

ELECTROCHEMICAL TREATMENT OF XYLENOL ORANGE DYE WASTEWATER AT RuO_2/Ti ANODE

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Dyes and Pigments are indispensable in modern life and have found wide application in fabrics, home interiors, leather accessories, plastics, automobile and paper industry. On the other hand, dye industries are one of the major industries responsible for water pollution. It consumes substantial volumes of water and chemicals. The electrochemical methods have been applied in the treatment of the wastewater since early 1960s. In the present paper, an attempt is made to treat synthetic effluent containing Xylenol orange dye by electrochemical method. The optimum conditions for maximum removal of TOC are reported.

Keywords: Fenton's reagent, NaCl, RuO_2/Ti , TOC removal, Xylenol orange dye effluent.

INTRODUCTION

In recent years, the problem of environmental pollution and its control have reached enormous significance owing partly to increased awareness among the public. One of the major industries contributing to pollution has been textile manufacture and dyeing industry. The later has reached a level of magnitude that the same poses a serious threat to environment.

The waste water from dye house are generally multicolored in nature with respect to type of dying processes. This dye house effluent disposed into the land and running water leads to the reduction of sun light penetration in the water environment, which in turn decrease, both photosynthesis and dissolved oxygen (DO) to aquatic plant and affect soil when disposed on the agricultural land with improper treatment. Depending on the functional group viz carboxylic ($-\text{COOH}$) group, amino ($-\text{NH}_2$) group and azo ($-\text{N}=\text{N}-$) group, the treatment method has to be suitably modified. [1].

The conventional method of effluent treatment has been carried out using strong oxidizing agent like hypo chlorite or conventional biological treatment through activated sludge process for the

biodegradable organic dyes. The major problem has been that the former leads to increase in the total dissolved solid content which makes the treated effluent undischageable into the water ways, whereas the biological treatment did not yield the satisfactory quality for the treated effluents.

Advances in physical and chemical technologies for decolorization have been reviewed by Yu. Gang *et al* [2]. The various processes have been reviewed by different authors with the view to arrive at possible and economically feasible technologies for effective treatment of effluents carrying the dyestuffs [3-7].

Photo-degradation of dye effluents using semiconductor catalyst has been found to be effective to the tune of 70% COD removal [8]. Ultra-violet irradiation enhanced the decolorisation through oxidation [9].

Photocatalytic approach for the reductive decolorisation of azo dyes has been found to yield good efficiencies where as combination of UV and H_2O_2 at very low pH of the order of 1-2 yielded best decolourisation in the reactive dyes [10,11]. Acid red G and C.I. 29160 dyes could be decomposed using UV irradiation in presence of TiO_2 [12].

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Irrespective of the nature of dyes or the composition and conditions of irradiation, the 100% effectiveness could not be brought about and hence the other approaches through conventional, biological methods have also been tried. Biodegradation of dye containing waste water measured in terms of COD removal has been reported by Zhang Yichu [13].

In textile dyeing a change in formulation by adjusting the amounts and auxiliary reagents the effectiveness of the biochemical treatment could be considerably improved [14].

Conventional aerobic/anaerobic processes have resulted in satisfactory treatment of a sulphonated azo dyes [15,16]. A review on the subject of a combination of physico chemical and biological treatment for the decolourisation of dyeing waste water has been made by Kouba [17].

As US patent describes three units processes consisting of aerobic/anaerobic treatment, oxidizer treatment and a final adsorption process for the purification of dye - house effluents [18]. A combination of biological treatment coupled with air flotation proceeded by electro flotation has yielded the treated effluent quality meeting discharge standards [19].

Adsorption of anionic dyes on montmorillonite modified with aluminium polyoxochloride has been tried in the decolourization of some direct dyes [20]. Hofmann degradation of poly acrylamide grafted onto cotton yarn has used with Fe²⁺/H₂O₂ and this has yielded very good adsorption/desorption characteristics [21].

Though all the above methods have been found to be fairly satisfactory, considering the very stringent environmental regulations there is a need for more effective treatment alternatives. This has led to development of electrochemical treatment techniques for the treatment purposes.

The electrochemical treatment method of industrial waste water includes oxidation, reduction and electrodialysis [22,23]. The waste water treatment from dyeing operations involves the use of an electrochemical cell which generates iron

hydroxides in the waste water decolourise the dye waste water [24].

