

ELECTROCHEMICAL TREATMENT OF WASTEWATER CONTAINING ORGANIC DYES

Md. Mominul Islam*, Md. Abu Bin Hasan Susan, and M. Yousuf Ali Mollah

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

E-mail address: mominul@du.ac.bd

Abstract: Electrochemical oxygen reduction reaction (ORR) was carried out at glassy carbon (GC) and platinum electrodes in acidic solutions in absence and presence of methylene blue (MB), a cationic dye, using cyclic voltammetry. Although MB was found to be electrochemically inactive, the electrochemical behaviour, especially, change in the peak potential and current in the cyclic voltammetric results in the presence of MB. MB was observed to undergo following chemical reaction with the reactive oxygen species (ROS) generated *in situ* during ORR. UV-visible spectral behaviour of MB changed when it was allowed to react with ROS generated by bulk electrolysis of O₂ at a GC plate electrode. The electrochemical ORR is revealed to be a promising route for degradation of organic dyes in aqueous solution.

Key Words: Electrochemical reduction of oxygen, Reactive oxygen species, Degradation of dye

1. INTRODUCTION

Modern civilization relies to a significant extent on textile, paper, plastics, leather, cosmetics and dyeing industries. However, effluents discharged from these industries severely contaminate the ecosystem with toxic organic dyes, suspended solids and heavy metal ions. As a result, the economic growth and living conditions of the people residing in the vicinity of these industries have been adversely affected. 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, e.g., adsorption, membrane/ion exchange filtration, coagulation/ flocculation, biodegradation, adsorption, electrolysis, photo-/electrodegradation and oxidation processes. Uses of reactive oxygen species (ROS) such as, hydrogen peroxide (H₂O₂ or HO₂⁻), ozone (O₃), and hydroxyl radical (OH[•]) as oxidants for degradation of dyes have been recognized as environmentally benign and cost-effective processes. ROS can be easily and readily generated from O₂ and after reaction may again be converted to O₂ or water [2],[3]. However, these species that can be produced using UV/H₂O₂, UV/O₃, UV/Fenton's reagent, TiO₂-based material, and electrochemical ORR (Fig 1) [4]–[8], are reported to be highly reactive towards organic compounds. Fenton agent (H₂O₂ + Fe²⁺) has been reported to be competent for degradation of methylene blue (MB) [9]–[16].

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 aims at employing the electrochemical ORR as a novel alternative to the well-known Fenton process for the degradation of dyes. With a view to exploring a suitable electrode material capable of assisting the catalytic degradation of MB, we studied ORR in absence and in presence of MB in acidic aqueous solutions using cyclic voltammetric technique at

GC and platinum electrodes. The degradation of MB upon bulk electrolysis of O₂ at a GC plate electrode was monitored by UV-visible spectral analysis. The role of *in situ* generated ORR towards the degradation of MB was clarified from the investigation of chemical reaction of H₂O₂ with MB.

2. EXPERIMENTAL

Sulphuric acid (H₂SO₄) with a purity of 99% (Merck, Germany), MB (Sigma, USA) and H₂O₂ (Merck, Germany) were used without any further purification. Ultrapure water (specific conductance < 0.1 μS cm⁻¹) was used in this study.

A conventional two-compartment cell made of Pyrex glass was used for electrochemical measurements. A spiral platinum wire and an Ag | AgCl | KCl (sat.) electrodes were used as the counter and reference electrodes, respectively. Two compartments of the cell were connected by a salt bridge. Prior to each experiment, the solution in the cell was purged with O₂ or N₂ gas for 20 min. A computer-controlled electrochemical system (Model: 600D, CH Instruments, USA) was employed for electrochemical measurements. The working electrodes, GC ($\phi = 2.0$ mm) and platinum ($\phi = 1.6$ mm), were 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. Platinum and GC electrodes were then electrochemically pre-treated in N₂-saturated 0.05 M H₂SO₄ 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 [2],[17],[18]. All the measurements were performed at room temperature.

