

Electrochemical Degradation of Acid Green Dye in Aqueous Wastewater Dyestuff Solutions Using a Lead Oxide Coated Titanium Electrode

N.M. Abu Ghalwa^a and M.S. Abdel-Latif^{b,*}

^a Chemistry Department, Faculty of Science, Al-Azhar University-Gaza, Palestine

^b Chemistry Department, The Islamic University of Gaza, P.O. Box 108, Gaza, Palestine

(Received 12 June 2005, Accepted 25 July 2005)

A modified electrode, which can be used as an anode for electrocatalytic oxidation processes of dyestuff in aqueous solutions, was fabricated by the electrodeposition of a lead oxide layer on a titanium substrate. The modified electrode was used for the electrochemical degradation of an acid green dye. The results of the electrocatalytic oxidation process of the dyestuff solutions were expressed in terms of the remaining dye concentration and chemical oxygen demand (COD) values. The different operating conditions of the treatment process were studied. The optimum operating conditions for the dye and modified electrode were determined, where good results for complete removal of the dye and COD were achieved. The optimum conditions were applied to the treatment of a sulfur black dye in true wastewater solutions.

Keywords: Modified electrode, Electrodeposition, Textile wastewater

INTRODUCTION

The removal of undesirable organic or dyestuff impurities from liquid (usually aqueous) solutions through electrochemical processes is based on the selection of suitable electrodes and potential/current conditions. The wastewater treatment by indirect electrochemical oxidation has also been investigated. It has been reported that when a sodium chloride solution is electrolyzed, Cl₂ is formed at the anode, which disproportionates in the presence of OH⁻ ions generated at the cathode [1-6].



Oliver *et al.* [7] proposed that the oxidation of organic

impurities to CO₂ occurs as a result of heterogeneous electrochemical oxidation reactions on the anodic electrocatalyst surface (modified electrode), which, at elevated current densities, is covered with a mixed film of metallic oxides. Also, at high current densities, oxygen evolution from water is a predominant anodic side-reaction, which creates an oxygen saturated environment at the electrode-solution interface. It is well known that reactive intermediates such as OH· and O· radicals are involved in the electrochemical evolution of oxygen. It is possible that one or both of these radical species, formed on the anodic electrode surface, participate in oxidizing the organic constituents. The decoloration of dye at a Pt anode in an electrolyte solution using electrogenerated oxygen or chlorine species has been investigated. Decoloration is weak in the presence of electrogenerated oxygen species but increases in a KCl electrolyte solution. Decoloration in this solution is accomplished by the electrogenerated hypochlorite ion. Also,

* Corresponding author.

E-mail: mlatif@mail.iugaza.edu

when placed in contact with a Pt anode, cotton fabric dyed with reactive dyes is decolorized significantly after a short-term electrolysis in an electrolyte containing KCl; but the decoloration of dyed fabrics is very weak in an electrolyte that is free from KCl. In addition, a study investigating the use of electrochemical methods for decolorizing azo dyes in an electrolyte solution containing halide ions has shown that the degree of decoloration was affected by molecular structure of azo dyes [8].

If the decomposition potential of the solvent lies higher than that of the targeted impurity, or if a suitable electrocatalyst can be found, then direct electrochemical oxidation of impurities can be used in waste treatment [9-15]. Amadelli *et al.* [16] studied the feasibility of bisphenol-A (BPA) degradation by means of electrochemical oxidation in aqueous solutions using a platinum mesh or titanium supported lead oxide film anodes. Synthetic effluents in concentrations ranging from 20 to 200 ppm and 2.8% NaCl at pH > 10.5 were used. When a lead oxide film electrode was used instead of a platinum mesh, the only effect observed was an increase in the rate of the BPA disappearance, at the same current density.

The performance of highly doped SnO₂ anodes for the oxidative treatment of wastewater containing biologically refractory compounds was compared with PbO₂ and Pt by Stucki *et al.* [17]. The oxidation of a wide range of organic compounds proceeds with an efficiency which is about 5 times higher than that with platinum anodes. The oxidation efficiency was found to be independent of the pH. It can be concluded from the literature that an anode material with a high oxygen overpotential should be used for oxidizing an organic compound in an aqueous solution. Among the materials which meet this criteria are tin dioxide, synthetic diamond, and lead dioxide [18,19].