In the waste water treatment from dyeing by electroflocculation the efficiencies of decolourisation and COD removal were reported to be 90 and 25% respectively [25].

Fixed beds are used in the treatment of waste water from dying industry. The fixed bed contains mainly iron filling and reducing substances such as graphite and charcoal [26]. Good results are observed for the removal of colour and COD by constant current electrolysis using metal oxide type anode and Ti cathode [27].

In the electrolytic processes for removal by dyestuff and colour by changing both electrolyte concentration and initial dye concentration, the rate of the electrooxidation process was found to be a pseudo first order kinetic process [28]. Electrochemical decolourisation of a solution of azo dyes were reported at Pt or graphite supported PbO₂ proceeded at potentials in the oxygen over voltage range [29] and at Ti/SnO₂ [30].

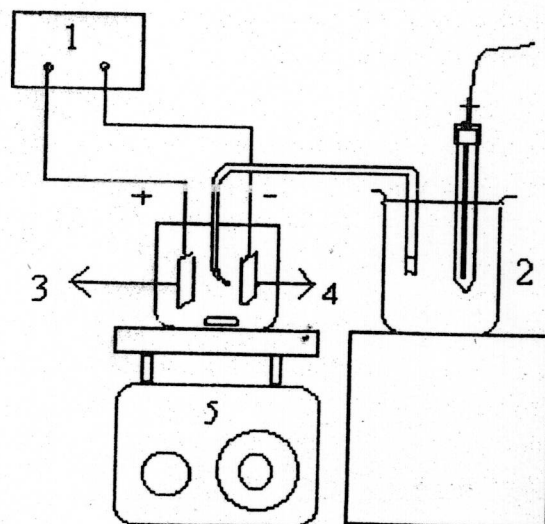


Fig. 1: Schematic diagram of experimental setup
(1) Power supply (2) Reference electrode
(3) Anode (4) Cathode and (5) Magnetic stirrer

In the present work, an attempt is made to treat the synthetic effluent containing Xylenol orange dye by electrochemical method.

EXPERIMENTAL

A Synthetic effluent was prepared using Xylenol orange dye for the present study. Fig. 1 shows the electrolytic cell used in the electro-oxidation process. It consists of a glass-beaker of 250 ml capacity closed with a PVC lid having provisions for a cathode and an anode. Salt bridge with reference electrode was inserted through the hole provided in the lid. The cathode is stainless steel and the anode is a RuO_2/Ti of area 0.235 dm^2 . Current was supplied by a Dc regulated power source. (Anlab 7771). Stirring is done with a magnetic stirrer. 200 ml of effluent was taken for all the experiments.

Electrolytic batch investigations have been carried out galvanostatically at pH 3, at different current densities (5.3 and 1 A/dm^2) using different mediators such as NaCl, Fenton's reagent and Fenton's reagent + NaCl. During the electrolysis samples were collected at different time intervals and the Total Organic Carbon (TOC) was analyzed using TOC analyzer.

The oxidized products and the reduction in dye concentration were qualitatively analysed by recording the UV-Visible spectra using a UV-Visible Spectrophotometer (Systronics 118.)

RESULTS AND DISCUSSION

Investigations on the electrochemical treatment of synthetic effluent containing xylenol orange dye have been carried out using RuO_2/Ti anode and stainless steel cathode in an acidic condition of pH 3.

The dye effluent is initially electrolyzed at 2 A/dm^2 at different NaCl concentration. Fig. 2 shows the variation of cell Voltage with time. Increase in NaCl concentration improves the conductivity of the effluent. The anode and cathode potentials remain more or less constant through out the electrolysis and a steady gas evolution could be observed on the electrode surface.

