

## Electrochemical Approach for Treatment of Textile Effluents

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**Abstract:** Electrochemical oxygen reduction reaction (ORR) was studied at glassy carbon (GC) electrode using cyclic voltammetric technique in aqueous acidic solution and in aqueous textile effluent containing dye species. The species present in the effluent (i.e., dye) was found to be electrochemically inactive in the potential range from 0 to -0.80 V at which ORR takes place in acidic solution. The characteristic of cyclic voltammetric response of ORR such as peak potential was found to shift towards positive potential along with the increase in the peak current in the presence of the effluent. Textile effluent was observed to undergo follow-up chemical reaction with the reactive oxygen species (ROS) generated *in situ* in the ORR. During bulk electrolysis of O<sub>2</sub> at a GC plate electrode, the effluent became colourless as monitored with visible spectral analysis as well as visual observation. The electrochemical ORR is revealed to be a promising route for treatment of textile.

**Keywords:** Dye degradation, Oxygen reduction reaction, Reactive oxygen species.

### 1. INTRODUCTION

Due to rapid population growth and fast industrial development in last few decades large amount of synthetic dyes have been discharged into water bodies to cause water pollution and substantially damage aquatic environments [1]. Water purification is quite important for the ecosystem [2-4]. Hence, to develop an efficient and cost-effective wastewater treatment technology is a critical need of the present society [5]. Numerous direct and indirect techniques have been widely used for the purification of water including chlorination, ozonisation, adsorption, membrane/ion exchange filtration, coagulation/flocculation, biodegradation, adsorption, electrolysis, photo-/electro-degradation and advanced oxidation processes [6-10]. However, these treatments have several disadvantages such as the production of toxic by-products, transport and storage of chemicals and high energy requirements [10]. Among these methods, the chemical oxidation of dyes in wastewater is one of the most promising techniques. The reactive oxygen species (ROS), e.g., hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> or HO<sub>2</sub><sup>-</sup>), ozone (O<sub>3</sub>) and hydroxyl radical (OH<sup>•</sup>) have been recognized as environmentally benign and cost-effective oxidants [10] for degradation of dyes. ROS can be easily and readily generated by the reaction of UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/Fenton's reagent, TiO<sub>2</sub>-based material, and electrochemical ORR [11-17] and after reaction ROS is converted to safe product such as O<sub>2</sub> or water [11].

Catalytic degradation of methylene blue (MB) by Fenton like system (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>) has been reported to be competent [17]. On the other hand, the electrochemical methods have been reported as simple, smart, portable and environmentally friendly since the electrode itself plays the role of a chemical in the electrochemical redox

reaction. Very recently, we have studied catalytic ORR assisted degradation of MB in acidic solution [10]. In fact, we developed an efficient and cost-effective wastewater treatment process by employing the electrochemical ORR at a glassy carbon (GC) electrode as a novel alternative to the well-known Fenton process for the degradation of MB in aqueous solution, a synthetic wastewater. In this study, the degradation of textile effluent collected from an industry located around Dhaka city was investigated through the catalytic pathway of ORR at a GC electrode. The degradation of industrial sample at a GC plate electrode upon bulk electrolysis of O<sub>2</sub> was monitored by visible spectral analysis. pH and conductivity of the sample were also recorded before and after degradation to judge the water quality as well as the efficiency of the treatment.

### 2. EXPERIMENTAL

Textile effluent that is dark blue in colour with pH of 8.5 was collected from the outlet of a dyeing system operating for a reactive dyeing of cotton and stored in a PET bottle. Prior to use, the bottle was shaken well and an adequate amount of liquid effluent was taken for the analysis and treatment. Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) with a purity of 98% (Merck, Germany) and analar grade potassium chloride (Merck, Germany) were used without further purification. Ultrapure water (specific conductance < 0.1 μS cm<sup>-1</sup>) prepared by using BOECO pure (Model-BOE8082060, Germany) was used in this study.

A conventional one-compartment three electrode system electrochemical cell made of Pyrex glass was used for electrochemical measurements as shown in Fig. 1. A spiral platinum wire and an Ag | AgCl | KCl (sat.) electrodes were used as the counter and reference electrodes, respectively. Prior to each experiment, the solution in the cell was purged with O<sub>2</sub> or N<sub>2</sub> gas for 20 min. A computer-controlled electrochemical system (Model: CHI 1140C, USA) was used for electrochemical measurements. For cyclic voltammetric measurement, the working electrode, GC ( $\phi = 3.0$  mm) was polished with aqueous slurry of alumina fine powder (0.05 μm) (Buehler) on an emery paper and then sonicated in deionized water for 30 min. The electrode was then electrochemically pre-treated in N<sub>2</sub>-saturated 0.05 M H<sub>2</sub>SO<sub>4</sub> solution by repeating the potential scan between the potential range of -0.20 to 1.50 V vs. Ag | AgCl | KCl (sat.) until the cyclic voltammogram (CV) characteristics of a clean electrode could be obtained [18-

