Removal of hazardous azo dye metanil yellow from industrial wastewater using electrochemical technique

R. Jain*, N. Sharma and K. Radhapyari

School of Studies in Environmental Chemistry, Jiwaji University, Gwalior-474011, India
Fax: +91-751-2346209, Tel: +91-751-2442766
* e-mail: rajeevjain54@yahoo.co.in

Abstract: The environmental challenge of synthetic azo dyes is of increasing concern due to the serious health effects on animals and human being. Metanil yellow (monosodium salt of 4-m-sulphophenylazodiphenylamine) was selected as the model compounds for this study because of its wide application in various textile industries either as such or in combinations with some other dyes as color additives. The azo dye degradation with electrochemical method in aqueous solution has been studied with platinum and steel electrode. A well–defined irreversible cathodic peak at -0.293 V was obtained and this may be attributed to the reduction of azo (–N=N-) group. Results indicate that the electrode process is diffusion controlled. Number of electron transferred was calculated and is found to be 4e and reduction mechanism proposed. During controlled potential electrolysis (CPE) peak current reduced substantially with a considerable decrease in color and absorbance. The reaction follows a first order dependence with k values 2.41 x 10^{-2} abs min^{-1} and 2.30 x 10^{-2} abs min^{-1} at platinum and steel foil respectively. The efficiency of different electrode materials for color removal is compared. Chemical oxygen demand (COD) decreases substantially from 2160 ppm to 180 ppm at platinum (91.7% COD removal) and 292 ppm at steel electrode (86.5% COD removal). No peak could be observed in the voltammograms after CPE, indicating the absence of any electroactive breakdown products.

Key words: Metanil Yellow, Azo dye, Electrochemical treatment, Waste water, CPE, COD.

1. INTRODUCTION

Dye wastewater usually contains of a number of contaminants including acids, bases, dissolved solids, toxic compounds, and colored materials which are noticeable even at very low concentrations and must be removed before the wastewater can be discharged. Azo dyes constitute an important class of synthetic, colored, organic compounds, which are characterized by the presence of one or more azo bonds (–N=N–). They represent about 50% of the worldwide dye production and are widely used in a number of industries, such as textile dyeing, food, cosmetics, paper printing, with the textile industry as the largest consumer (Ollgaard et al. 1999; Gomez et al. 2003).

It is reported that approximately 5 tonne of dye discharge from dyes and coloration industries every year (Brown, 1987). A number of physical and chemical techniques have been reported for the removal of dye compounds such as adsorption (Walker and Weatherley, 1999; Moura et al. 2003), biological treatment (Lee and Pavlostathis, 2004), chemical precipitation (Sarasa et al. 1998), photocatalytic (Prevot et al. 2001; Jain et al. 2008), electrochemical methods (Gupta et al. 2007; Jain et al. 2006; Jain et al. 2007; Fan et al. 2008; Jain et al. 2009), ozonation (Ciardelli and Ranieri, 2001) and Fentons' reaction (Meric et al. 2004). Electrochemical techniques are considered as an attractive methodology for the treatment of dyeing wastewater due to its significant advantages viz. wide application, simple equipment, easy operation, lower temperature requirements and no sludge formation (Daneshvar et al. 2004; Do and Chen, 1994; Gutierrez and Crespi, 1999; Vlyssides et al. 1999; Lorimer et al. 2000).

Metanil yellow (monosodium salt of 4-m-sulphophenylazodiphenylamine) is an acidic azo dye (Figure 1). It is a monoazo dye having CI name acid yellow 36 and comes under the trade name of external drug and cosmetic (D&C) Yellow No.1.
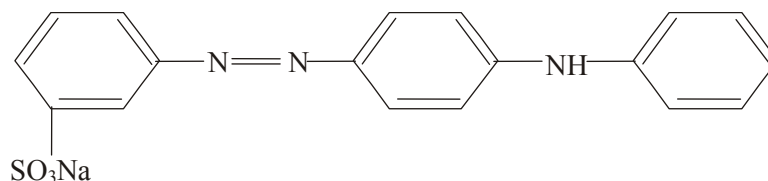

Figure 1. Metanil yellow

These dyes are released in effluents from textile, leather, shoe polish, wood stain, paper, food and cosmetic industries. Despite the ban as food colouring agents in many countries, these dyes is frequently used as a food additive in many yellow orange coloured eatables mostly in India (Khana et al.1985). Metanil yellow has shown to promote tumor enhancing effects (Gupta et al. 2003), cause testicular damage in gametogenic elements to arrest spermatogenesis in guinea pigs, rats and mice (Khanna and Das, 1991), induced haematological changes (Prasad and Rastogi, 1983), effect DNA synthesis (Sundarrajan et al. 2001) and a case of allergic contact dermatitis due to metanil yellow was also reported by Hausen, 1994.