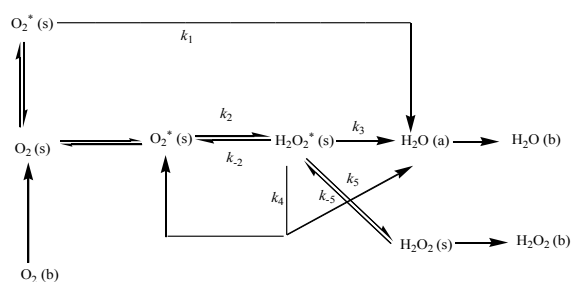


Fig. 1 ORR mechanism in acidic solution [2],[3],[17],[18]. (b) and (s) refer to bulk solution species and adsorbed state or species on electrode surface, respectively, and the superscripts (*) refers to the process in the vicinity of the electrode. The k values are the rate constants of the relevant steps.

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 × 3.0 mm × 0.5 mm) as a working electrode, platinum mesh as a counter electrode and Ag | AgCl | KCl (sat.) as a reference electrode (Fig 2). The electrolysis was carried at a constant potential of -0.50 V in O₂-saturated 0.05 M H₂SO₄ solution containing 0.01 mM MB. During electrolysis, O₂ 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 also 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.

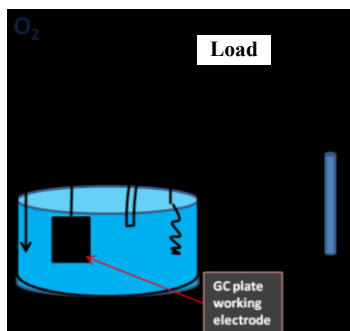


Fig. 2 Schematic diagram of the electrochemical cell used for catalytic degradation of dye.

3. RESULTS AND DISCUSSION

Fig. 3 shows representative CVs measured at a GC electrode in O_2 - and N_2 -saturated H_2SO_4 solutions in absence and in presence of MB. The CV measured in N_2 -saturated solutions shows no peak for the reduction of MB except for the shoulder for the hydrogen evolution reaction (HER) at a potential more negative than -0.80 V (Figs. 3a and 3b). The CV recorded in a O_2 -saturated solution (Fig. 3d) shows a cathodic peak at ca. -0.54 V vs. $\text{Ag} | \text{AgCl} | \text{KCl}$ (sat.) followed by a shoulder at potential more negative than -0.70 V for the HER. Measurements were also carried out by varying potential scan rate (data not shown). Several significant changes were found in the CV measured for ORR at a GC electrode in presence of MB (Fig. 3c): shifting of peak towards positive potential by ca. 0.06 V, increase of peak current by 74%, broadening of the shape of peak and increasing the slope for the ascending current portion of the CV as compared to those observed without MB in solution.

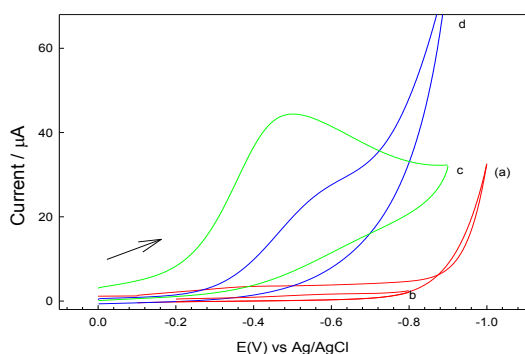


Fig. 3. CVs measured at a GC electrode in (a, b) N_2 - and (c, d) O_2 -saturated 0.05M H_2SO_4 solutions in absence (b, c) and in presence (b, c) of 0.01 mM MB. The potential scan rate was 0.10 V s^{-1} .

