DECOLORIZATION OF SYNTHETIC AND REAL POLLUTED WATER BY INDIRECT ELECTROCHEMICAL OXIDATION PROCESS

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ABSTRACT

In this paper the Decolorization and Degradation of synthetic and real polluted water by electrochemical oxidation method were investigated. Synthetic polluted water consisting of Fast Blue B Salt (FBBS) was used as a model compound. Electrochemical degradation processes were performed using Graphite as an anode and Stainless Steel (304) as a cathode. In the bulk solution, the strong oxidizing potential of the chemicals were produced when the polluted water was passed through the electrolytic cell. The organic pollutants were oxidized to little or harmless organic molecules, carbon dioxide and water. The results indicated that the removal of chemical oxygen demand (COD) and colour were 75% and 88% respectively. The removal of COD and color increased by increasing voltage and chloride concentration at low pH. Due to effectiveness and ease in operation, this technique can be applied for treatment of a large volume and industrial scale of textile polluted water.

INTRODUCTION

Dyes pollutants from the textile industry are an important source of environment contamination. With a rapidly growing world population and an increasing number of reports on harmful effects on the environment, its protection has become a major issue and a crucial factor for future technological progress, which will have to meet the requirements for sustainable development. The strategies for environmental protection in industry generally include processes for polluted water treatment as well as development of new processes or products which have no or less harmful effects on the environment (Simond, 1997).

Industrial polluted water are usually treated by conventional methods such as biological oxidation (Raghukumar et al., 2008), adsorption (Gutierrez et al., 1999 and . Vlyssides et al., 2002), ozonation (Li-Choung Chiangi et al., 2007), photochemical oxidation (Schrank et al., 2004 and Shen et al., 2006), Ultrasonic method (Lorimer et al., 2000 and Lorimer et al., 2001) and electrochemical technology (Vlyssides et al., 2004, Szpyrkowicz et al., 2005, Rajkumar et al., 2003 and Tunay et al., 1995, Kotz et

al., 1991 and Panizza et al., 2004). In recent years there has been increasing interest in the use of electrochemical method for the treatment of polluted water. Electrochemical methods have been successfully applied in the purification of several industrial polluted waters such as textile (Mohan et al.,2001), tannery phenol solution (Vaghela et al., 2005) and poly aromatic organic pollutants (Tunay et al., 1995), textile dye and finishing process are among the major industrial water user; in many areas, this industry has the pollutants most difficult to treat to a satisfactory level. The major problem of textile and finishing polluted water is in strong color and high COD (Karlis et al., 2000). The organic and toxic pollutants present in treated polluted water such as dyes are usually destroyed by a direct anodic process or by an indirect anodic oxidation. The time of oxidation depends upon the stability and concentration of compounds, concentration of NaCl, solution pH and applied voltage (Szpyrkowicz et al., 2005). The direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, diffusion rates of organic compounds in the active points of the anode and the applied current density Fig. 1.
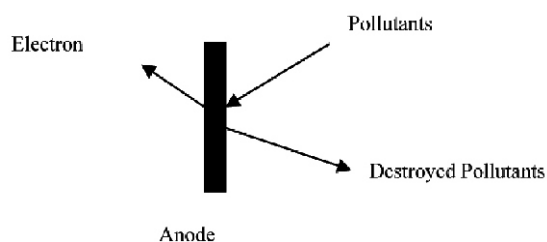
Fig. 1. Direct oxidation mechanism on anode

The indirect electro-oxidation rate is dependent on the diffusion rate of secondary oxidants into solution, temperature and pH. Effective pollutant degradation is based on the direct electrochemical process because the secondary Oxidants are able to completely convert all organics into water and carbon dioxide. Fig. 2.

In acid solution, oxygen, free chlorine and may be some amounts of ozone and chlorine oxides are the secondary main oxidants as by-products of the direct oxidation process. In moderate alkaline solution a cycle of chloride-chlorine- hypochlorite-chloride takes place, which produces OCl⁻, oxygen and some amounts of hydrogen peroxide and maybe ozone. In the strong alkaline solutions the cycle of chloride-chlorine-chloride is reduced owing to the production of ClO_3^- that is a chlorate anion. Therefore, in low pH the chlorides are reduced during the electrolysis process to produce free chlorine, while at high pH values the chlorides are reduced producing chlorates (Szpyrkowicz *et al.*, 2005 and Panizza *et al.*, 2004).
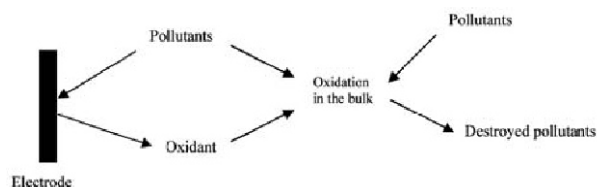

