



# Catalytic Degradation of an Organic Dye through Electroreduction of Dioxygen in Aqueous Solution



Tamanna Ishrat Farhana, M. Yousuf Ali Mollah, Md. Abu Bin Hasan Susan, Md. Mominul Islam

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

## ARTICLE INFO

### Article history:

Received 10 May 2014

Received in revised form 17 June 2014

Accepted 20 June 2014

Available online 11 July 2014

### Keywords:

Oxygen reduction

Reactive oxygen species

Methylene blue

Dye degradation

## ABSTRACT

Oxygen reduction reaction (ORR) was carried out electrochemically at glassy carbon (GC), platinum, copper and nickel electrodes in acidic solution using cyclic voltammetry in absence and in presence of an organic dye, methylene blue (MB). Four- and two-electron ORR occurred at platinum and GC electrodes, respectively, whereas no well-defined ORR took place at nickel and copper electrodes. Although MB was found to be electrochemically inactive, the electrochemical behavior, especially, change in the peak potential and current in the cyclic voltammetric results in the presence of MB at platinum and GC electrodes varied interestingly. MB underwent following chemical reaction with the reactive oxygen species (ROS) generated *in situ* during ORR as supported by steady-state hydrodynamic voltammetric measurements. Ultraviolet-visible spectral behavior of MB changed when it was allowed to react with ROS generated by bulk electrolysis of O<sub>2</sub> at a GC plate electrode. It was revealed that electrochemical ORR is a promising route for degradation of an organic dye in aqueous solution.

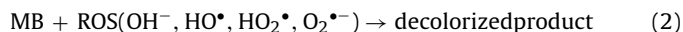
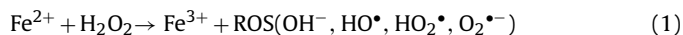
© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Organic dyes, chromophores with high visibility even at very low concentrations, are widely used in textile, rubber, plastics, printing, and food industries as coloring agents. However, their widespread uses are often limited since they can be harmful to human beings and toxic to plants and microorganisms. The removal of textile dyes from effluents has therefore been one of the challenging tasks in the realm of industrialization [1]. In dyeing processes, 10–15% of dyestuffs are lost and become part of wastewater to produce eco-toxic hazards and introduction of potential dangers to bioaccumulation necessitating inevitable treatments. The treatment of wastewater usually employs many direct and indirect methods, for instances, adsorption, membrane/ion exchange filtration, coagulation/flocculation, biodegradation, adsorption, electrolysis, photo-/electro-degradation and oxidation processes.

The chemical oxidation of dyes in wastewater has received considerable attentions [2–11]. Uses of reactive oxygen (O<sub>2</sub>) species (ROS) such as, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> or HO<sub>2</sub><sup>-</sup>), ozone (O<sub>3</sub>), hydroxyl radical (OH•), and superoxide (O<sub>2</sub><sup>•-</sup>) as oxidants for degradation of dyes have been recognized as environmentally benign and cost-effective processes. ROS can be easily and readily

generated from O<sub>2</sub> and after reaction may again be converted to O<sub>2</sub> or water. However, OH• species that can be produced using ultraviolet (UV)/H<sub>2</sub>O<sub>2</sub>, UV/ozone, UV/Fenton's reagent, TiO<sub>2</sub>-based material, and electrochemical O<sub>2</sub> reduction reaction (ORR) [2–6], is known to be very reactive towards organic compounds. Fenton's reagent (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>) has been reported to be competent for degradation of methylene blue (MB) [8]. The color of MB could also be removed by H<sub>2</sub>O<sub>2</sub> catalyzed by some supported alumina [9]. Katafias *et al.* [10] also studied the kinetics and mechanism of degradation of MB by alkaline H<sub>2</sub>O<sub>2</sub>. The degradation of MB by Fenton's reagent follows the mechanism [11–17] (Eqs. (1) and (2)):



The ORR is one of the most widely investigated reactions due to its practical applications in biological, industrial and environmental areas, and in clean energy generation systems such as fuel cells and metal-air batteries [18–25]. This reaction has extensively been studied at different bare and modified electrodes in aqueous, non-aqueous, molten salt, and ionic liquid media [26–28]. In fact, the mechanism of ORR depends on a number of factors including electrode material, type of media, and solution pH [29–32]. In acidic solution, ORR is a multi-electron transfer reaction that may proceed following direct or indirect routes. Four-electron mechanism of ORR usually occurs at platinum [32–37], palladium [38],