Traditional methods [20,21] for dealing with textile wastewater effluents involve various combinations of biological, physical and chemical methods. These are becoming troublesome because of the large variability of the composition of the textile wastewaters. The treatment of textile wastewater from a large dyeing and finishing mill by a continuous process of combined chemical coagulation, electrochemical oxidation, and activated sludge treatment has been investigated [22]. The experimental results were assessed

in terms of chemical oxygen demand (COD) and color reduction to determine the overall treatment efficiency of the combined process. Operating variables, such as wastewater flow rate, conductivity, pH, applied current and amount of polyaluminum chloride (PAC), were explored to determine their respective effects on the efficiency of the electrochemical oxidation of the textile wastewater.

The treatment of the textile wastewater, containing a high concentration of Cl⁻ ions, by an electrochemical method using Ti/RuO₂, Ti/Pt, and Ti/Pt/Ir electrodes was investigated [23, 24]. All three anodes proved to be very effective in the direct or indirect oxidation of organics present in wastewater. Textile wastewater from a reactive azo dyeing and finishing process for cellulosic fibers was treated by an electrochemical oxidation method using Ti/Pt as the anode and stainless steel 304 as the cathode [25]. The strong oxidizing potential of the chemicals produced when the wastewater was passed through the electrocatalytic cell resulted in the oxidation of organic pollutants to carbon dioxide and water. Ninety-two percent of the COD was removed after 40 min of electrolysis at 0.89 A cm⁻² in presence of sodium chloride in an acidic medium.

The aim of this work was to develop an electrochemical system for dyestuff wastewater treatment for elimination of acid green and similar organic dyes.

EXPERIMENTAL

Reagents

All chemicals and reagents used in this study were used as received without further purification. NaCl, CaCl₂·2H₂O, and KCl were of analytical grade and purchased from Merck, Germany. HCl (37%), lead nitrate, sodium fluoride, HNO₃, and H₂SO₄ (96%) were purchased from Aldrich, USA. Acid green 25 and sulfur black dyes were from BDH, England. Other reagents were of the laboratory grade. Distilled water was used throughout the work.

Preparation of Modified Electrode

Pretreatment of the titanium sheet (IMI 115) (1.0 cm × 1.4 cm) was carried out following the procedure used in standard methods for the examination of water and wastewater [26]. The titanium sheet was polished on a 320-grit paper strip, using water as a lubricant, followed by siliceous paste

blasting. The sheet was then degreased in 40% NaOH, cleaned in a hot 1:1 mixture of HNO₃ and H₂SO₄ and finally washed with water. The treated surface (1.0 cm × 1.2 cm) was immersed in a 15% boiling aqueous solution of oxalic acid. Coating with active metal oxide was carried out immediately to minimize formation of TiO₂.

The electrodeposition of PbO₂ was performed at constant anodic current of 100 mA from 0.1 M HNO₃ solution containing 0.5 M Pb(NO₃)₂ and 0.04 M NaF. During electrolysis, the potential ranged from 1.5 to 1.8 V and the solution became dark just after the start of electrolysis, due to the formation of PbO₂ that was released from the electrode, at the high electrolysis current used. Electrodeposition was carried out for 30 min, achieving a PbO₂ loading of about 14 mg cm⁻² as a thin film on the titanium electrode.

In order to verify the reproducibility of the electrode preparation, experimental runs were repeated using three different electrodes prepared by the same procedure. Results showed good reproducibility, with the current efficiencies measured on the three electrodes within 5%. Electrodes were also sufficiently stable to allow their use in consecutive runs; the analysis of solutions revealed that no metal dissolution occurred during electrolysis.

Electrolysis

Acid green dye 25, (C.I. 61570), with the molecular formula C₂₈H₂₀N₂Na₂O₈S₂, (F.W. 622.59), was used in this study. The absorption maximum (λ_{max}) of the acid green dye was at 640 nm. The cell was made of transparent Perspex (150 cm³) in the form of a rectangular trough. The anode (modified electrode; 1.0 cm × 1.4 cm) was supported in a vertical position parallel to the stainless cathode. The distance between the cathode and the anode was about 3 cm, and the volume of electrolyte in each experiment was 50 ml. Studies were carried out for the investigation of optimum conditions for the degradation and removal of the acid green dye and COD from its synthetic solutions by the electrocatalytic oxidation process. DC power supply (model GP4303D, LG Precision Co., Ltd., Korea.) was used to provide the required current. The current measurements were carried out using a digital multimeter (Kyoritsu, model 1008, Japan). Absorbance measurements were performed using a double-beam spectrophotometer (model 552S, Perkin-Elmer, GMBH,

Germany).