Fig. 2. Indirect oxidation mechanism in bulk solution

In this research, decolorization of FBBS and RW by indirect electrochemical oxidation has been studied. The effect of experimental parameters such as voltage, sodium chloride concentration, and initial pH and anode materials on the Decolorization of Synthetic and Real polluted water were all evaluated.

MATERIALS AND METHODS

The electrochemical cell consists of an undivided

reactor with two cathodes and one anode. It had a cell volume of 400 mL. These electrodes were parallel. The anode electrode is in the center of cell and was made of Graphite plate (20 mm × 20 mm × 1 mm); Stainless Steel 304 plates (20 mm × 80 mm × 1 mm) were used as cathodes (Fig. 3).
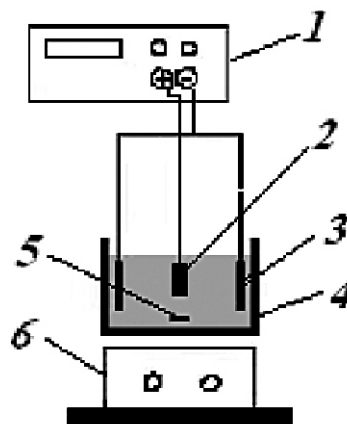

Fig. 3. Experimental laboratory set up. 1: power supply; 2: anode electrode; 3: cathode electrode; 4: electrolytic cell; 5: stirrer bar; 6: magnetic stirrer.

Chemical Oxygen Demand (COD) tests were also performed, according to Standard Methods (APHA/AWWA/WEF, 2007).

Textile polluted water was prepared from (TIRUPUR) Textile dying factory located in Tamil nadu (South India). The characteristics of these textiles polluted water are showed in Table 1.
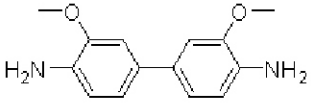
Table 1. Characterization of Real polluted water

Character	Value
pH	8.5
COD	2980 mg/L
BOD	158 mg/L
TOC	810 mg/L
Conductivity	3210μs/cm

Fast Blue B Salt (FBBS) was used as a Synthetic polluted water. It was commercially available as 3,3'-Dimethoxy Benzidine (3,3'-DMB) and used without further purification. 3,3'-DMB is one of the most important and commonly used dyes in textile industry. This dye has amine (-NH_2) functional group. The chemical structure of 3,3'-DMB was shown in Table 2.

Different groups in the dye molecule have different absorbance peaks. The maximum absorbance is at 460 nm. The initial concentration of

Table 2. Characterization of 3,3'-Dimethoxy Benzidine (3,3'-DMB)

Name	3,3'-Dimethoxy Benzidine
Structure	

3,3'-Dimethoxy Benzidine

Colour Index (C.I)	37235
α_{max}	460 nm
Molecular Weight	244.29

3,3'-DMB solution was 10^{-3} (mol L^{-1}). Absorbance measurements were carried out with a UV–visible spectrophotometer (Shimadzu UV-256). NaCl was used as a supporting electrolyte (PRIYA FINE CHEMICALS).

RESULTS AND DISCUSSION

Decolorization of 3,3'-Dimethoxy Benzidine

The results from the electro oxidation of the 3,3'-DMB solution are shown in Fig. 4. After 120 min of electrolysis, all absorbance peaks (250 < λ < 700) have been found to have disappeared.
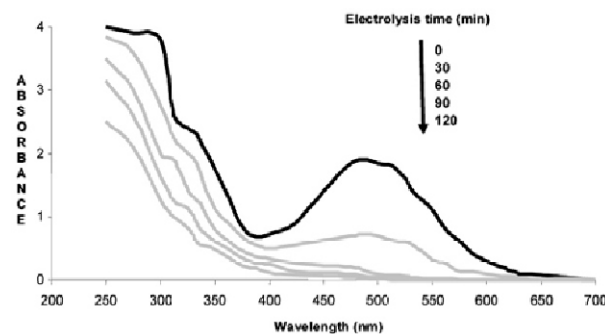
Fig. 4. Change in the absorption UV-visible spectra of 3,3'-DMB during of electrolysis (Voltage = 16 volt, NaCl = 0.5 (g L^{-1}), pH = 4.5, 3,3'-DMB = 10^{-3} (mol L^{-1}), reactor volume = 400 mL) The decreasing of the visible band is due to fragmentation of the anthraquinone band. The percentage of dye mineralization was evaluated from the measurements of COD.