E-mail addresses: [mominul@du.ac.bd](mailto:mominul@du.ac.bd), [mmislam01@yahoo.com](mailto:mmislam01@yahoo.com) (Md.M. Islam).

and ruthenium [39] electrodes to produce a neutral product, water. The peroxide formation mechanism at glassy carbon (GC), gold and graphite electrodes involves a two-electron reduction process to generate a number of ROS including  $O_2^{2-}$ ,  $HO_2^-$ ,  $OH^\bullet$ , and  $HO_2^-$  [40–44].

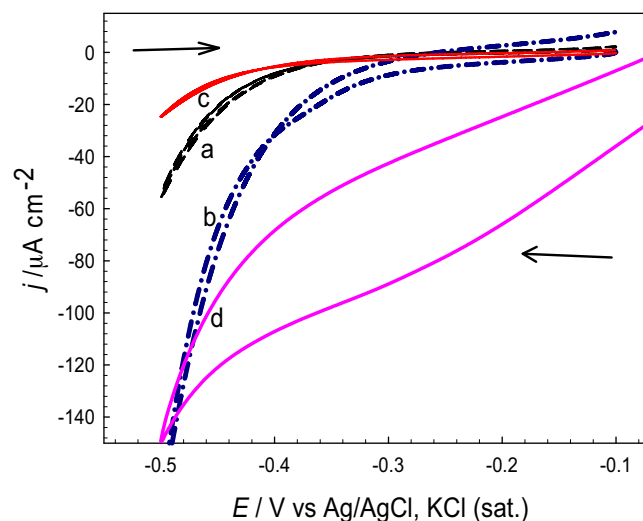
The electrochemical methods have been recognized as simple, smart, portable and environmentally friendly since the electrode itself plays the role of a chemical in the electrochemical redox reaction. This study, therefore, aims at employing the electrochemical ORR as a novel alternative to the well-known Fenton process for the degradation of organic compounds. With a view to exploring a suitable electrode material capable of assisting the catalytic degradation of MB, we studied ORR in presence and in absence of MB in aqueous acidic solutions using cyclic voltammetric technique at copper, nickel, GC and platinum electrodes. Steady-state voltammograms for ORR were also measured using rotating ring disk electrode (RRDE). The degradation of MB upon bulk electrolysis of  $O_2$  at a GC plate electrode was monitored by UV-visible spectral analysis. The role of *in situ* generated towards the degradation of MB was clarified from the investigation of chemical reaction of  $H_2O_2$  with MB.

## 2. Experimental

Analytical grade sulphuric acid ( $H_2SO_4$ ) with a purity of 99% (Merck, Germany), MB (Sigma, USA) and  $H_2O_2$  (Merck, Germany) were used without any further purification. Ultrapure water (specific conductance  $<0.1 \mu S cm^{-1}$ ) prepared by using BOECO pure (Model-BOE8082060, Germany) was used in this study.

A conventional two-compartment cell made of Pyrex glass was used for electrochemical measurements. A coiled platinum wire and an Ag | AgCl | KCl (sat.) electrodes were used as the counter and reference electrodes, respectively. They were placed in a two-compartment cell connected by a salt bridge. Prior to each experiment, the solution in the cell was purged with  $O_2$  or  $N_2$  gas for 20 min. A computer-controlled electrochemical system (Model: 600D, CH Instruments, USA) was employed for electrochemical measurements on static electrodes. The static working electrodes were GC ( $\phi = 2.0$  mm), platinum ( $\phi = 1.6$  mm), nickel ( $\phi = 3.0$  mm) and copper ( $\phi = 2.5$  mm). Steady-state voltammograms were obtained at a rotating platinum disk ( $\phi = 4.0$  mm)-platinum ring ( $\phi = 1.0$  mm) and GC disk ( $\phi = 4.0$  mm)-platinum ring ( $\phi = 1.0$  mm) electrode using a rotator system (Model: RRDE-3A, ALS, Japan) coupled with a bi-potentiostat (Model: 760 E, CH Instruments, USA). The electrodes were polished with aqueous slurry of alumina fine powder ( $0.05 \mu m$ ) (Buehler) on an emery paper and then sonicated in deionized water for 30 min. Platinum and GC electrodes were then electrochemically pretreated in  $N_2$ -saturated  $0.05$  M  $H_2SO_4$  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. All the measurements were performed at room temperature.