Analyses

Analytical parameters measured to evaluate the treatment efficiency were color or remaining dye concentration (mg l⁻¹) and COD (mg O₂ l⁻¹), which was measured by a closed reflux titrimetric method [26]. The decrease in the absorbance of the dyestuff solution, as a result of electrocatalytic oxidation process, formed the basis of the colorimetric analytical procedure for the determination of the remaining dye concentration.

RESULTS AND DISCUSSION

Effect of Current Density

The treatment process was carried out at pH 2.47, a temperature of 30 °C, an initial dye load concentration of 100 mg l⁻¹, a NaCl concentration of 2 g l⁻¹ for 10 min. It is clear from Fig. 1 that the removal of the dye and COD were greatly increased with an increase in current density. The remaining dye concentration was negligible and the COD removal was very efficient at current densities of approximately 15 mA cm⁻². For this reason a current density of 15 mA cm⁻² was taken as optimum.

Effect of pH

A current density of 15 mA cm⁻², a temperature of 30 °C, a

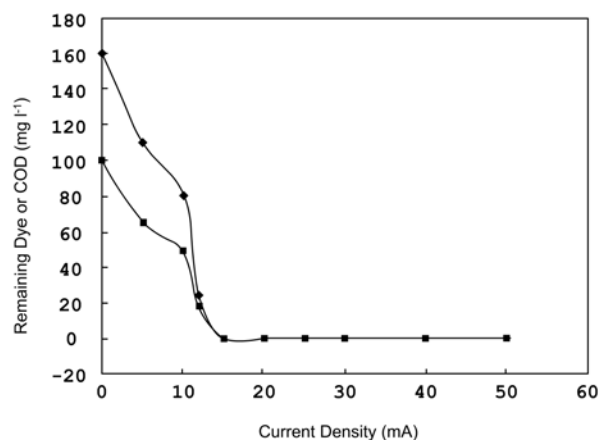


Fig. 1. Effect of current density on the removal of acid green dye and COD. (◆) COD, (■) Dye.

10 min electrolysis time, a NaCl concentration of 2 g l⁻¹, and an initial dye concentration of 100 mg l⁻¹ were used with solutions of pH values ranging from 1.5-10. It is clear from the results shown in Fig. 2 that the maximum removal of dye and COD could be achieved in the pH range of about pH 1.5-4.0. Solutions at pH 2.47 were used in further experiments.

Effect of Electrolysis Time

The above operating conditions were used for this study but with different electrolysis times ranging from 0-15 min. The results indicate that the maximum removal of dye and COD can be obtained at a time exceeding 10 min.

Effect of NaCl Concentration

A current density of 15 mA cm⁻², a temperature of 30 °C, a 10 min electrolysis time, and an initial dye concentration of 100 mg l⁻¹ were used with solutions of NaCl at concentrations from 0-3 g l⁻¹. It is clear from Fig. 3 that the removal efficiency was increased with an increase in NaCl concentration. A NaCl concentration above 2 g l⁻¹ had no additional effect on the removal efficiency.

Effect of Initial Dye Concentration

A current density of 15 mA cm⁻², a temperature of 30 °C, a 10 min electrolysis time, a NaCl concentration of 2 g l⁻¹, and a variable dye load concentration in the range of 10-300 mg l⁻¹ at pH 2.47 were used. The results from Fig. 4 show that the change in initial dye concentration has no effect on the dye

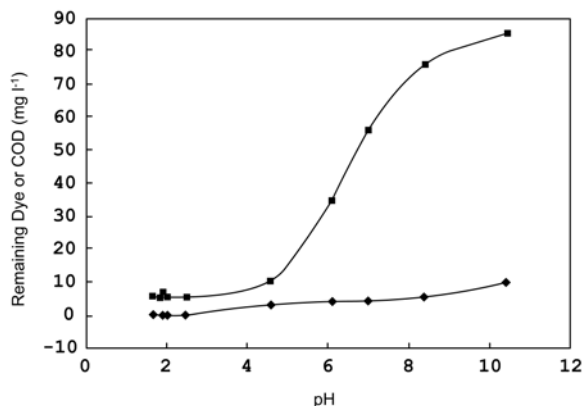


Fig. 2. Effect of pH on the removal of acid green dye and COD. (♦) Dye, (■) COD.