Photocatalytic degradation (Sleiman et al. 2007) technique is available for degradation of metanil yellow from environmental samples. Metanil yellow azo dye has electroactive groups but its electrochemical behavior or their treatments have not been investigated. In the present study, the electrochemical treatment of a hazardous azo dye metanil yellow from industrial wastewater was investigated and the treatment performance was optimized using electrochemical methodology. Results have been analyzed employing the criterion of complete decolourisation and reduction in toxicity of the dye.

2. EXPERIMENTAL APPARATUS AND METHODS

2.1 Instrumentation

Cyclic voltammetric (CV) studies were carried out on EG & G potentiostat of Princeton Applied Research integrated with applied electrochemistry software. Voltammograms were recorded by cycling the working electrode potential between -1.20 V to $+1.20$ V at different at different sweep rates (50 - 2000 mV s^{-1}). The electrochemical cell consisted of three-electrode system placed 1.0 cm apart from each other and directly dipped in the solution to be electrolyzed. Voltammetric behavior was studied using platinum as working electrode, SCE as reference and platinum wire as counter electrode. Controlled potential electrolysis was carried out using BAS CV-27 cyclic voltammograph in connection with the digital electronic 2000 Omnigraph x-y/t recorder. The working electrodes used for controlled potential electrolysis (CPE) were platinum foil of surface area 3x3 cm^2 and steel foil having 4.5 x 3.5 cm^2 surface areas. Ag/AgCl was taken as the reference electrode and platinum wire as counter electrode.

Differential pulse polarographic (DPP) measurements were carried out on Elico pulse polarograph (model CL 90) connected with Polarocord recorder (model LR-108). Triple distilled mercury was used for the DME. The capillary had a flow rate of 3.02 mg s^{-1} together with drop time of 3 seconds. The pH metric measurements were made on Hach digital EC-40 Benchtop pH/ISE meter. The absorption spectra of samples were recorded on UV-Visible spectrophotometer (model Elico SL I59). The chemical oxygen demand (COD) was determined with the open reflux method using COD digester apparatus (model Spectralab 2015-S). The synthetic azo dye metanil yellow was purchased from Aldrich USA.

2.2 Reagents and materials

2×10^{-3} M of stock solution of metanil yellow was prepared by dissolving accurately weighed quantity of compound in double distilled water. In order to evaluate the effect of varying pH, BR buffers in the pH range 2.5 - 12.0 were prepared as per literature method (Britton, 1956). The solutions for recording voltammograms were prepared by mixing appropriate volume of stock solution and distilled water/buffer of varying pH. Supporting electrolyte was 1.0 M KCl. For carrying out the COD experiments reagents were prepared in accordance to standard methods (APHA, 1995).

2.3 Procedure

The cyclic voltammetric and differential pulse polarographic studies of metanil yellow was carried out by mixing 1.0 mL of potassium chloride, 1.0 mL stock solution and 8.0 mL of appropriate BR buffer/distilled water. Solutions of different concentrations were prepared in distilled water/buffer for CV and DPP studies. Dissolved oxygen was removed from the solution by passing nitrogen gas for about 10 minutes. The polarograms and cyclic voltammograms were then recorded. The redox behavior was studied at varying pH range of 2.5 to 12.0 and scan rates from 100 to 2000 mV s^{-1}. Controlled potential electrolysis of the dye solution was performed at slightly more negative potential than the peak potential of the respective peak. Absorbance of the solution was measured at different time intervals. The value of rate constant k was calculated from the $\log_{10}$ (absorbance) vs time plots. The number of electrons transferred was calculated from the decrease in current with time during electrolysis. Controlled potential coulometry was also carried out at different pH values. The progress of electrolysis was monitored by recording cyclic voltammograms at regular intervals of time. The end products of the electrolysis were identified by TLC. For COD studies, the experiments were carried out as per standard methods.

2.4 Coulometry

For the coulometric determination of number of electrons 'n' consumed in the reduction, a solution of depolarizer, potassium chloride and buffer/distilled water was mixed in the same ratio as for cyclic voltammetric and polarographic studies. The solution was de-aerated by passing nitrogen gas for 10 mins and cyclic voltammograms were recorded at a negative potential slightly higher than the peak potential. With the progress of electrolysis the color of the solution gradually faded and finally a colorless solution was obtained. The current decreases exponentially with time and using coulometer, value of Q was read and by application of Q = nFN, the value of 'n' could be calculated and found to be 4.0.