During the electrolysis it was noticed that the colour of the dye has been disappeared gradually with in a hour. The samples were collected at different time intervals and analyzed for the TOC content. Results are shown in Fig. 3. It was observed that the TOC removal increases with increase in NaCl concentration from 6 gpl to

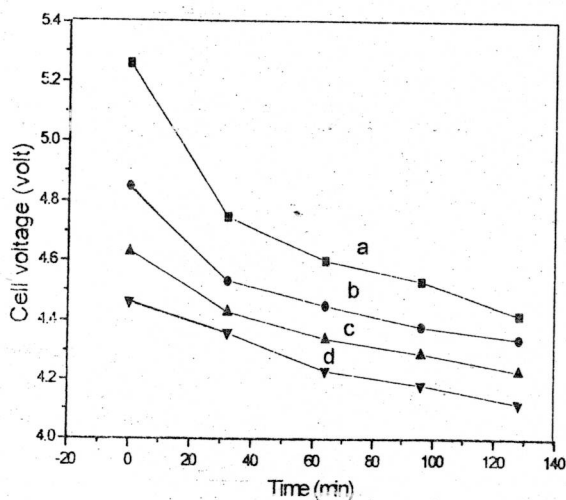


Fig. 2: Variation of cell voltage with respect to time during the electrolysis at C.D. of 2 A.dm^{-2} at different NaCl concn (g/l)
(a) 6 (b) 7 (c) 8 (d) 9

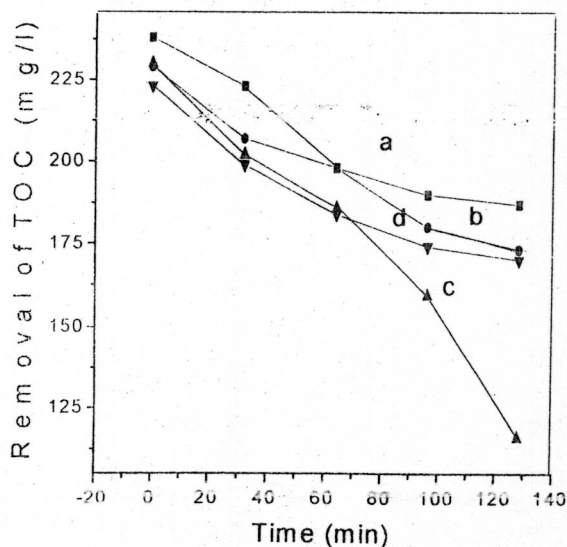
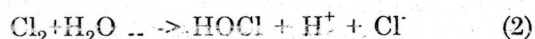


Fig. 3: Removal of TOC with respect to time at C.D. 2 A.dm^{-2} at different NaCl concn (g/l)
(a) 6 (b) 7 (c) 8 (d) 9

7 gpl, but above 7 gpl the TOC removal started decreasing. This may be due to reason that the OCL⁻ formed undergoes some other side reaction. Hence the 6 gpl NaCl concentration is fixed as the optimum supporting electrolyte concentration and experiments have been carried out at different current densities namely 0.5, 1.2 and 4 current density A/dm² is the optimum, for the maximum removal of TOC.

The possible electrode reactions are:



The raw dye effluent is subjected to a spectral analysis covering the range from 200 nm to 700 nm. It is observed from the Spectrum (Fig. 4) that there are three adsorption peaks in the visible region of 360 nm, 440 nm and 480 nm.

For the purpose of evaluation, absorbance is measured at the wave lengths 360 nm, 440 nm and 480 nm. A cross check for the possible formation of a new compound during electrolysis has also been carried out for the treated sample by having a full spectral analysis. It is observed

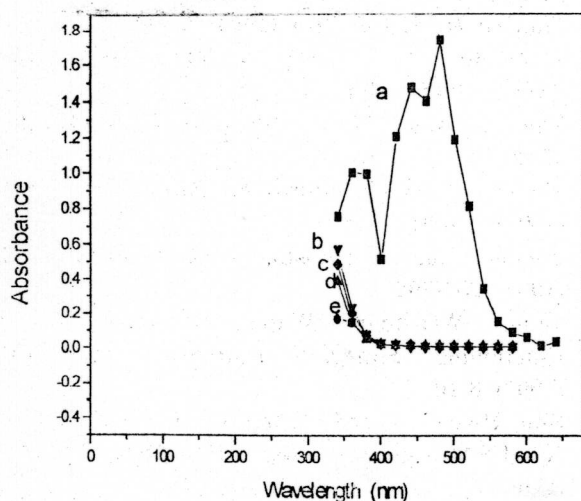


Fig. 4: Spectral analysis of the (a) Raw effluent and treated effluent at different NaCl concn (g/l)

(b) 6 (c) 7 (d) 8 (e) 9

TABLE I: Experimental data obtained during the electrolysis of the dye effluent containing Xylenol orange