To clarify the mechanism of such observations, similar measurements were also carried out at a platinum electrode (data are not shown). The CV recorded at platinum electrode does not show any significant peak in the potential range of 0.80 to -0.10 V in the presence of MB in a N_2 -saturated solution, indicating that MB is also electrochemically inactive in the potential range studied. A well-defined cathodic peak was found at ca. 0.41 V in an O_2 -saturated solution to infer that the observed peak corresponds to ORR [2],[3],[17],[18]. In general, the ORR at a platinum electrode has been considered to be a four-electron

transfer process that generates water (Fig. 1) as a stable product [17],[18]. However, this peak shifted to a more negative potential with a 45% increase of peak current when ORR was carried out in the presence of MB. The shifting of the peak corresponding to ORR indicates that MB hinders the ORR via its adsorption on the platinum surface. On the other hand, the observed increase in peak current might have been considered to be due to the following chemical reaction of MB at the interface with the electrogenerated intermediates that may be produced during ORR at the platinum surface.

The current density of the peak observed at GC electrode measured without MB is about two times (1.8) lower than that at a platinum electrode which is suggestive of a four-electron ORR. The number of electrons involved in the ORR at a GC electrode is one-half of that involved at a platinum electrode. The ORR at a GC electrode is thus considered for a two-electron ORR that generates H_2O_2 as an ultimate product in acidic solution (Fig. 1). Thus, the chemical reaction between ROS and MB is considered to be coupled with ORR occurring at GC electrode by EC' mechanism [19], resulting in shifting of peak of ORR towards more positive potential.

As discussed above, the ROS generated during ORR readily reacts with MB. Decolorization of MB was, therefore, studied by ROS generated electrochemically as well as by commercially available H_2O_2 . In former case, a GC electrode substrate at which ROS is known to be produced via two-electron ORR was chosen as the cathode. Upon bulk electrolysis of O_2 , the ORR in solution containing MB was carried out at a GC plate electrode by applying a constant potential of -0.50 V (Fig 2). UV-visible spectra of MB were measured at different time intervals. The UV-visible spectra show that the color intensity of MB decreased as time of electrolysis of O_2 was increased (Fig 4). However, a complete decolorization of MB solution could be achieved within 14 min. On the other hand, the UV-visible spectra measured in the course of decolorization with commercial H_2O_2 demonstrate a slow change in color of MB (data not shown). In both cases, the characteristic peaks of MB at the visible region diminished, while a new peak at ultra-violet region (< 400 nm) was found to develop with the elapse of time due possibly to the formation of conjugated aromatic rings consisting of sulfur, nitrogen atom or enone system.

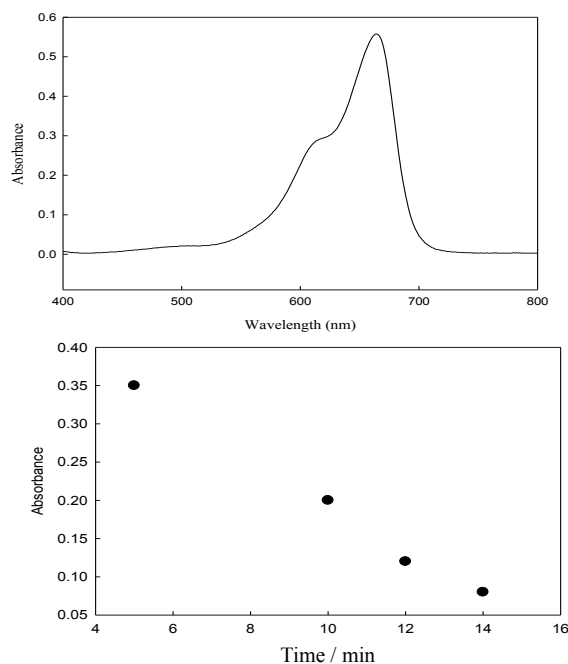


Fig. 4. Upper panel: Typical visible spectrum of 1×10^{-5} M MB in aqueous solution. Lower panel: Measurement of absorbance of MB with time during the electrolysis of O_2 as shown in Fig 2. The absorbance was measured at λ_{max} of 664 nm.

