

ELECTROCHEMICAL DEGRADATION OF C.I. REACTIVE ORANGE 16 IN THE PRESENCE OF H₂O₂/Cu⁺ IONS

Fátima ESTEVES*, Elisabete SOUSA

Department of Textile Engineering
School of Engineering, University of Minho, 4800-058 Guimarães, PORTUGAL
Tel. (+351) 253 510297
Fax (+351) 253 510293
Email : festeves@det.uminho.pt

Abstract

The aim of the present study was to investigate the electrochemical degradation of a vinylsulphone reactive dye, C.I. Reactive Orange 16, in the presence of hydrogen peroxide and copper ions. The reaction between these two species leads to the generation of hydroxyl radicals, causing dye oxidation and degradation. The efficiency of dyebath decolorization and dye degradation was evaluated by color removal and COD variation.

With a two-electrode electrochemical system it was possible to optimize experimental conditions in order to achieve color removal of simulated dyebaths over than 90% after 30-90 min of electrolysis.

Key words

Vinylsulphone dye, Electrochemical degradation, Hydroxyl radical, Copper ions

Introduction

Vinylsulphone reactive dyes are widely used in the textile industry to color cellulosic fibers [6]. They contain one or more reactive groups able to forming covalent bonds with hydroxyl groups on the fiber. A strong covalent bond would be expected but the efficiency of the dye-fiber reaction can change from 50 to 90% [3]. This fact causes a significant problem, considering the residual dyes that are left in the dyebath. Once dyeing is completed, the dyed material is washed off several times in order to remove unfixed and/or hydrolyzed dye. This means that a significant amount of these compounds is directly lost into wastewaters during processing operations. This is the case of dye C.I. Reactive Orange 16 (Figure 1), with a fixation efficiency of 55-60%,

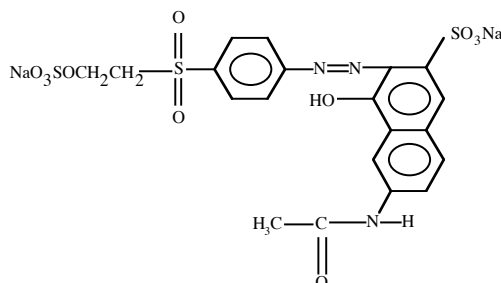
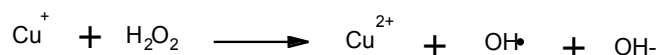


Figure 1: Molecular structure of C.I. Reactive Orange 16

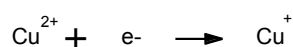
* PhD and Textile Chemistry Teacher in University of Minho - Portugal

In the present work, an electrochemical degradation method, action of H₂O₂ in the presence of Cu⁺ ions, was applied and optimized as a development of a previous study concerning these species [2]. Hydrogen peroxide is used, for a long time, in decolorization of dyeing wastewater, especially in the so-called advanced oxidation processes (AOP), combined with UV radiation, ozone and Fenton's reagent [4], ultrasound [5] or electrochemical degradation in the presence of cobalt ions [1].

H₂O₂ itself requires high concentration and long contact time. However, activation by metals (Fe, Co or Cu) can promote the catalytic decomposition of the oxidant agent, leading to strong radicals formation. In the present study,



This reaction produces hydroxyl radicals by chemical means, but to attain this, an initial amount of Cu⁺⁺ ions is added to the solution at the same time as H₂O₂. A cathodic reaction guarantees Cu⁺ production in order to achieve following dye oxidation and degradation,



Materials and Methods

Dyebath preparation

Simulated dyebaths were prepared according the composition commonly used for cotton dyeing. C.I.Reactive Orange 16 was included in concentration 3% (o.w.f.). Several auxiliary products were added to dyebath: Na₂CO₃ (5 gL⁻¹), NaOH 38°Bé (2 mL⁻¹), Na₂SO₄ (50 gL⁻¹). The analyzed solutions consisted on 5% and 20% of these initial dyebaths, simulating different textile wastewaters.

Electrochemical procedure

Electrolysis apparatus consisted of a 570 mL closed cell and two Ti/RuO₂ electrodes, 2 cm apart from each other and dipped into the solution. The total effective electrode surface area was 64 cm². A power unit Farnell 30-10 controlled the power input. Potential value of 6 was applied in controlled potential experiments. Several volumes of H₂O₂ 35% (w/w) were tested, as well different volumes of initial solution of CuSO₄ 0.01 M for hydrogen peroxide activation. COD, pH, conductivity, redox potential and color measurements were made using standard methods. Experiments were carried out at room temperature.

Results and discussions

For dye degradation study two concentrations of initial dyebath were considered, 5 and 20%. Established experimental conditions in previous study were 4h of electrolysis, 4.5 mL⁻¹ H₂O₂ and 7 mL⁻¹ CuSO₄. These were initial conditions for the present work, in order to optimized electrochemical degradation of C.I. Reactive Orange 16. Therefore, after electrochemical treatment under those conditions, 5 and 20% solutions presented color removal values indicated in Table 1.

Table 1: Color removal after 4h of electrolysis

Time (min)	Color removal (%)	
	5% solution	20% solution
30	83.5	87.0
60	85.7	91.2
90	94.3	93.5
120	94.9	93.9
240	96.7	96.3

For each solution it was possible to reach an electrolysis time with a reasonably color removal value, avoiding too large energy consumption. As a consequence, 90 minutes of electrochemical treatment was considered a suitable time, getting 94.3 and 93.5% of color removal for 5 and 20% solutions, respectively.

Established time factor, the following step was to reduce CuSO_4 and H_2O_2 volumes, in order to attain more adequate electrolysis conditions and optimize electrochemical degradation of C.I. Reactive Orange 16 dye. In Tables 2 and 3 results of such a study are presented for 5 and 20% solutions, respectively.