Anode : RuO ₂ /Ti							
Cathode : Stainless steel							
Area of the electrode : 0.235 dm ²							
pH : ~ 3							
Volume of the electrolyte : 200 ml							
Concn of NaCl (gpl)		Current (A)	Time (min)	Cell voltage (V)	Electrode potential (V)		Removal of TOC (%)
					Anode	Cathode	
6		0.47	128	5.2-4.67	1.87-1.68	3.10-2.76	50
7		0.47	128	4.85-4.49	2.12-1.60	2.55-2.39	51
8		0.47	128	4.69-4.62	2.28-2.04	2.63-1.75	48
9		0.47	128	4.46-4.12	1.63-1.43	3.10-2.76	45

from the spectrum that the peaks appears in the raw effluent disappeared due to the cleavage of the functional groups present in the raw during the electrolysis.

TABLE II: Experimental data obtained during the electrolysis of the dye effluent containing Xylenol orange

Anode		: RuO ₂ /Ti				
Cathode		: Stainless steel				
Area of the electrode		: 0.235 dm ²				
NaCl concentration		: 7 gpl				
pH		: ~ 3				
Volume of the electrolyte		: 200 ml				
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Current density	Current	Time	Cell voltage	Electrode potential (V)		Removal of
(A.dm ⁻²)	(A)	(min)	(V)	Anode	Cathode	TOC (%)
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0.5	0.12	512	2.56-2.47	1.32-1.16	1.23-1.20	38
1.0	0.24	256	4.15-4.34	1.82-1.80	2.29-2.03	38
2.0	0.47	128	5.26-4.67	1.67-1.68	3.10-2.76	50
4.0	0.94	64	11.30-8.73	5.24-3.64	5.04-4.62	43

TABLE III: Experimental data obtained during the electrolysis of the Xylenol orange using the mediators

Anode	: RuO ₂ /Ti
Cathode	: Stainless steel
Area of the electrode	: 0.235 dm ²
pH	: ~ 3
Current density	: 2 A.dm ⁻²
Volume of the electrolyte	: 200 ml

Media-tors	Charge Q (Ah)	Cell voltage (V)	Electrode potential (V)		Removal of TOC (%)
			Anode	Cathode	
A	2	2.74-2.72	1.54-1.52	1.23-1.05	75
B	2	2.88-2.62	1.59-1.57	1.29-1.04	63

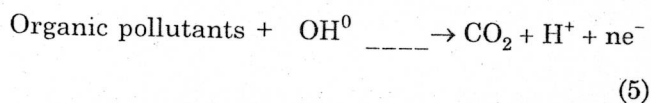
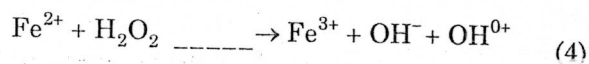
A = Fenton's (0.1 mg/l + 2 ml/l H₂O₂)

B = Fenton's reagent + NaCl (1 g/l)

In order to improve the TOC removal efficiency, the effect of different mediators like Fenton's reagent and Fenton's reagent + NaCl have also been tried during the electrolysis. It is observed from the results that about 75% of TOC removal could be achieved when using the Fenton's mediator compared to the other two mediators such as NaCl (50%) and Fenton's reagent + NaCl (65%) at 2 A.dm⁻².

Coming to the question of electro oxidation, the reaction may occur either through direct oxidation of organic compounds by nascent oxygen or through the intermediate, namely hypochlorite ions.

It is generally observed that the current efficiency for the reaction is increased when the reaction takes place through the indirect route mainly hypochlorite ion. When the electrolysis is carried out using Fenton's reagent the following reactions take place.



When we are using the Fenton's reagent the Fe²⁺ ions generates OH[·] from the H₂O₂ and that facilitate the oxidation. The oxidized-Fe³⁺ ions intern get reduced as Fe²⁺ ions at the cathode and again generates the OH[·]. Hence, the efficiency of the product oxidation takes place effectively. Concluded that it is possible to destroy the dye compound through electrolysis or electro chemical oxidation. The effective destruction of the dye preferably takes place at a current density of 2 A.dm⁻².

