Scientific paper

Decolorization of Synthetic and Real Wastewater by Indirect Electrochemical Oxidation Process

J. Basiri Parsa[a,*], Mahmood Abbasi[b]

[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 65178, Iran.

[b] Colorant Manufacturing and Environmental Science Department, Institute for Colorants, Paints and Coatings,Tehran, Iran.

* Corresponding author: parssa@basu.ac.ir, Tel. +98 811 8282808, Fax. =98 811 8257407

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Abstract

In this paper the decolorization and degradation of synthetic and real wastewater by electrochemical oxidation method were investigated. Synthetic wastewater consisting of Mordant Red 3 (MR3) was used as a model compound. Electrochemical degradation processes were performed using Pt 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 wastewater 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 color were 86% and 100% respectively. The removal of COD and color increased by increasing voltage and chloride concentration at low pH.

Keywords: Real wastewater, electrochemical oxidation, decolorization, COD, Mordant Red 3.

1. Introduction

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 waste treatment as well as development of new processes or products which have no or less harmful effects on the environment.[1]

Industrial wastewater are usually treated by conventional methods such as biological oxidation,[3] adsorption,[4–5] ozonation,[6] photochemical oxidation,[7–8] Ultrasonic method[9–10] and electrochemical technology.[11–15,18]

In recent years there has been increasing interest in the use of electrochemical method for the treatment of wastewater. Electrochemical methods have been successfully applied in the purification of several industrial wastewaters such as textile,[16] tannery phenol solution[17] and polyaromatic organic pollutants,[15] Textile dye and finishing process are among the major industrial water user; in many areas, this industry has the wastes most difficult to treat satisfactory. The major problem of textile and finishing wastewater is strong color and high COD.[2] The organic and toxic pollutants present in treated wastewater 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. [13] 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.

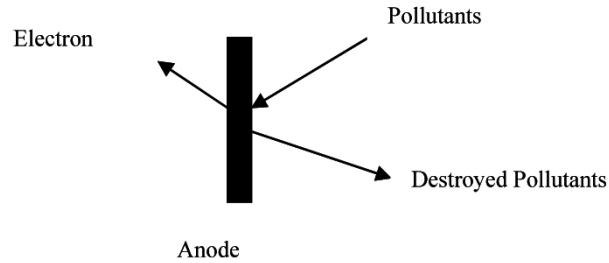


Fig. 1. Direct oxidation mechanism on anode

The indirect electrooxidation 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**.**

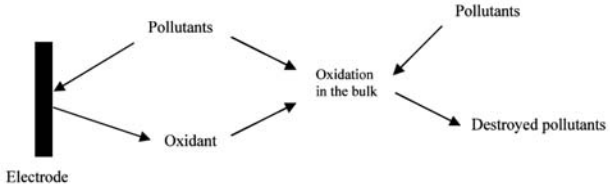


Fig. 2. Indirect oxidation mechanism in bulk solution

In acid solution, oxygen, free chlorine and may be some amounts of ozone and chlorine oxides are the main secondary 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.[13–14.]

In this research, we investigated the decolorization of MR3 and (RW) by indirect electrochemical oxidation. The effect of experimental parameters such as voltage, sodium chloride concentration, initial pH and anode materials on the decolorization of Synthetic and Real Wastewater were all evaluated.

2. Materials and Methods

The electrochemical cell consists of an undivided reactor with two cathodes and one anode. It has a cell volume of 400 ml. These electrodes were parallel. The anode electrode is in the center of cell and is was made of platinum (Pt) plate (20 mm × 20 mm × 1 mm); Stainless Steel 304 plates (20 mm × 80 mm × 1 mm) were used as cathodes (Fig. 3). Stainless Steel 304, graphite, Pb/Pbo_2 and Pt were used as anodes.

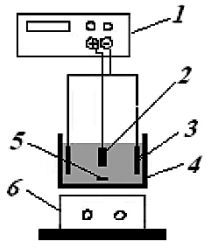


Fig. 3. Experimental laboratory set up. 1: power supply; 2: anode electrode; 3: cathode electrode; 4: electrolytic cell; 5: stirrer bar; 6: magnetic stirrer

Chemical Oxygen Demand (COD) tests were also performed, according to Standard Methods.[19]

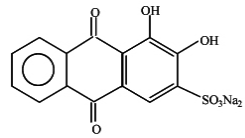
Textile wastewater was prepared from (Rkbatan–Hamedan) Textile dying factory located in the west of Iran. The characteristics of this textile wastewater are showed in Table 1**.**

Table 1. Characterization of Real Wastewater

Character	Value
COD (mg/L)	2950
TOC (mg/L)	800
Conductivity (μS/cm)	3200
pH	6.9

Mordant Red 3 (MR3) was used as a Synthetic wastewater. It was obtained from fluca and used without further purification. MR3 is one of the most important and commonly used dyes in textile industry. This dye has several functional group such as ($R–CO_2–R'$, OH, $–SO_3Na_2$). The chemical structure of MR3 was shown in Table 2.