Table 2: Color removal for 5% solution after 90 minutes of electrolysis

H_2O_2 (mL^{-1})	CuSO_4 (mL^{-1})	Color removal (%)
4.5	7	94.3
4.5	5	88.4
4.5	3	89.9
4.5	1	89.0
4.5	0.5	90.6
4	0.5	91.2
3	0.5	94.5
2	0.5	95.5
1	0.5	95.5

Table 3: Color removal for 20% solution after 90 minutes of electrolysis

H_2O_2 (mL^{-1})	CuSO_4 (mL^{-1})	Color removal (%)
4.5	7	93.5
4.5	5	94.0
4.5	3	94.2
4.5	1	94.3
4.5	0.5	85.2
4	1	93.7
3	1	94.0
2	1	91.0
1	1	83.2

Considering experimental results, it was possible to set the minimal conditions for both solutions in order to attain a color removal over than 90% with a single electrolysis step. For 5% solution, after 90 minutes of electrolysis in the presence of $1 \text{ mL}^{-1} \text{H}_2\text{O}_2$ and $0.5 \text{ mL}^{-1} \text{CuSO}_4$, 95.5% of decolorization is reached. In the case of 20% solution, $4.5 \text{ mL}^{-1} \text{H}_2\text{O}_2$ and $1 \text{ mL}^{-1} \text{CuSO}_4$ cause 94.3% of color removal, but also a quite good result (94.0%) is attained with $3 \text{ mL}^{-1} \text{H}_2\text{O}_2$.

In Tables 4 and 5 pH, conductivity, redox potential and COD values are presented for 5 and 20% solutions, respectively, after electrolysis in the considered experimental conditions.

Table 4: Analysis of 5% solution after 90 minutes of electrolysis

H_2O_2 (mL^{-1})	CuSO_4 (mL^{-1})	pH	Conductivity (mScm^{-1})	Redox potencial (mV)	COD ($\text{mg O}_2\text{L}^{-1}$)
4.5	7	9.38	5.05	0	33.2
4.5	5	9.27	4.77	174	54.3
4.5	3	9.02	4.94	108	18.6
4.5	1	9.80	4.98	136	117.6
4.5	0.5	10.35	5.08	121	23.4
4	0.5	10.39	5.15	109	34.8
3	0.5	10.77	5.18	-9	13.7
2	0.5	9.56	5.09	-41	8.8
1	0.5	9.78	5.04	-121	44.3

Before electrolysis, average values: pH 10; cond. 5 mScm^{-1} ; Red. pot. 200 mV; COD $44 \text{ mg O}_2\text{L}^{-1}$

Table 5: Analysis of 20% solution after 90 minutes of electrolysis

H ₂ O ₂ (mL ⁻¹)	CuSO ₄ (mL ⁻¹)	pH	Conductivity (mScm ⁻¹)	Redox potencial (mV)	COD (mg O ₂ L ⁻¹)
4.5	7	10.85	16.44	-103	132
4.5	5	11.22	16.32	-88	150
4.5	3	10.85	18.77	-103	145
4.5	1	10.95	18.31	-113	171
4.5	0.5	10.71	19.46	-156	168
4	1	10.57	19.73	-123	178
3	1	10.73	19.14	-123	187
2	1	11.32	19.06	-117	190
1	1	11.09	19.21	-174	194

Before electrolysis, average values: pH 11; cond. 15 mScm⁻¹; Red. pot. ±35 mV; COD 200 mg O₂L⁻¹

Conclusion

Electrochemical procedure is an important alternative for dye degradation in wastewater treatment. In this case, it was possible to demonstrate that oxidation by hydroxyl radicals action, with activation by copper ions, has an effective result in the case of C.I. Reactive Orange 16 dye.

Considering experimental results we can also conclude that with established and optimized conditions for electrochemical process it was possible to attained a considerably good level of decolorization of C.I. Reactive Orange 16 solutions, with consequently dye degradation. In most situations, COD removal was also considerable, but side reactions could be the cause of some dissimilarity. Changes in conductivity and pH values were not significant. Redox potential values are, however, relatively unforeseen (both before and after electrolysis) perhaps result of some unexpected interference during analysis procedure.

In several situations total color removal was achieved in both solutions some time after electrolysis. This means that a minor electrolysis time can also be used only to begin the wastewater treatment procedure.

References

- [1] Chen, J. et al., *Electrochemical degradation of bromopyrogallol red in presence of cobalt ions*, *Chemosphere*, N° 53, 2003, pages 1131-1136
- [2] Esteves, F. and Cunha, E.P., *Voltammetric study and electrochemical degradation of reactive dyes*, *5th World Textile Conference AUTEX 2005, Slovenia, 2005*
- [3] Guaratini, C.C.I. et al., *Studies of the voltammetric behavior and determination of diazo reactive dyes at mercury electrode*, *Electroanalysis*, N° 13,18, 2001, pages 1535-1543
- [4] Kurbus, T. et al., *Comparison of H₂O₂/UV, H₂O₂/O₃ and H₂O₂/Fe²⁺ processes for the decolorisation of vinylsulphone reactive dyes*, *Dyes and Pigments*, N° 58, 2003, pages 245-252
- [5] Voncina, D.B. and Le Marechal, A.M., *Reactive dye decolorization using combined ultrasound/ H₂O₂*, *Dyes and Pigments*, N° 59, 2003, pages 173-179
- [6] Zanoni, M.V.B. et al., *Determination of the vinylsulphone azo dye Remazol Brilliant Orange 3R by cathodic stripping voltammetry*, *Analytica Chimica Acta*, N° 385, 1999, pages 385-392