CONCLUSION

The present study aims at the electro oxidative destruction of the textile dye Xylenol orange which is highly soluble in aqueous medium. The investigation has indicated that it is possible to remove the organic pollutant, Xylenol orange dye effluent. The decrease in absorbance at the characteristic wavelengths indicates positively that destruction of organic pollutant take place during the electrolysis. TOC level of the effluent is brought down to around 50% with NaCl and to around 73% with Fenton's reagent.

REFERENCES

1. R K Trivedy and Geol, "Chemical and Biological methods for water pollution studies", (1984)
2. Yu Gang, Yang, Zhihua, Zhu, Wanpeng and Jiang Zhanpeng, *Huanjing Kexue*, 15(4) (1994) 75-9
3. Kouba, F John, Pmg, Zhuang, Inc Charlotte, *Fluid/part*, Sep J, 7(3) (1994) 87-90
4. Yamamoto, Ichirio, Aizawa and Maski, "Kako Gyubu" 29(8) (1994) 50-6
5. Yamamoto and Ichirio Kankyo, "JETI" 43(3) (1995) 42-8
6. Monimoto and Kunihiro, *Senshoku Kogyo*, 43(6) (1995) 276-91
7. Yamada and J Hiroshi, *Kankyo Gijitsu*, 23(5) (1994) 281-292
8. Jmug, Weichuan, Wangi, Qiauan, Yu and Chuanmmg, *Shanghai Huanjing Kexue*, 14(5) (1995) 8-10
9. Shu, Hwng-Yee and Huang, *Ching-Rong*, Newyark NJ (USA), *Am Dyest Rep*, 84(8) (1995) 30, 32, 34 & 9
10. K Vinodgopal, Bedja, Idriss, Hotchandani Surat, Kamat and V Prashant, *Langmuir*, 110161 (1994) 1767-7

11. Uygur and Ayse, *Melliand Textilber*, **76(69)** (1995) E121-E122, 421-9
12. Fan, Banglang and Li Jian, *Huanjing Wuran Yu Fangzhi* **11(4)** (1989) 16-18
13. Zhang, Yichu, Xi Danli, Yu, Zhimei and Guo, *Meifang Shanghai Huanjing Kexue*, **8(4)** (1989) 15-17
14. Gong, Runbo *Huanjing Baobu*, **2** (1989) 14-16
15. Zhu, Jianrong, Yang, Yanru, An, Huren and Qian, *Yi Huanjing Kexue*, **15(4)** (1994) 31-34
16. FitzGerald, Wsean, Bishop and L Paul, *J Environ Sci Health*, **30(6)** (1995) 1251-76
17. Kouba, F John and Zhuang, Ping *book pap Intl Conf Enhib AATCC*, (1994) 351-5
18. Meid/John, Vollstedt Thomas J U s 5,302,288,12 April (1994) *Appl* **35,110,19** March 1998.
19. Liu, Yichun *fangzhe Xuebao*, **10(8)** (1989) 359-60
20. Deroshenco, Tarasevich, Yu, Rok and V S Ksum, *Tekhnol Vody*, **11(6)** (1989) 500-3
21. Furuta, Hirokazu and Kobajashi, Kengo *seni gakkaiishi*, **46(1)** (1990) 38-46
22. G Valenbn, F Lapique and A Stork, *Recents Prog Genic Proceeds*, **7(25)** (1993)
23. J C Cotonne, *Galvano orango*, **62(641)** (1993) 1073-8
24. Furr and W Brian, *Book Pap Intl Conf Exhib AATCC*, (1992) 38-41
25. Zhao Jianfu, Gu Guowei and Tongj, *Daxue Xaebo*, **21(3)** (1993) 339- 42
26. Cao and Man Shanghai, *Huanjing Kexue*, **13(2)** (1994) 43-9
27. Nakajima Yasno, Sekimoto Masco, Hirao Kazuhiro, Shimamune, Takauki, Matsuda Yohiharu and Denki Kagaker, *Oyobi Kogyo Butsuri Kagaku*, **62(11)** (1994) 1036-8
28. J Allen Stephen, Khader Kayed and Murray Marganet, *I Chem E Res Event Two-day Symp*, **1** (1994) 1383-5
29. Borovski Yu and T M Grishna, *Zh Priklkhim*, **67(8)** (1994) 1383-5
30. Comninellis Chutas, *Inf chim*, **357** (1994) 109-12