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetric (CV) studies

The cyclic voltammogram of metanil yellow in distilled water exhibits a reduction peak at -0.293V and a corresponding oxidation peak at -0.697 V at 50mV s^{-1} scan rate. As the scan rate was increased, the cathodic peak potential showed negative shift and oxidation peak potential showed positive shift. The difference between E_{pc} and E_{pa} (ΔE_p) decreased gradually with increasing scan rate. At the higher scan rate of 2000mV s^{-1}, E_{pc} and E_{pa} are -0.363V and -0.743V respectively. The cathodic peak can be safely assigned to the reduction of azo (-N=N-) group. The separation of reduction and oxidation peak is greater than 0.059/n volts which pointed towards irreversible nature of the electrode process. Irreversibility occurs when the relative rate of electron transfer with

respect to the mass transport was insufficient to maintain Nernstian equilibrium at the electrode surface. The voltammograms recorded were more spread out and flatter which also supported the irreversible nature of the electrode process. As the scan rate (v) is increased, the reduction peak potential shows negative shift and oxidation peak potential shows positive shift suggesting the irreversible nature of the electrode process. The plot of i_{pc} *vs* $v^{1/2}$ in the 6.5 pH solution is a straight line passing through the origin indicating diffusion controlled nature of the electrode process (Figure 2) indicates diffusion controlled nature of the electrode process.
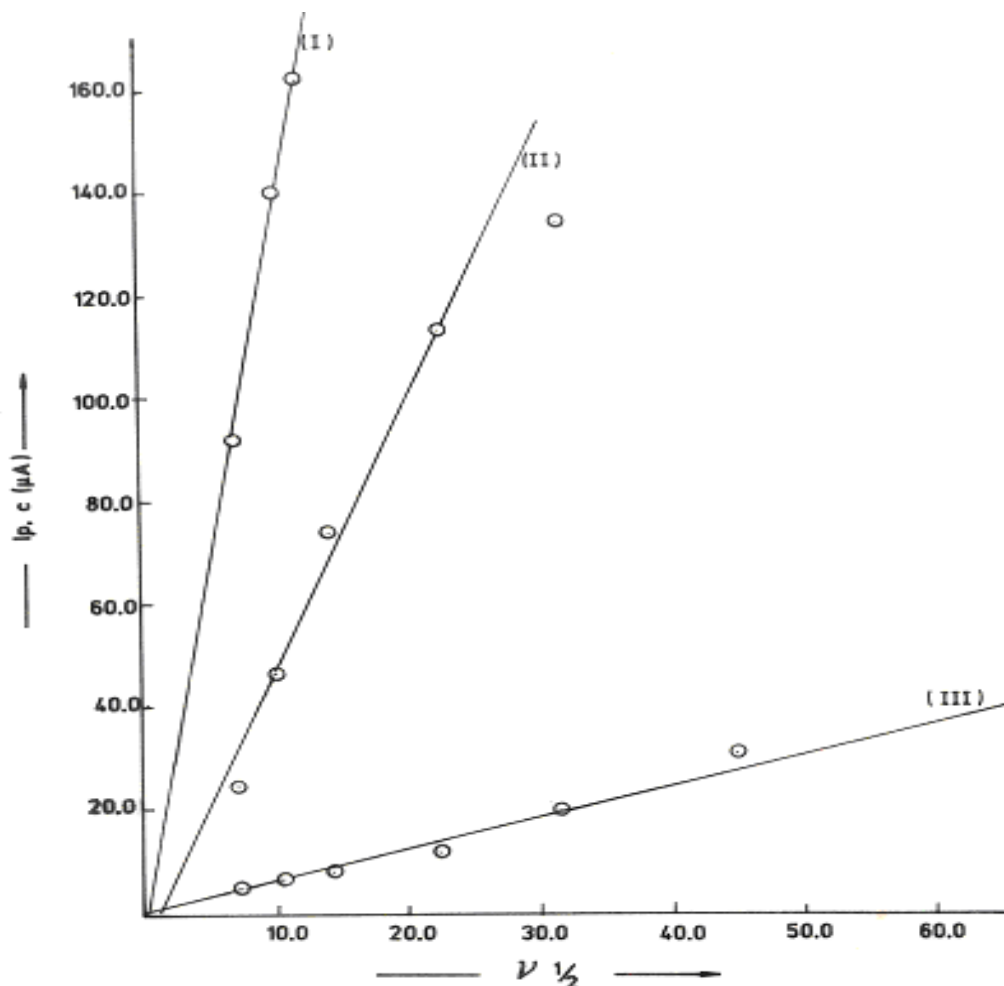

Figure 2. Plot of i_{pc} vs $v^{1/2}$ metanil yellow solution at (I) pH 6.5 (II) distilled water (III) pH 7.9 at platinum working electrode, conc = 2 x 10^{-4} M.

