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VOLTAMMETRIC INVESTIGATIONS OF SOME FOOD AND TEXTILE DYES

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ABSTRACT. The removal of the color by oxidation or reduction can be carried out in an electrochemical cell directly without the addition of redox chemical reagents, working at room temperature [1,2].

The main purpose of this paper is the study of the electrochemical behavior of the azo linkage –N=N– in oxidation and reduction for Methyl Orange (MO), Tartrazine (T) and Ponceau 4R (P) in order to establish the influence of the experimentale conditions (pH, electrolytes, concentrations, nature of the electrode material) on the discoloration yield.

Preliminary electro-oxidation experiments for a model molecule (MO), on boron doped diamond electrodes (BDD) showed a decrease of the absorbance with 97-98%, a decrease of total organic carbon (TOC) with 88-90% and of the cemical oxygen demand (COD) with 86-90%.

Keywords: Electrochemical oxidation, azo dyes, boron doped diamond electrode.

INTRODUCTION

The effluents from textile dyeing are colored so these waters will have to be treated before being released back to environment [1]. On the other hand some of the synthetic dyes used in the food industry are toxic [2].

Azo compounds are among the most profoundly explored classes of organic compounds both from theoretical and practical viewpoints. The presence of an azo linkage in aromatic compounds makes them highly important in dye-stuff industry, pharmacy and dosimetry [3]. Various synthetic azo dyes have been shown to induce a variety of tumors in mice and rats and to exhibit inhibitory effects on the biosynthesis of proteins [4].

Electrochemical methods for color removal are new and environmental friendly techniques. Electrochemical reduction of azo compounds usually occurs in $2e^-$, $2H^+$ transfer to give hydrazo products. However in the presence of strong electron donating groups, reduction has been found to occur in $4e^-$, $4H^+$ reaction to give amino compounds as the final products. An excellent review on the electroreduction of azo compounds has also appeared in the literature [5].

The electrochemical oxidation of organics on different electrode material uses the hydroxyl anions produced on the anode, as electrogenerated oxidizing species [4, 5]. Studies of the oxidation of azo compounds in pure solvents, aqueous solutions or mixtures of aqueous buffers and organic solvents have appeared

occasionally in the literature and the number of studies concerning oxidations of azo compounds is by far less than those dealing with reductions. Electrochemical oxidation of azo compounds in aprotic solvents like acetonitrile has been performed in connections with studies involving light fading of azo dyes, synthesis and electrode mechanisms [9,10].

The oxidation of Solochrome Violet RS in connection with complexometric determinations of aluminum has been suggested to involve an oxidation to the azoxy compound [11,12]. Matrka et al. [13] reported that the hydroxyl derivatives 4'-hydroxy-4-N, N-dimethylazobenzene and 2'-hydroxy-4-N, N-dimethylazobenzene were initially oxidized to a quinoid structure, followed by demethylation. Ladanyi et al. [14] also studied the oxidation of 4-aminoazobenzene in 50% alcohol buffer and came to the conclusion that this oxidation was similar to the oxidation of substituted anilines [9,15] and the final product is N-[4-(p-phenylazo)-phenyl]-1,4-benzoquinone-monoimine [14]. Malik et al. [16] studied the bisazo dye Fast Sulfone Black-F both reductively and oxidatively in connection with an investigation of the electrochemical reduction mechanism of this dye. Fogg and Bhanot [17,18] used linear scan and cyclic voltammetry with glassy carbon and carbon paste electrodes for the determination of food colorants. Among the studied colorants were several common azo dyes, such as Tartrazine, Oxalazinesodium and related compounds [19], Amaranth, Sunset Yellow FCF and Black PN. Fogg and Bahnot also developed a flow injection system with amperometric detection for the determinations of these compounds, [18] but did not study the electrode process in detail.

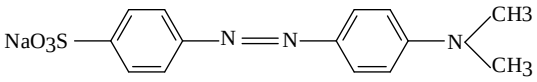
EXPERIMENTAL

In order to obtain the voltamperommetric data, fundaments for the electrochemical color removal in waste water, cyclic voltammetry (BAS 100W and AUTOLAB PGSAT 12 computer aided electrochemical systems) have been used. The control of the electrochemical discoloration was achieved using UV-Vis spectrophotometer (UNICAM Helios β) and (TOC) and (COD) determination equipment (Shimadzu Corporation, Tokyo, Japan).

The textile and food azo dyes were obtained from Sigma Chemical Co. USA and were used as received. The stock solution of the dye (1.0 mM) was prepared in double distilled water. Voltammograms were recorded in different buffer solution of ionic strength 0.1. The pH of buffer solution was measured using the JENWAY 3330 pH meter, after standardization with potassium hydrogen phthalate and borax buffers. For recording voltammograms, equal volumes of dye solution and buffer solution of appropriate pH were mixed. Nitrogen gas was bubbled for 8–10 min. before recording the voltammograms. BDD electrodes for cyclic voltammetry (from CSEM, Neufchatel, Suisse) others working electrodes (GC, Au and Pb from BAS Co.) had an area of 0.2826 cm^2. All potentials refer to Ag/AgCl,KCl at an ambient temperature of 20±2 ℃.