$$\text{COD removal \%} = 100 \times (COD_i - COD_t) / COD_i$$

Where COD_i corresponds to the initial value and COD_t is the value obtained at time t. The indirect electrochemical treatment involves the application of an electrical current to the polluted water containing chloride to convert chloride to chlorine/hypochlorite.

The effect of applied voltage showed that with

the increasing of applied voltage the percentage removal of COD increased (Fig. 5). With the increasing of applied voltage the Oxygen Evolution Reaction (OER) may occur on the anode surface along with the oxygen molecule formation. The production of O$_2$ molecules diffuse into solution and this has been the cause for oxidation of Cl$^-$ ions and increase in OCl$^-$ production. The process finally would cause the increase in 3,3'-DMB degradation rate.
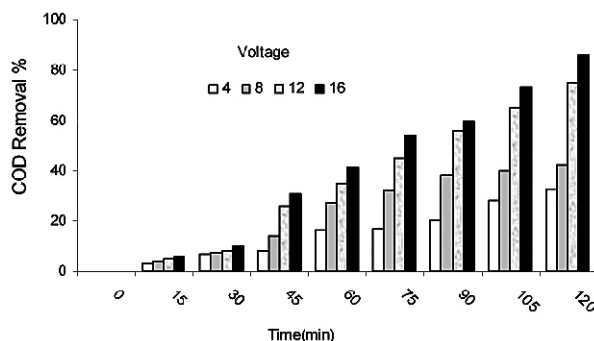

Fig. 5. Effect of voltage (NaCl = 0.5 (g L^{-1}), pH = 4.5, 3,3'-DMB = 10^{-3}(mol L^{-1}), reactor volume = 400 mL)

The Effect of Anode Material

High electrode potential can conveniently be set for oxidation of toxic compounds at the anode of an electrochemical cell. The limit is set based on the stability of anode and reactions such as oxygen evolution and reaction in chloride solutions. Therefore, the anode material must have a high overpotential for the oxygen evolution reaction. But the present work shows that, the Graphite electrode is the best answer for anode material among several electrodes such as Pt, Stainless Steel (304) and Pb/PbO$_2$, Fig. 6. While Graphite has electrode possesses lower overpotential compared with PbO$_2$ electrode,
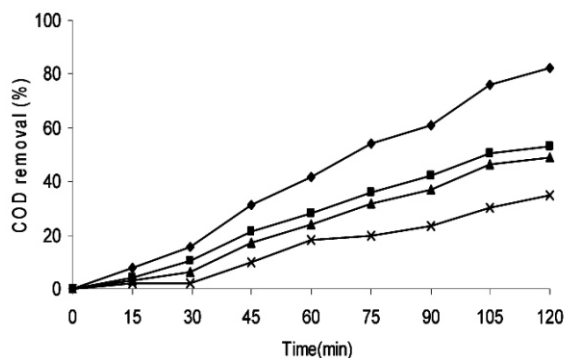

Fig. 6. Effect of different material for anode (NaCl = 0.5(g L^{-1}), pH = 4.5, 3,3'DMB = 10^{-3}(mol L^{-1}), reactor volume = 400 mL)

The amount of percentage removal COD was found to be 75% which revealed that the Decolorization process took place completely. Regarding the presence of other versatile colorant substances in real medium, the decreasing in COD would be less in comparison with synthetic solution.

CONCLUSIONS

Indirect electrochemical Decolorization of 3,3-Dimethoxy Benzidine and real polluted water were investigated using Graphite in the presence of chloride. The effects of various operating parameters such as NaCl concentration and initial pH and applied voltage were studied. The electrochemical oxidation Decolorization kinetics followed first order model for 3,3'-DMB. COD and percentage colour removal for 3,3'-DMB was 75% and 88%. However for similar real polluted water samples the percentage removals were found to be 68% and 75%, respectively at the 120 min electrolysis time. Hence this technique may be applied for treatment of a large volume and industrial scale of textile polluted water and have the ability to destruct organic pollutants completely to carbon dioxide and water.

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