3.2 Effect of pH

The shape and characteristics of voltammograms were strongly dependent on the pH of the medium. Well-defined cathodic peaks in acidic pH range are obtained with both platinum and glassy carbon electrodes. The cathodic peak shifts towards negative potential and anodic peak potential exhibits positive shift with increasing pH, which indicates that proton transfer occurs as a step consecutive to an irreversible electrode process. The potential of cathodic peak of metanil yellow is shifted linearly towards more negative values with increasing the pH between 2 and 6.5. At pH > 6.5, the E_{pc} is pH independent. The linear regions of the E_{pc} – pH plot intersect at about 6.5 (Figure 3), a value which is in accord with the pKa value. This indicated the reduction of unprotonated species. These results are presented in Table 1.
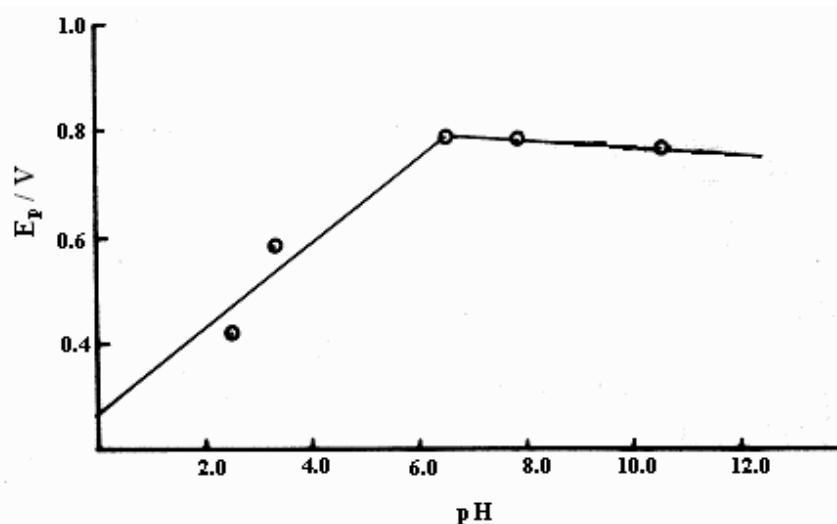
Figure 3. Plot of E_p vs pH of metanil yellow solution at scan rate of 200 mv s^{-1} at platinum foil working electrode (conc = 2 x 10^{-4} M).

Table 1. Voltammetric characteristics of metanil yellow at various pH before electrochemical treatment at Pt electrode, v = 500 mV s^{-1}, Conc 2x10^{-4}M

S.No	pH	$-E_{pc}$/V	$-i_{pc}$/ μA	$-E_{pa}$/V	$-i_{pc}$/ μA
1.	2.5	0.617	153.0	0.456	159.3
2.	3.3	0.780	132.9	0.584	124.5
3.	6.5	0.975	134.3	0.623	121.7
4.	7.9	0.986	137.8	0.847	55.0
5.	8.8	0.962	133.8	0.840	79.4
6.	10.5	0.963	123.8	0.828	102.0

3.3 Differential pulse polarographic studies

A single four-electron irreversible reduction peak is observed in the pH range 2.5 to 12.0 at mercury electrode. This may be attributed to reduction of the azo group (-N=N-). The shift in E_p towards more cathodic potential with pH with a break at pH 6.5 was observed and after that there was constancy in E_p till pH 6.5 suggesting the participation of protons in rate determining step. Analysis of peak $E_{d.e.}$ vs $\left[\log\left(\dfrac{i}{i_d - i} \right) - 0.546 \log t \right]$ plot and the shift of peak potential towards more negative potential with the concentration suggests the irreversible nature of the electrode process (Figure 4).

3.4 Controlled potential coulometric studies

The number of electrons involved in cpe were determined at different pH and in neutral aqueous medium. The value of 'n' was found to be 4.0 ± 0.2 for neutral medium and at various pH. The progress of electrolysis was monitored by recording decrease in current (i_{pc}) with time. The current decreases exponentially with time during CPE, at both platinum foil and steel foil electrodes,(Table 2) till only background current was realised (Figure 5).