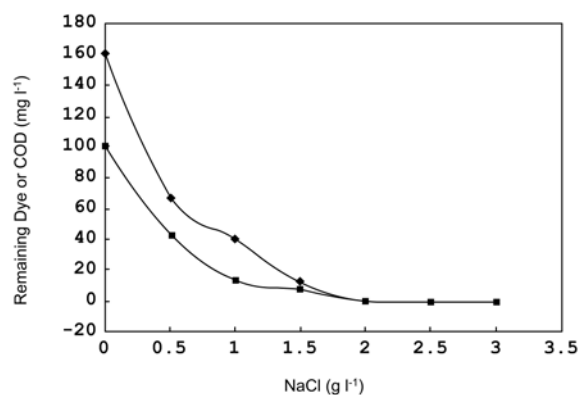


Fig. 3. Effect of sodium chloride concentration on the removal of acid green dye and COD. (♦) COD, (■) Dye.

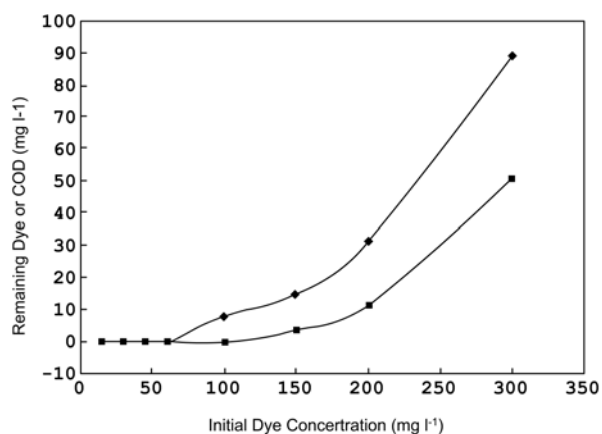


Fig. 4. Effect of initial dye concentration on the removal of acid green dye and COD. (♦) COD, (■) Dye.

removal below 100 mg l⁻¹. When the dye concentration exceeded 100 mg l⁻¹, removal of the dye was incomplete and required a higher current density. In addition, incomplete COD removal was observed above an initial dye concentration of 60 mg l⁻¹.

Effect of Temperature

The above operating conditions were used for this study with the exception of temperature: temperatures from 30-70 °C were used. The results obtained indicate that the change in temperature in the specified range has almost no effect on the

dye and COD removal. For this reason, a temperature of 30 °C is used throughout this work.

It can be assumed that in the present study the removal of dyestuffs from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical oxidation. The treatment by the electrocatalytic oxidation process was carried out at considerably low current densities not exceeding 15 mA cm⁻². At these low current densities, enough Cl₂ is generated in the solution to drive the oxidation process. These species are powerful oxidizing agents capable of the oxidation and removal of the tested dyestuff from its solution. During electrolysis and in the presence of NaCl, the odor of chlorine and hypochlorite could be noticeably smelt.

On the other hand, in absence of chloride containing electrolytes, the efficiency of the dye and COD removal was relatively low. This means that the amount of formed oxygen and/or intermediate species at these low current densities was not enough to enforce a complete removal of dye and COD. This confirms that the electrogenerated Cl₂ may play a main role in the electrocatalytic oxidation process of dyestuff.

Treatment of Sulfur Black Dye

The treatment of sulfur black dye effluents obtained from a dyeing factory was carried out using the prepared PbO₂/Ti modified electrode. The treatment was carried out by first collecting actual waste samples of equal volumes and dye concentration from the wastewater effluents of the sulfur black dyeing bath. The initial dye load concentration of these samples and their correlated COD values were 150 mg l⁻¹ and 1070 mg O₂ l⁻¹, respectively. The dyestuff solution was treated by the electrocatalytic oxidation technique at optimum conditions, as applied to the treatment of the acid green dye.

After the treatment process, the results of the analysis for the remaining dye concentration and COD showed that the solution contained 0 mg l⁻¹ of dye and a COD value of 22 mg O₂ l⁻¹. These results indicate that the suggested modified electrode is also highly efficient in the treatment of effluents containing sulfur black dye.