UV-visible spectra were recorded using a spectrometer (Model: UVD 3500, Labomed, USA). The electrolysis was carried out in a special type of cell comprised of a GC plate ( $2.0$  mm  $\times$   $3.0$  mm  $\times$   $0.5$  mm) as a working electrode, platinum mesh as a counter electrode and Ag | AgCl | KCl (sat.) as a reference electrode. The electrolysis was carried at a constant potential of  $-0.50$  V in  $O_2$ -saturated  $0.05$  M  $H_2SO_4$  solution containing  $0.01$  mM MB. During electrolysis,  $O_2$  gas was continuously bubbled into the solution. The extent of reaction was monitored by measuring absorbance of MB with time of electrolysis. The chemical reaction of MB with  $H_2O_2$  was studied typically by mixing  $5.0$  mL of  $0.01$  mM MB with  $5.0$  mL of  $10.0$  M  $H_2O_2$  in a beaker.



**Fig. 1.** CVs at a nickel electrode in (a, c)  $N_2$ - and (b, d)  $O_2$ -saturated  $0.05$  M  $H_2SO_4$  solutions in absence (a, b) and in presence (c, d) of  $0.01$  mM MB. The potential scan rate was  $0.10$   $V s^{-1}$ .

## 3. Results and discussion

### 3.1. Cyclic voltammetric study of ORR

**Fig. 1** shows the CVs measured at a nickel electrode in  $N_2$ - and  $O_2$ -saturated  $H_2SO_4$  solutions in absence and in presence of MB. The CV measured in a  $N_2$ -saturated solution shows only a satellite peak at a potential of ca.  $-0.40$  V vs. Ag | AgCl | KCl (sat.). This is due to hydrogen evolution reaction (HER) [45,46]. The CV measured in a  $O_2$ -saturated solution also shows a shoulder at a slightly more positive potential, i.e., ca.  $-0.30$  V. This may be attributed to either HER that catalytically commences at a more positive potential in the presence of  $O_2$  than that observed in the presence of  $N_2$  or for ORR that merges with the HER. On the other hand, the CV in a  $N_2$ -saturated MB solution exhibits a shoulder starting at a slightly more negative potential than that observed in absence of MB (**Fig. 1a**), indicating that MB is not electroactive at the potential range studied and limits the HER, whereas a broad cathodic peak was observed in the presence of  $O_2$ . Thus, it may be presumed that the presence of MB induces the electrochemical reaction of  $O_2$  or *vice versa* at a nickel electrode (further study is in progress).

**Fig. 2** illustrates the typical CVs measured in  $N_2$ - and  $O_2$ -saturated  $H_2SO_4$  solutions at a copper electrode. The CV measured in a  $N_2$ -saturated solution shows positive (anodic) current at the starting potential of  $0.10$  V that follows a broad cathodic peak at ca.  $-0.04$  V vs. Ag | AgCl | KCl (sat.) and a shoulder at a potential more negative than  $-0.50$  V. In the reverse scan, an anodic shoulder at potential more positive than  $0.00$  V vs. Ag | AgCl | KCl (sat.) was observed. The positive current in both cathodic and anodic scans is due to the dissolution of metallic copper to Cu(II) and hence the cathodic peak at  $-0.04$  V vs. Ag | AgCl | KCl (sat.) is ascribed to the reduction of Cu(II) [47] formed due to electrochemical dissolution of copper electrode used. The satellite peak at the cathodic site may be attributed to the HER [46]. Interestingly, the dissolution-deposition phenomenon of copper was found to decrease in presence of  $O_2$  (**Fig. 2b**) and completely diminished in presence of MB (**Fig. 2c**). This indicates that MB could inhibit dissolution of copper electrode via its adsorption that may form passive layer on the copper electrode surface (further work to explore MB as a corrosion inhibitor for copper is in progress) and the presence of  $O_2$  inhibited the dissolution process of copper via the formation of  $O_2$  layer on the surface formed by the adsorption of  $O_2$  on the

Download English Version:

<https://daneshyari.com/en/article/185353>

Download Persian Version:

<https://daneshyari.com/article/185353>

[Daneshyari.com](https://daneshyari.com)