Reduction peak of metanil yellow in aqueous neutral medium as well as at varying pH, disappeared within 1-3 hours of electrolysis leading to the decolourisation of the dye solution. The

comparative overlay of initial coloured and electrolyzed dye solution in aqueous medium at Pt foil working electrode is depicted in Figure 6.
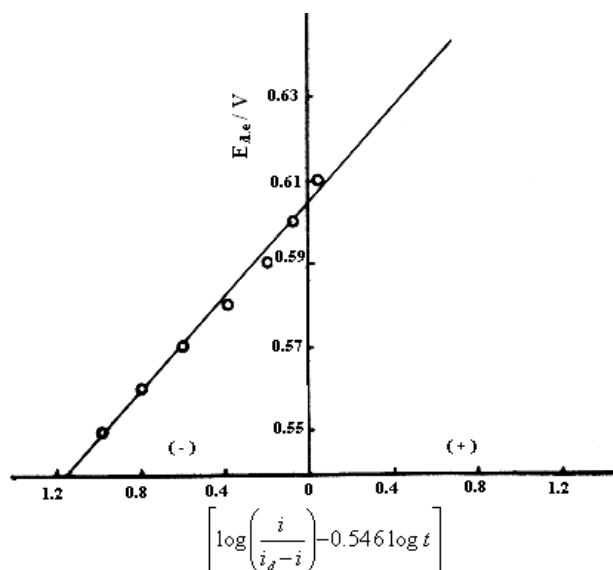

Figure 4. Plot of $E_{d.e.}$ vs $\left[\log\left(\dfrac{i}{i_d - i}\right) - 0.546 \log t \right]$ of metanil yellow solution at pH 8.8 (2×10^{-4} M)

Table 2. Gradual fading of colour and decrease in current with time for Metanil Yellow (2×10^{-3} M) in distilled water

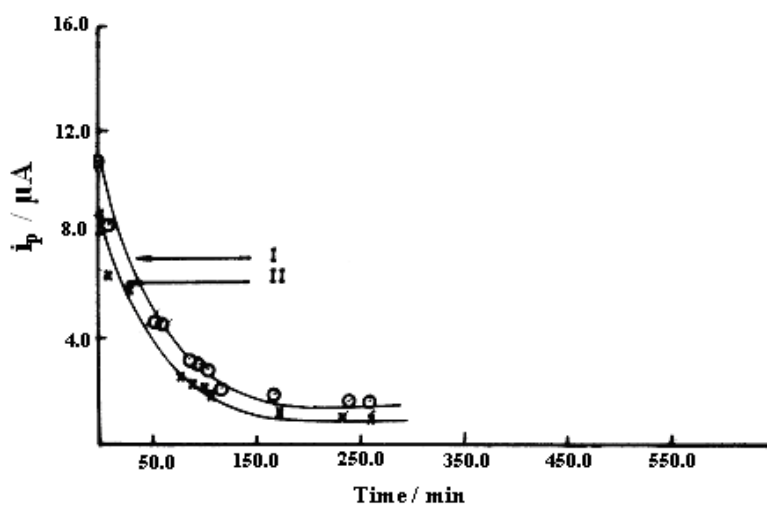| Time taken for Electrolysis (minutes)	Current i_{pc}	
	Pt foil	steel foil
00	10.80	8.56
10	8.40	6.68
20	5.14	3.54
40	5.17	3.12
80	4.64	2.72
90	3.19	2.51
100	3.10	2.30
120	2.02	2.00
180	1.98	1.80
240	1.90	1.40
255	1.88	1.20

Figure 5. Comparative plot of ip vs time during electroreduction of metanil yellow at (I) steel foil working electrode (II) platinum foil working electrode (conc. = 2 x 10-4 M)
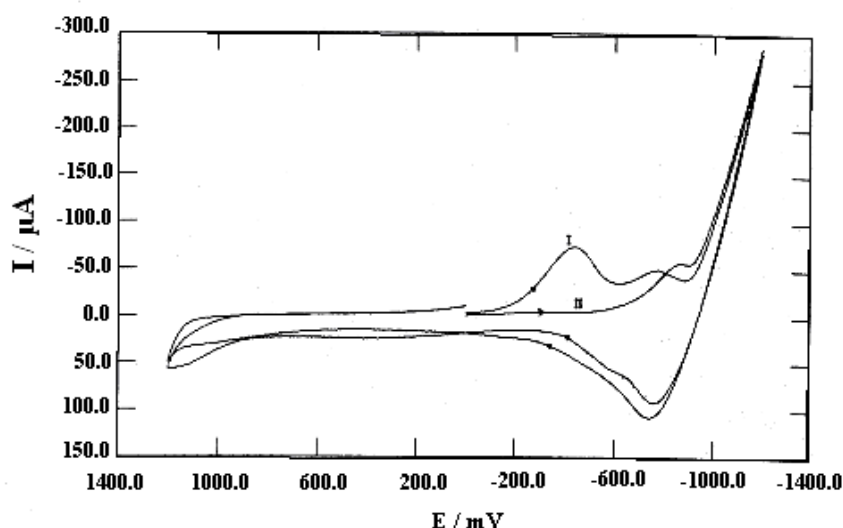
Figure 6. Cyclic voltammograms of metanil yellow (2 x 10-4 M, 6.5 pH) at platinum working electrode, scan rate 200 mV s-1; (I) Before electrochemical treatment (II) After electrochemical treatment.