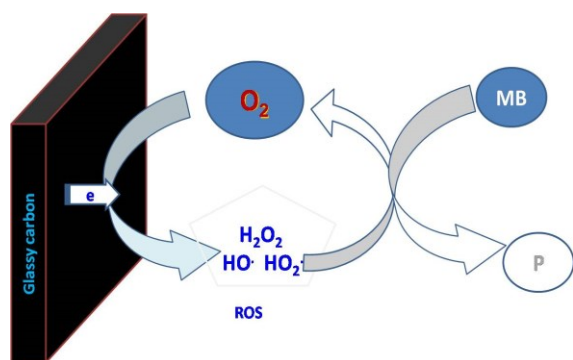


Fig. 5 Schematic representation of degradation of MB via following chemical reaction with ROS generated at GC electrode by electrochemical reduction of O₂.

In Fig. 5, a schematic presentation of catalytic degradation of MB by the *in situ* generated ROS is shown. Generation of ROS from O₂ that is available in the air (i.e., free of cost) occurs by the consumption of electron from the GC electrode (i.e., electricity). In an acidic solution, leuco form of MB is produced through the attachment of H⁺ to the central N atom and it has been reported that both forms of MB exist in equal amount in 0.5 M H₂SO₄ acid solution [20]. The degradation of MB with H₂O₂ has been considered to involve several steps to form different reaction intermediates [21],[22]. However, both forms of MB react with H₂O₂ forming aromatic compounds containing nitrogen and sulfur hetero-atoms. The pseudo first order rate constant for the reaction of MB with H₂O₂ has been reported to be about 10⁻³ s⁻¹ in alkaline solution [23]. Further study to identify the products is in progress.

4. CONCLUSIONS

ORR depends strongly on the electrode material. In acidic solution, ORR at a platinum electrode involves four-electron transfer to produce water, while at a GC electrode the reaction occurs through a two electron-transfer process to generate a number of ROS (OH⁻, HO[·], HO₂[·], O₂^{-·}). The *in situ* electrochemically generated ROS was found to be very reactive towards MB to cause degradation of the dye to yield colorless products. This opens up a novel catalytic route for degradation of MB by using a cost-effective and eco-friendly method. The catalytic cycle of MB degradation involves only molecular O₂ (Fig. 5), which is abundant in the atmosphere in contrast to other common techniques where uses of chemicals or radiations are more often required. The novel approach thus offers a brighter prospect and superiority for degradation of dyes.

ACKNOWLEDGMENT

The financial support for this work from TWAS (the academy of sciences for the developing world), Italy is greatly appreciated.

REFERENCES

[1] A. Gottlieb, C. Shaw, A. Smith, A. Wheatley, and S. Forsythe, "The toxicity of textile reactive azo dyes after hydrolysis and decolourisation", *J. Biotechnol.*, vol. 101, pp. 49–56, 2003.

[2] T. I. Farhana, "Degradation of an organic dye by electrogenerated reactive oxygen species in aqueous solution" M. S. thesis, University of Dhaka, Dhaka, Bangladesh, Mar. 2014.

[3] T. I. Farhana, M. Y. A. Mollah, M. A. B. H. Susan, and M. M. Islam, "Catalytic degradation of an organic dye through electroreduction of dioxygen in aqueous solution", *Electrochim. Acta*, DOI: 10.1016/j.electacta.2014.06.145, 2014.

[4] N. Daneshvar, D. Salari, and A. R. Khataee, "Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂", *J. Photochem. Photobiol. A*, vol.162, pp. 317–322, 2004.

[5] D. Wiping, X. Yiming, and W. Yansong, "Photoinduced degradation of orange II on different iron (Hydr)oxides in aqueous suspension: Rate enhancement on addition of hydrogen peroxide, silver nitrate, and sodium fluoride", *Langmuir*, vol. 24, pp 175–181, 2008.

[6] J. Li, W. Ma, C. Chen, J. Zhao, H. Zhu, and X. Gao, "Photodegradation of dye pollutants on one-dimensional TiO₂ nanoparticles under UV and visible irradiation", *J. Mol. Catal. A*, vol. 261, pp.131–138, 2007.