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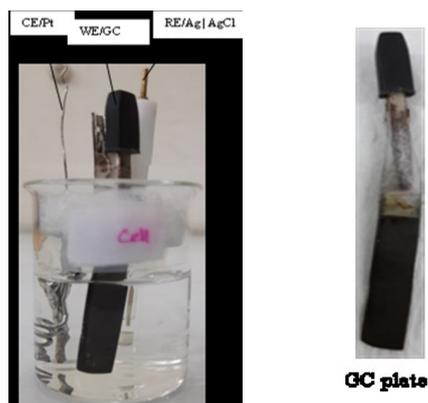


Fig. 1. Schematic diagram of the electrochemical cell used for treatment of effluent.

The treatment of effluent was carried via bulk electrolysis of  $O_2$  in effluent solution in a special type of cell comprised of a GC plate ( $13\text{ mm} \times 9\text{ mm} \times 1\text{ mm}$ ) as a working electrode, platinum mesh as a counter electrode and  $Ag | AgCl | KCl (\text{sat.})$  as a reference electrode (Fig 1). The electrolysis was carried at a constant potential of  $-0.70\text{ V}$  in  $O_2$ -saturated effluent solution. During electrolysis,  $O_2$  gas was continuously bubbled into the solution. Visible spectra were monitored using a spectrophotometer (Model: UVD-3500, LABOMED, USA). pH and conductivity measurements of the textile effluent before and after degradation were recorded using an ion meter (Model: 3345, Jenway) and conductivity meter (Model: 4510, Jenway).

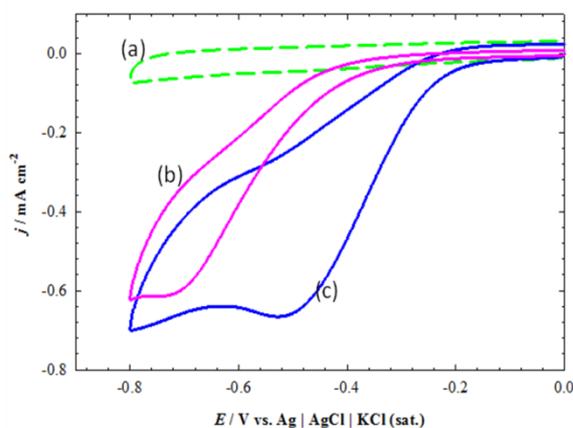


Fig. 2. CVs measured at a GC electrode in (a,)  $N_2$ - and (b,c)  $O_2$ -saturated  $0.05\text{ M H}_2\text{SO}_4$  solution (b) and (a,c) textile effluent. The potential scan rate was  $0.10\text{ V s}^{-1}$ .

### 3. RESULTS AND DISCUSSION

Fig. 2 represents typical CVs measured at a GC electrode in  $N_2$ - and  $O_2$ -saturated solutions in absence and in presence of effluent. The CV obtained in  $N_2$ -saturated solutions shows no peak for the reduction at a potential range from 0 to  $-0.80\text{ V}$  (Fig. 2a). On the other hand, a well-defined cathodic peak was observed at ca.  $-0.52\text{ V}$  vs.  $Ag | AgCl | KCl (\text{sat.})$  in a  $O_2$ -saturated solution (Fig. 2c). A well-known cathodic peak was observed at ca.  $-0.72\text{ V}$  vs.  $Ag | AgCl | KCl (\text{sat.})$  in  $O_2$ -saturated  $H_2SO_4$  solution at a GC electrode shown in Fig. 2b. Measurements were also carried out by varying potential scan rate (data not shown). Several significant changes

were observed in the CV measured for ORR at a GC electrode in the presence of industrial sample (Fig. 2c): shifting of peak towards positive potential by ca.  $0.20\text{ V}$ , increase of peak current, broadening of the shape of peak and increasing the slope for the ascending current portion of the CV as compared to those observed without effluent in solution. Similar results have previously been observed with MB, a model cationic dye [10,11].

Two-electron mechanism of ORR occurring at a GC electrode generating  $H_2O_2$  as an ultimate product in acidic solution has been reported [9]. Thus, the chemical reaction between ROS and dye species in the textile effluent is considered to be coupled with ORR occurring at a GC electrode by EC mechanism [20], resulting in shifting of peak of ORR towards more positive potential [10,11].