3.5 Spectral studies

UV-visible spectra of metanil yellow (conc. $2x10^{-4}$ M) at distilled water were recorded at λ_{max} 475 nm. The progress of controlled potential electrolysis was monitored by recording spectral changes at different time intervals. Absorbance systematically decreased with the progress of electrolysis. The absorbance measurement for before electrochemical treatment and after treatment is depicted in Figure 7. The kinetics of decolourisation was followed by recording changes in absorbance with time at selected wavelengths. The kinetics of decolourisation was found to be varying with initial dye concentration. Using linear log A_t Vs time (t) plots, the reaction was found to be obeying I order rate expression both in case of steel and platinum foil working electrodes. First order rate constants for electrochemical reduction at steel foil and platinum foil electrodes are presented in Table 3.
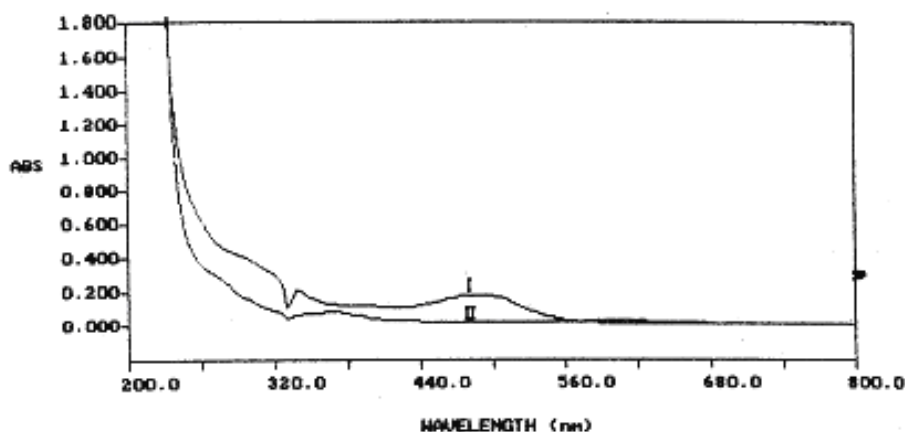

Figure 7. UV-vis spectrum of metanil yellow (2 x 10-4 M, 6.5 pH) at platinum working electrode showing absorbance; (I) Before electrochemical treatment (II) After electrochemical treatment.

Table 3. Kinetic Parameters for Metanil Yellow

Compound	Electrode	Conc.	Initial Applied. Potential	K abs /Min^{-1}	t$^{1/2}$	R$_{abs}$
Metanil Yellow	platinum foil	2×10^{-4} M	-1.20 V	2.41×10^{-2}	28.75	5.52×10^{-6}M
	steel foil	2×10^{-4} M	-1.20 V	2.30×10^{-2}	30.13	5.52×10^{-6}M

3.6 Chromatographic studies

After cpe, thin layer chromatographic studies were carried out on decolorized/-electrolyzed solution of metanil yellow in aqueous medium. It was observed that electrolyzed solution exhibited two spots in acetone-water system (9:1) leading to the conclusion that two decomposition products were formed after electrolysis at - 1.20V. The end products were further identified by GC-MS. The mass spectrum of the electrolyzed solution clearly exhibits following molecular ion peak and fragment ion peak.

1. m/z = 43   Presence of $-NH_2$
2. m/z = 93 $C_{11}H_{13}N_2O$
    Note: Being highly polar, the SO_3Na group could not be retained by the column of GC hence, could not be detected in the peak.
3. m/z = 185

3.7 COD removal

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the feasibility of the electrochemical process for the degradation of metanil yellow dye solution.The electrochemical degradation of the azo dye, metanil yellow was carried out at different experimental conditions. After electrolysis completely decolourise effluent with substantial reduction in COD value was obtained. The dye solution (2×10^{-4} M) in distilled water gets completely decolourised in an hour with complete disappearance of reduction (ip,c) and oxidation peak (ip,a). At different pH, no peak was observed in electrolysed solution implying complete reduction of chromophoric group. The rate kinetics was also monitored during electrolysis and it was observed that reaction follows first order rate. Comparison of the COD value of the initial dye solution with electrolysed solution indicates the COD value is substantially reduced. It is observed that the COD value shows a significant decrease from 2160 mg L^{-1} to a final value of 180 mg L^{-1} at platinum and 2160 mg L^{-1} to 292 mg L^{-1} at steel electrodes indicating less toxicity of the related products in comparison to the original dye and good potential of employing electrolytic technique.