[7] T. Matsunaga, M. Inagaki, "Carbon-coated anatase for oxidation of methylene blue and NO", *Appl. Catal. B*, vol. 64, pp. 9–12, 2006.

[8] K. M. Parida, N. Sahu, N. R. Biswal, B. Naik, and A. C. Pradhan, Preparation, characterization, and photocatalytic activity of sulfate-modified titania for degradation of methyl orange under visible light, *J. Colloid Interface Sci.*, vol. 318, pp. 231–237, 2008.

[9] S. R. Thakare, "Catalytic degradation of methylene blue by Fenton like system: Model to the environmental reaction", *J. Environ. Sci.*, vol. 16, pp. 285–287, 2004.

[10] A. A. Burbur, D. D. Dionysiou, and T. M. Suidan, "Effect of oxidant-to-substrate ratios on the degradation of MTBE with Fenton reagent", *Water Research*, vol. 42, pp. 3225–3239, 2008.

[11] C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.*, vol. 8, pp. 125–131, 1975.

[12] J. D. Laet, and H. Gallard, "Catalytic decomposition of hydrogen peroxide by Fe (III) in homogeneous aqueous solution: Mechanism and kinetic modeling", *Environ. Sci. Technol.*, vol. 33, pp. 2726–2732, 1999.

[13] F. F. R. Pontes, F. E. J. Moraes, A. Machulek Jr, and J. M. Pinto, "A mechanistic kinetic model for phenol degradation by the Fenton process", *J. Hazard. Mater.*, vol. 176, pp. 402–413, 2010.

[14] R. Chen, and J. J. Pignatello, "Role of quinone intermediates as electron shuttles in Fenton and photo assisted Fenton oxidations of aromatic compounds", *Environ. Sci. Technol.* vol. 31, pp. 2399–2406, 1997.

[15] N. Kang, S. D. Lee, and J. Yoon, "Kinetic modeling of Fenton oxidation of phenol and mono chlorophenols", *Chemosphere*, vol. 47, pp. 915–924, 2002.

[16] J. Sun, S. Sun, M. Fan, H. Guo, L. Qiao, and R. Sun, "A kinetic study on the degradation of *p*-nitroaniline by Fenton oxidation process", *J. Hazard. Mater.*, vol. 148, pp.172–177, 2007.

[17] M. I. Awad, S. M. El-Deab, and T. Ohsaka, "Tailor-designed platinum nanoparticles electrodeposited onto gold electrode: Catalytic activity for oxygen reduction", *J. Electrochem. Soc.*, vol. 154, pp. B810–816, 2007.

[18] J. Perez, M. H. Villullas, and R. E. Gonzalez, "Structure sensitivity of oxygen reduction on platinum single crystal electrodes in acid solutions", *J. Electroanal. Chem*, vol. 435, pp. 179–187, 1997.

[19] A. J. Bard, and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley and Sons, Inc., 2001, 2nd ed.

[20] N. G. Lewis, and J. Bigeleisen, "Methylene blue other indicators in general acids: The acidity function", *J. Am. Chem. Soc.*, vol. 65, pp 1144–1150, 1943.

[21] L. C. A. Oliveira, T. C. Ramalho, E. F. Souza, M. G. D. Alves, Q. L. Oliveira, M. C. Pereira, and J. D. Fabris, "Catalytic properties of goethite prepared in the presence of Nb on oxidation reactions in water: computational experimental studies", *Appl. Catal. B*, vol. 83, pp. 169–176, 2008.

[22] H. W. P. Carvalho, A. P. L. Batista, P. Hammera, and T. C. Ramalhoc, "Photocatalytic degradation of methylene blue by TiO₂-Cu thin films: Theoretical experimental study", *J. Hazard. Mater.*, vol. 184, pp. 273–281, 2010.

[23] A. Katafias, M. Lipiska, and K. Strutyski, "Alkaline hydrogen peroxide as a degradation agent of methylene blue-kinetic and mechanistic studies", *Reac. Kinet. Mech. Catal.*, vol. 101, pp. 251–266, 2010.