Controlled potential and current electrolysis of 0.1- 0.5 mM solution of the dye was carried out both in a conventional divided H-type cell and electrochemical undivided – BDD cell, at potential 50-70 mV more positive than the peak potential observed in the voltammograms. The working electrode for electrolysis was glassy carbon, PbO_2 and BDD plate (area 63,6 cm^2), and counter electrode was cylindrical platinum gauze.

Voltamperometric behavior of Methyl Orange – influence of the electrode and electrolyte nature



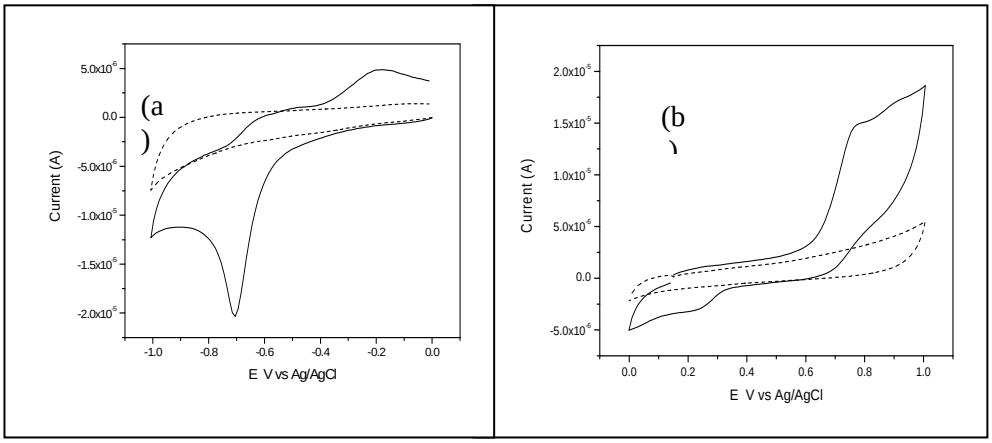


Figure 1. VOC of Methyl Orange 10^{-3} M in Na_2SO_4 0.1 M on glassy carbon electrode at 50mV/s; (a)- negative potential range, (b)-positive potential range.

The CVs on glassy carbon electrode confirm that in both reduction (Fig.1a) and oxidation (Fig.1b) direction the azo bond was affected, respectively at ≅ -700mV and 750mV. The electrochemical oxidation of (MO) on the investigated electrodes (glassy carbon, Au and BDD), has been demonstrated Fig. 2, the oxidation current on BDD is higher at the same concentration (10^{-3}M) and scan rate (100 mv.sec^{-1}). Figure 2 shows that the electro-oxidation process takes place in the same potential range (737-782 mV/Ag, AgCl,KCl) for all the investigated electrodes.

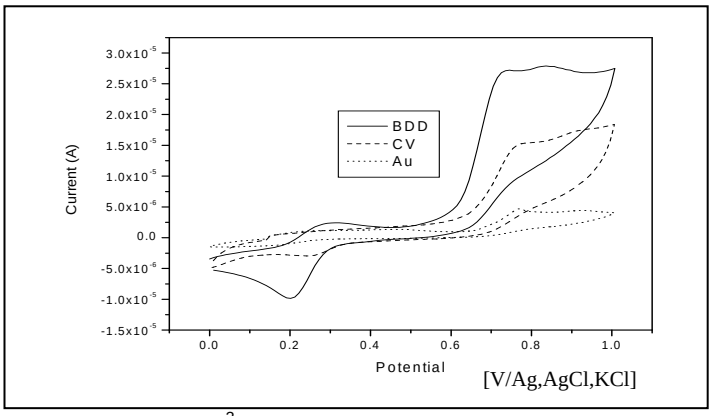


Figure 2. Voltammograms of 10^{-3}M (MO) at different scan rates on GC, Au and BDD electrode in Na_2SO_4 0,1M.

The dependence peak current-square root of the sweep rate is a straight line, a proof for a diffusion mechanism. As expected, the peak current increases with larger scan rates (Fig. 3).

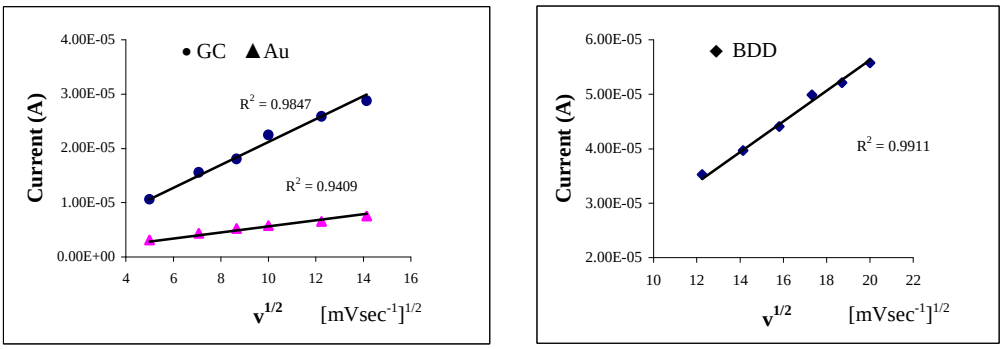


Figure 3. The plot of peak current versus the square root of sweep rate for oxidation of 10^{-3}M (MO) on different electrodes materials: glassy carbon (GC), gold (Au), boron doped diamond (BDD) in Na_2SO_4 0.1M.