3.8 Proposed mechanism

On the basis of the results of coulometry, controlled potential electrolysis, chromatographic and spectral analysis following reduction mechanism (Figure 8) is postulated. During the reduction, the polarized molecule formed in the first step takes a proton from the medium and gets protonated to form (B). The next step is slow and rate determining in which the reduction of azo group -N=N- takes place by intake of two electrons (2e) giving hydrazo moiety and resulting in the formation of (C). In step III, (C) hydrazo moiety consumes two electrons and a proton resulting into the two decomposition products (D) and (E) having m/z of 93 and 185. This mechanism of reduction of azo dye is also supported by GC-MS results.

4. CONCLUSIONS

The electroactivity of metanil yellow on different electrode material has established and studied for the first time. The electrochemical reduction of metanil yellow under the conditions described in this work is an irreversible process controlled by diffusion. Both platinum and steel electrodes exhibit great stability and resistant to redox and acidic/basic environments showing no deactivation. During the electrochemical degradation process the COD decreases by approximately 91.7% at

platinum electrode and 86.5% at steel foil electrode with complete color removal. The developed electrochemical treatment is in good agreement with the already reported photocatalytic degradation method (Sleiman et al. 2007). The proposed electrochemical procedure is a good alternative approach for wastewater treatment with considerable lowering of toxicity.
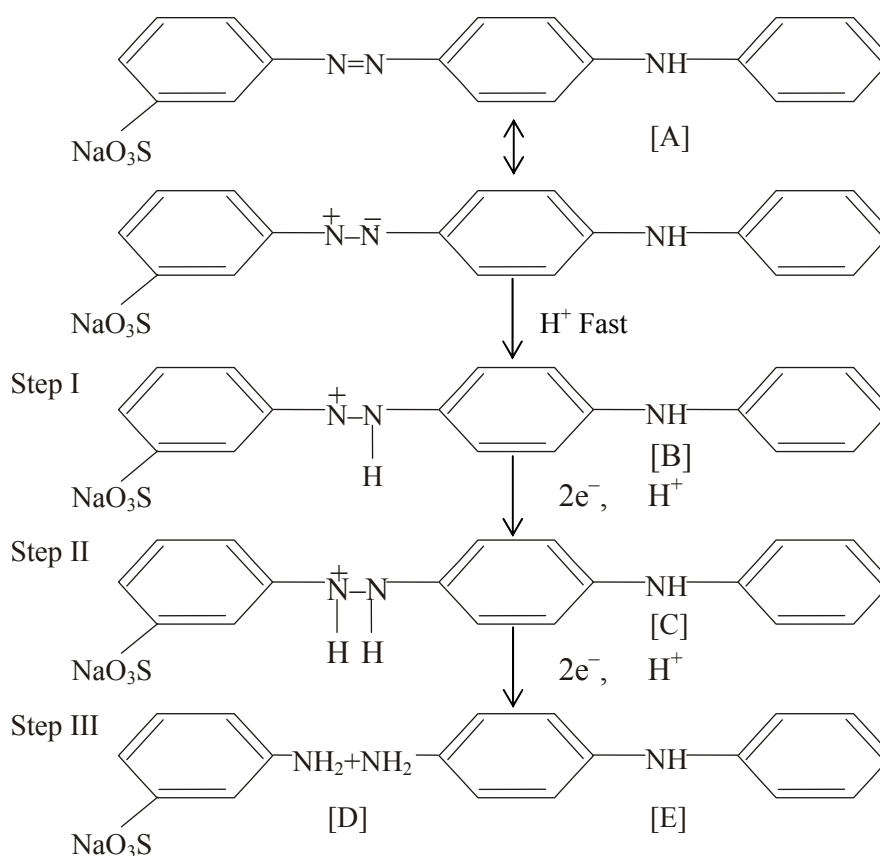

Figure 8. Reaction mechanism of metanil yellow

REFERENCES

APHA (1995) Standard Methods for examination of water and wastewaters, 17ed. American Public Health Association, Washington DC.

Britton, H. T. S., 1956. Hydrogen Ions, 1,.D. Van Nostrand company, New York.

Brown, D., 1987. Effects of colorants in the aquatic environment. Ecotoxicology Environ. Safety; 13:139–147.

Ciardelli, G., Ranieri, N., 2001. The treatment and reuse of wastewater in the textile industry by means of ozonation and Electroflocculation. Water Res.; 35:567-572.

Daneshvar, N., Sorkhabi, H. A., Kobya, M., 2004. Decolorization of reactive dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections. J. Haz. Mat.; 112:55–62.

Do, J. S., Chen, M. L., 1994. Decolorization of dye containing solutions by electro-coagulation. J. Applied Electrochem.; 24:785–790.

Fan, Li., Zhou, Y., Yang, W., Chen, G., Yang, F., 2008. Electrochemical degradation of aqueous solution of amaranth azodye on ACF under potentiostatic model. Dyes and pigments; 76:440-446.