Table 2. Characterization of Mordant Red 3

Name and color index (C.I)	Structure	$\alpha_{max\ (nm)}$	Molecular Weight
Mordant Red 3; 58005		418-558	342.26

Different groups in the dye molecule have different absorbance peaks. The maximum absorbance of MR3 is at 487nm. The initial concentration of Mordant Red 3 solution was 10^{-3} (mol L^{-1}). Absorbance measurements were carried out with a UV–visible spectrophotometer (Shimadzu UV-256). NaCl was used a supporting electrolyte (Merck).

3. Results and Discussion

3. 1. Decolorization of Mordant Red 3

The results from the electro oxidation of the MR3 solution are shown in Fig. 4**.** After 120 min of electrolysis, all absorbance peaks ($250 < \lambda < 700$) have been disappeared.

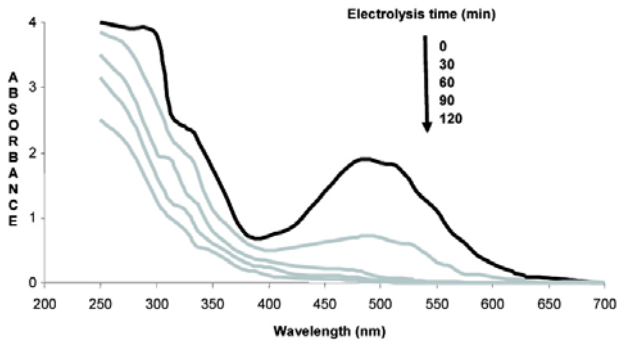


Fig. 4. Change in the absorption UV-visible spectra of MR3 during of electrolysis (Voltage = 16 volt, NaCl = 0.5 (g L^{-1}), pH = 4.5, MR3 = 10^{-3} (mol L^{-1}), reactor volume = 400 ml)

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.

$$\text{COD removal } \% = 100^{*} \frac{(COD_i - COD_t)}{COD_i}$$

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 wastewater containing chloride to convert chloride to chlorine/hypochlorite.

The effect of applied voltage showed that with increasing of applied voltage the percentage removal of COD increased. Fig. 5. with increasing applied voltage the Oxygen Evolution Reaction (OER) may occur on the anode surface along with the oxygen molecule formation. The produce 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 MR3 degradation rate.

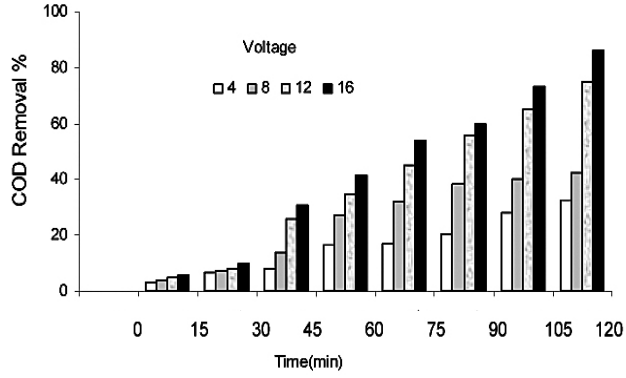


Fig. 5. Effect of voltage (NaCl = 0.5 (g L^{-1}), pH = 4.5, MR3 = 10^{-3} (mol L^{-1}), reactor volume = 400 ml)

3. 2. 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 from present work show that, the Pt electrode is the best answer for anode material among several electrodes such as Stainless Steel 304, Pb/PbO_2, and carbon plate Fig. 6. While Pt electrode possesses lower overpotential compared with PbO_2 electrode, the results implied that the MR3 degradation on the surface of platinum occurred to more extent comparing with PbO2. The reason may be attributed to the high number of active sites on Pt surface and more convenient adsorption of O_2 and chloride species which would lead to the higher formation rate of OCl^- on the surface of electrode. The process would also enhance the degradation rate of MR3.