As discussed above, the ROS generated during ORR readily reacts with organic dyes. Upon bulk electrolysis of  $O_2$ , the ORR in effluent solution containing dyes was carried out at a GC plate electrode by applying a constant potential of  $-0.70\text{ V}$  and the visible spectra of the sample were recorded (Fig. 3). Fig. 3(a) shows the visible spectrum of the sample giving a broad peak at ca.  $620\text{ nm}$ . On the other hand, after 8 min bulk electrolysis of  $O_2$ , there is no such peak was observed in Fig. 3(b), indicating that the chromophore portion of the dyes in the effluent is broken down [2]. Images also support the spectral results.

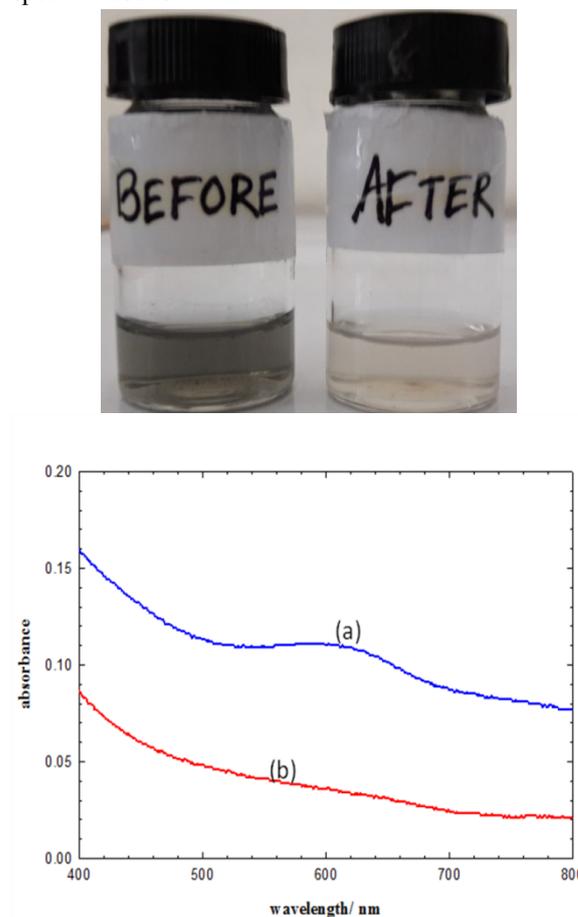
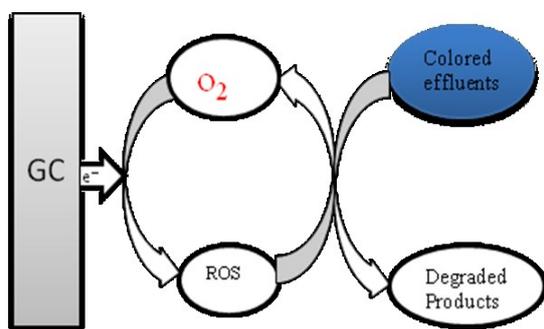


Fig. 3. Lower panel: Typical visible spectrum of industrial samples in aqueous solutions before (a), and after (b) degradation. Upper panel: the photographs of the solution after and before degradation.

**Table 1:** Quality of textile effluent before and after treatment via electrochemical ORR.

Sample	Appearance	pH	Conductivity ( $\mu\text{S cm}^{-1}$ )
Untreated effluent	Dark blue	8.5	28.2
Treated effluent	Colourless	1.9	57.5

To justify the nature of the solution after degradation through electrochemical ORR, the pH and conductivity were recorded as tabulated in Table 1. pH value of the solution after treatment was found to decrease due to the oxidation of  $\text{H}_2\text{O}$  into  $\text{O}_2$  and  $\text{H}^+$  ions that simultaneously results in increase of conductivity of the solution. Hence the overall reaction mechanism for dye degradation could be shown in Fig. 4.



**Fig.4.** Schematic representation of degradation of effluent via follow-up chemical reaction with ROS generated at GC electrode by electrochemical reduction of  $\text{O}_2$ .

In Fig. 4, a schematic presentation of catalytic degradation of effluent by the *in situ* generated ROS is shown. Generation of ROS from  $\text{O}_2$  that is available in the air (i.e., free of cost) occurs by the consumption of electron from the GC electrode (i.e., electricity). Further study to establish the mechanism and to identify the products is in progress.

#### 4. CONCLUSIONS

Textile effluent containing dyes can be treated by applying electrochemical ORR that consumes  $\text{O}_2$  (air) and electricity.

#### ACKNOWLEDGMENT

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