CONCLUSION

The prepared PbO₂/Ti electrode has a high efficiency in the

removal of acid green and sulfur black dyes from their aqueous solutions, at low current densities, short electrolysis times, and mild temperatures. The optimum operating conditions of the treatment process were a current density of 15 mA cm⁻² a temperature of 30 °C, an initial dye load concentration of 100 mg l⁻¹, and an electrolysis time of 10 min. The electrode was stable during the time it was used for the full study (about 4 months) without a notable decrease in efficiency.

REFERENCES

- [1] P. Schmittinger, Chlorine Ullmann's Encyclopedia, Vol. 6A, VCH, Weinheim, 1986, p. 399.
- [2] M. Beal, in: Modern Chlor-Alkali Technology; Vol. 6, R.W. Curry (Ed.), The Royal Chemical Society, Cambridge, UK, 1995.
- [3] J. Newman, W. Tiedemann, in: H. Gersicher, C.W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 11, Wiley, New York, 1978.
- [4] D.L. Callwell; in: J.O'M. Bockris, B.E. Conway, E. Yeager, R.E. White (Eds.), Comprehensive Treatise of electrochemistry, Vol. 2, Plenum Press, New York, 1981, p.105.
- [5] D.M. Novak, B.V. Tilak, B.E. Conway, in: B.E. Conway, J.O'M. Bockris (Eds.), Modern Aspects of Electrochemistry, Vol. 18, Plenum Press, New York, 1982, p. 195.
- [6] W.N. Brooks, Chem. Brit. 22 (1986) 1095.
- [7] J. Oliver, G. Murphy, H. Ducan, K. Lamine, E.V. Charles, J. Wat. Res. 26 (1992) 443.
- [8] K. Fukastu, S. Kokot, Sen-i-Gakkaishi 53 (1997) 15.
- [9] N. Ibl, H. Vogt; in: J.O'M. Bockris, B.E. Conway, E. Yeager, R.E. White (Eds.), Comprehensive Treatise of Electrochemistry, Vol. 2, Plenum Press, New York, 1981, p.167.
- [10] B.V. Tilak, P.W.T. Lu, J.E. Colman, S. Srinivasan, in: J. O'M. Bockris, B.E. Conway, E. Yeager, R.E. White (Eds.), Comprehensive Treatise of Electrochemistry, Vol. 2, Plenum Press, New York, 1981, p.1.
- [11] F. Gutman, O.J. Murphy, in: R.E. White, J.O'M. Bockris, B.E. Conway (Eds.), Modern Aspects of

- Electrochemistry; Vol. 15, Plenum Press, New York, 1981, p. 1.
- [12] J.A. McIntyre, *Interface* 4 (1995) 29.
- [13] D.E. Kyriacous, D.A. Jannakoudis, *Electrocatalysis for Organic Synthesis*, Wiley, New York, 1986.
- [14] A.J. Fry, W.E. Britton (Eds.), *Topics in Organic Electrochemistry*, Plenum Press, New York, 1986.
- [15] M. Baizer, H. Lund (Eds.), *Organic Electrochemistry*, Dekker, New York, 1985.
- [16] R. Amadelli, A. De Battisti, A. Barbieri, D. Paracchini, *J. Appl. Electrochem.* 24 (1994) 1052.
- [17] S. Stucki, R. Kötzt, *J. Appl. Electrochem.* 21 (1991) 99.
- [18] J.J. Carey, W. Henrietta, C.S. Christ, S.N. Lower, *US. Pat.* 399 (1995) 247.
- [19] S. Trasatti, *J. Electroanal. Chem.* 111 (1980) 125.
- [20] A. Hamza, M.F. Hamoda, Multiprocess Treatment of Textile Wastewater. In *Proc. 35th Purdue Ind. Waste Conf.*, Lafayette, Indiana, 1980.
- [21] G. Mckay, *Am. Dyestuff Reporter* 69 (1980) 38.
- [22] H.L. Sheng, C. Peng, *J. Wat. Res.* 30 (1996) 587.
- [23] K. Muthukumar; S. Sundaram, N. Anantharaman, C. Basha, *J. Chem. Tech. Biotech* 79 (2004) 1135.
- [24] N.N. Rao, K.M. Somasekhar, S.N. Kaul, L. Szpyrkowicz, *J. Chem. Tech. Biotech* 76 (2001) 1124.
- [25] A.G. Vlyssides, C.J. Israilides, *J. Environ. Sci. Health* 33 (1998) 847.
- [26] PHA, AWWA and WEF, *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, A.E. Greenberg, L.S. Clesceri, A.D. Eaton, Washington, 1992.