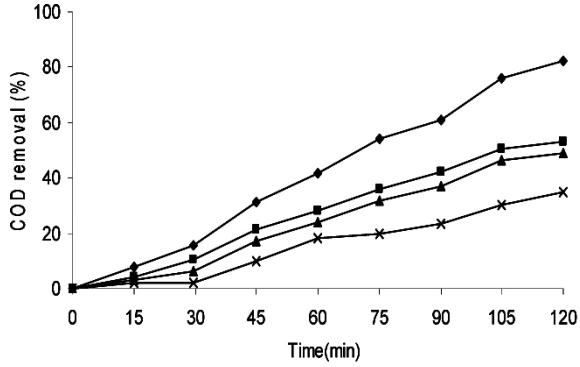


Fig. 6. Effect of different material for anode (NaCl = 0.5(g L^{-1}), pH = 4.5, MR3 = 10^{-3}(mol L^{-1}), reactor volume = 400 ml)

3. 3. The Effect of NaCl Concentration

The general chloride reactions involved in electrochemical oxidation are presented in Table 3.

Table 3. General chloride reaction at the electrochemical oxidation

$2Cl^-$	$\longrightarrow Cl_2 + 2e^-$
$Cl_2 + H_2O$	$\longrightarrow HOCl + H^+ + Cl^-$
$HOCl$	$\longrightarrow H^+ + ClO^-$
$6HClO + 3H_2O$	$\longrightarrow 2ClO^-_3 + 14Cl^- + 12H^+ + 3O_2 + 6e^-$
$ClO^- + H_2O + 2e^-$	$\longrightarrow Cl^- + 2OH^-$
$6ClO^- + 3H_2O$	$\longrightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 1.5O_2 + 6e^-$
$2H_2O + 2e^-$	$\longrightarrow 2OH^- + H_2$
$R + HOCl$	$\longrightarrow P + Cl^-$

R, Dye pollutant; P, product

The results show that, color removal occurred only in the present of NaCl. The decolorization occurs in the bulk solution because of the reaction between the generated chlorine/hypochlorite and the MR3. Hypochlorite ions which are subsequently produced as the result of the hydrolysis of chlorine molecules can also participate in the destruction of pollutants. Fig. 7.

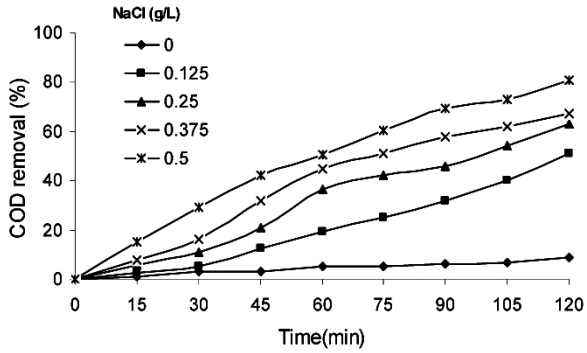


Fig. 7. Effect of sodium chloride concentration on the removal of COD percent (Voltage = 16 volt, pH = 4.5, MR3 = 10^{-3} (mol L^{-1}), reactor volume = 400 ml)

3. 4. The Effect of Initial pH

The variation of initial pH on the decolorization of MR3 during the electrochemical degradation is presented in Fig.8. The results showed that the color removal and COD decreased with increasing in the initial pH of the solution.

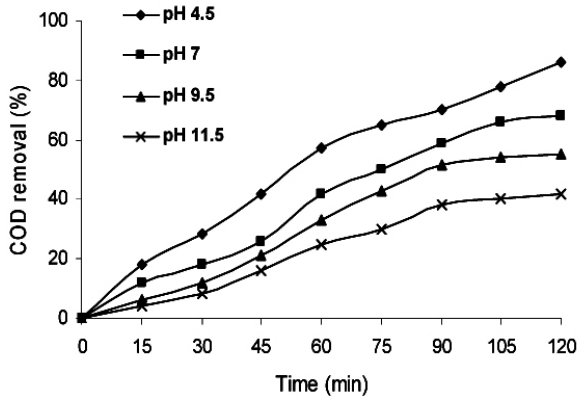


Fig. 8. Effect of initial pH on the removal of COD percent (Voltage = 16 volt, NaCl = 0.5 (g L^{-1}), MR3 = 10^{-3} (mol L^{-1}), reactor volume = 400 ml)

The reason may be due to the increasing of chlorine/hypochlorite in acidic medium and in low pH chlorine is present in the solution in the from of hypochlorous acid, which possesses higher oxidation potential than that of hypochlorite**.**

4. Treatment of Real Wastewater

The decolorization of real textile wastewater was performed under optimum condition in terms of NaCl concentration, applied voltage and electrode type, 0.5 (g L^{-1}), 16 (Volt) and platinum electrode as anode, respectively. The decolorization of textile wastewater was performed Fig. 9.