Gomez, E., Ledoux, E., Monget, J.M., Marsily De, G., 2003. Distributed surface groun water coupled model applied to climate or long term water management impacts at basin scale. European Water, 1/2:3-8.

Gupta, S., Sundarrajan, M., Rao, K. V., 2003. Tumor promotion by metanil yellow and malachite green during rat hepatocarcinogenesis is associated with dysregulated expression of cell cycle regulatory proteins. Teratog. Carcinog. Mutagen; 1:301-12.

Gupta, V. K.a, , , Jain, R.,b Varshney, S., 2007. Electrochemical removal of the hazardous dye reactofix red 3 BFN from industrial effluents. J. Colloid Inter. Sc.; 312:292-296.

Gutierrez, M. C., Crespi, M., 1999. A review of electrochemical treatments for color elimination. J. Soc. Dyers Colour; 115:342–345.

Hausen, B. M., 1994. A case of allergic contact dermatitis due to metanil yellow. Contact Dermatitis; 31:117–118.

Jain, R., Shriastava M., 2008. Phtocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide. J. Haz. Mat.; 152:216-220.

Jain, R., Sharma, N., Jadon, N., Radhapyari, K., 2006. Electrochemical studies on a textile azine dye Safranin T. Inter. J. Environ. Poll.; 27:121-129.

Jain, R., Sharma, N., Radhapyari, K., 2009. Electrochemical treatment of pharmaceutical azo dye amaranth from Waste Water. J. Applied Electrochem.; 39:577-582.

Jain, R., Varshney, S., Sikarwar, S., 2007. Electrochemical techniques for the removal of reactofix golden yellow 3 RFN from industrial wastes. J. Colloid Inter. Sc.; 313:248-253.

Khanna, S. K., Das, M., 1991. Toxicity, carcinogenic potential and clinical epidemiological studies on dyes and dyes Intermediates. J. Sc. Indus. Res.; 50:964-974.

Khanna, S. K., Singh, G. B., Dixit, A. K., 1985. Use of synthetic dyes in eatables of rural area, J. Food Sc. Tech.; 22:269-273.

Lee, Y. H., Pavlostathis, S. G., 2004. Decolorization and toxicity of reactive anthraquinone textile dyes under methanogenic Conditions. Water Res.; 38:1838-1852.

Lorimer, J. P., Manson, T. J., Plates, M., Phull, S. S., 2000. Dye effluent decolorisation using ultrasonically assisted electro-Oxidation. Ultrason. Sonochem.; 7:237–342.

Meric, S., Kaptan, D. O., lmez, T., 2004. Color and COD removal from wastewater containing reactive black 5 using Fenton's oxidation process. Chemosphere; 54:435-441.

Moura, L.M.A., Gonçalves, E.P.R., Amorim, M.T., Teles de Vasconcelos, L.A., González Beça, C.G., 2004. Adsorption of yellow lanasol 4g reactive dye in a simulated textile effluent on gallinaceous feathers. European Water, 1-16.

Ollgaard, H., Frost, L., Gastler, J., Hensen, O. C., 1999. Survey of azo-colorants on Denmark: Milgo, Project 509. Danish Environmental Protection Agency.

Prasad, O. M., Rastogi, P. B., 1983. Haematological changes induced by feeding a common food colour, metanil yellow, in albino mice. Toxicol Lett.;16:103-7

Prevot, A. B., Baiocchi, C., Brussino, M. C., Pramauro, E., Savarino, P., Augugliaro, V., 2001. Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO2 suspensions. Environ. Sc. Tech.; 35:971-976.

Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., Ovelleiro, J. L., 1998. Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. Water Res.; 32: 2721-2727.

Sleiman, M., Vildozo, D., Ferronato, C., Chovelon, J. M., 2007. Photocatalytic degradation of azo dye metanil yellow: optimization and kinetic modeling using a chemometric approach. Applied Catalysis B: Environmental; 77:1-11.

Sundarrajan, M., Prabhudesai, S., Krishnamurthy, S. C., Rao, K. V., 2001. Effect of metanil yellow and malachite green on DNA synthesis in N-nitrosodiethylamine induced preneoplastic rat livers. Indian J. Exper. Bio.; 39:845-52.

Vlyssides, A. G., Loisidou, M., Karlis, P. K., Zorbas, A. A., Papaioannou, D., 1999. Electro- chemical treatment of a textile dyewastewater using Pt/Ti electrode. J. Haz. Mat.; B70:41–52.

Walker, G. M., Weatherley, L. R., 1999. Adsorption of acid dyes on to granular activated carbon in fixed beds. Water Res.; 731:2093-2101.