrate that, at time of 120 min, maximum of 78% and 88% removal of COD and color occurred respectively with a current density of 48 A/m^2. Therefore the operation of the electrochemical reaction at optimized current density is essential to reduce the operating cost of the process. From the experimental parameters studied, the optimum current density was found to be 48 A/m^2 by considering 120 min as ideal electrolysis time. Hence it can be concluded that the electrochemical oxidation could be used for effective TDW oxidation or as a feasible pretreatment stage for biological post treatment.

References

1. Angela Anglada, Ane Urtiaga and Inmaculada Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, *J Chem Technol Biotechnol*, **84**, 1747-1755 (2009).

2. APHA, Standard methods for the examination of water and wastewater, 20th edition. Americal Public Health Association, Washington, D.C (1998).

3. Cerqueira A, Russo C and Marques M R C, Electroflocculation for textile wastewater treatment, *J.Chem Eng.*, **26 (4)**, (2009).

4. Daneshvar N, Sorkhabi H A and Kasiri M B, Decolorization of dye solution containing acid red 14 by electrocoagulation with a comparative investigation of different electrode connection, *J Haz Mat*, **B112** (2004).

5. Daneshvar N, Khataee A R, Ghadim A R A and Rasoulifard, M H, Decolorization of c.i. acid yellow 23 solution by electrocoagulation process: investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC), *J of Haz Mat*, **148** (2007).

6. Guohua Chen, Electrochemical technologies in wastewater treatment, *Separation and Purification Technology*, **38**, 11-41 (2003).

7. Gurses A, Yalgin M and DoAr C, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, *Waste Management*, **22(5)** (2002).

8. Karuppan Muthukumar and Shunmuga Sundaram P, Treatment of textile dye wastewater by using an electrochemical bipolar disc stack reactor. *J of Chemical Technology and Biotechnology*, **79**,1135-1141 (2004).

9. N Mohan, Balasubramanian, and V Subramanian. Electrochemical Treatment of Simulated Textile Effluent, *Chem Eng. Technol.* **24**, (7) 749-753 (2001).

10. NN Rao and K M Somasedhar, Electrochemical oxidation of tannery wastewater. *J Chem. Technology and Biotechnology*, **76**, 1121-1131 (2001).

11. Vlyssides A G, Loizidou M, Karlis P K and Zorpas A A, Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode, *J. Haz Mat*, **B70**, 41-52 (1999).