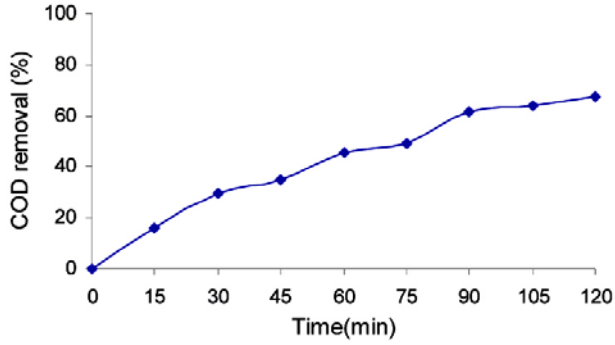


Fig. 9. Removal of COD percent of textile wastewater at different time of electrolysis in optimum condition (Voltage = 16 volt, NaCl = 0.5 (g L^{-1}), reactor volume = 400 ml)

The amount of percentage removal COD was found to be 68% 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 comparing with synthetic solution.

5. Conclusions

Indirect electrochemical decolorization of Mordant Red (3) and real wastewater (RW) were investigated using platinum 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 kinetic followed first order model for MR3.

COD and percentage color removal for MR3 was 86% and 100%. However for similar real wastewater samples the percentage removals were found to be 68% and 100%, respectively at the 120 min electrolysis time. Hence this technique may be applied for treatment of a large volume and industrial scale of textile wastewater and had to ability to complete destruction of organic pollutants to carbon dioxide and water.

6. References

1. D.Simonsson, Chem. Soc Rev, **1997**, *26*, 181–189.
2. S. Liakou, S. Pavlou and G. Lyberatos, Wat. Sci Tech, **1997**, *35*, 279–286.

3. A. Rubalcaba, M. E. Suárez-Ojeda, J. Carrera, J. Font, F.k Stüber, Ch. Bengoa, A. Fortuny and A. Fabregat, *Catalysis Today*, **2007**, *124, 191–197.*
4. V. K. Gupta, A. Mittal, L. Krishnan, J. Mittal. Journal of Colloid and Interface Science, **2006**, *293*, 16–26.
5. F. Villacañas, M.Fernando R. P. José J. M. Órfão, J. L. Figueiredo. Journal of Colloid and Interface Science, **2006**, *293*, 128–136.
6. Li-Bing Chu, Xin-Hui Xing, An-Feng Yu, Yu-Nan Zhou, Xu-Lin Sun and Benjamin Jurcik, *Chemosphere*, ***2007****, 68, 1854–1860.*
7. S. G. Schrank, J. N. Ribeiro dos Santos, D. Santos Souza and E. E. Santos Souza. J. Photochem. Photobio *A:* Chemistry ***2007,*** *186*, 125–129.
8. Sejin Park and Tai-il Yoon. Desalination, ***2007***, *208 181*–191.
9. K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura, Y. Maeda. Ultrasonics Sonochemistry, **2000**, *7*, 261–264.
10. C. Y. Kwan and W. Chu, Chemosphere, ***2007***, *67, 1601–1611.*
11. S. Koparal, Y. Yavuz, C. Gürel and Ü. B. Öğütveren, *Journal of Hazardous Materials*, ***2007****, 145, 100–108.*
12. A. G. Vlyssides, D.Papaioanno, M. Loizidou, P. K.Karlis, A. A.Zorpas, Waste Managment. **2000**, *20*,569–574.
13. L. Szpyrkowicz, C. Juzzolino, S. Daniele, M. Dante De Fave. Catalysis Today, **2001**, *66*, 519–527
14. M. Panizza, A. Barbucci, R. Ricotti and G. Cerisola, *Separation and Purification Technology*, ***2007****, 54, 382–387.*
15. Thomas Bechtold, Aurora Turcanu and Wolfgang Schrott, *Diamond and Related Materials*, ***2006****, 15, 1513–1519.*
16. O. A. Mohammed, A.-T. Mousa and T. Yahya, *Journal of Hazardous Materials*, **2000**, *B75*, 99–l 13.
17. Ugur Kurt, Omer Apaydin and M. Talha Gonullu, *Journal of Hazardous Materials*, ***2007*** *143, 33–40.*
18. D. Rajkumar, B. J. Song, J. G. Kim. Dyes and Pigments **2006**, *71*, 244–250.
19. APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association/American Water Works Association/Water Environmental Federation, Washington, DC, USA. ***1995***.

Povzetek

Proučevana sta bila razbarvanje in razgradnja sintetične odpadne vode, ki je vsebovala rdeče barvilo Mordant Red 3 (MR3) in prave odpadne vode s pomočjo elektrokemijske osidacije v pretočni celici, v kateri je bila uporabljena anoda iz platine in katoda iz nerjavnega jekla 304.
Oksidacija je potekla do majhne in neškodljive organske molekule, ogljikovega dioksida in vode, pri tem pa se je odstranilo 86 % KPK in 100 % barve. Odstranjevanje KPK in barve se je povečalo pri višji napetosti in nižji pH vrednosti.