The peak potential was dependent on pH and during the oxidation of (MO) shifted towards more positive values with pH increase. The plots of *E*p *vs.* pH can be approximated as two segments of straight lines which intersect at pH 5.1 which correspond to the value of pK_a. The dependence of *E*p on pH for the (MO) oxidation can be represented by the following equations:

for $(MO)_{ox}$: pK_a= 5.1

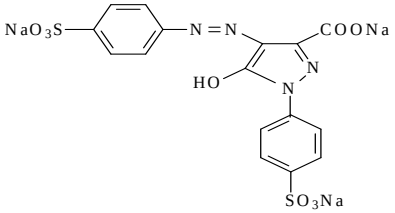
$$Ep_{(pH\ 2.0-5.1)} = [716.4 + 21.4\ pH]\ mV\ vs.\ Ag/AgCl$$

$$Ep_{(pH\ 5.1-11.0)} = [909.59 - 17.9\ pH]\ mV\ vs.\ Ag/AgCl$$

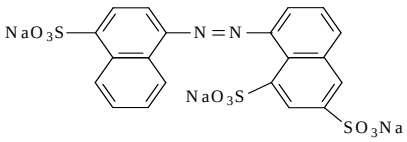
From the data presented in Table 1, the nature of the electrode seems to be not very important concerning the oxidation potential range, but we observe the electrocatalitic activity of BDD, proved by an important increase of the oxidation current, Fig.2. This behavior could be explained by the electrode surface modification of BDD during the polarization [20].

During the reduction of azo group in (MO), the peak potential shifted towards more negative potential with pH increase and the pK_a value could be estimated at 5.2-5.8 depending on the initial potential and scan rates.

Electrochemical reduction of food dyes (Tartrazine and Ponceau 4R)



TARTRAZINE (E_{102})
trisodium 5-hidroxy-1-(4-sulphonatophenil)-4-(4-sulphonatophenilazo)-H-prazol-3-carboxylate



PONCEAU 4R (E_{124})
trisodium 2- hidroxy-1-(4-sulphonato-1-naphtilazo) naphtalin-6,8-disulphonat

The CVs for the first scan, in negative potential range, exhibited two reduction peaks for (T), (E_{1red}= -1.11V; E_{2red} = -1.51V), Fig. 4 and only one (E_{red}= -1.35V) for (P) in the pH range 2.0–11.3.

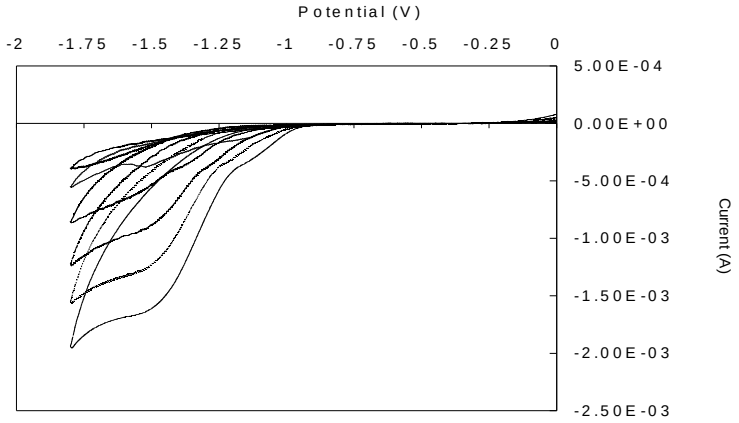


Figure 4. CV's for the reduction of Tartrazine on BDD in 0.1M Na_2SO_4; $\Delta C=10^{-3}$-10^{-2}M

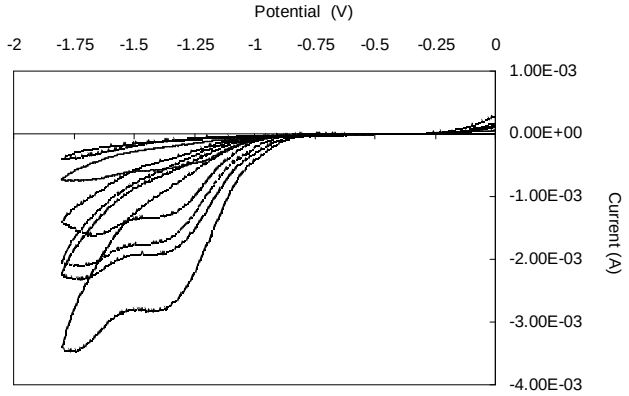


Figure 5. CVs for the reduction of Ponceau 4R on BDD electrode in 0.1M Na_2SO_4; pH=7.1; v=50mV.sec^{-}; $\Delta C=10^{-3}$-10^{-2}.

The reduction of azo bond in Tartrazine and Ponceau 4R is a diffusion controlled processes for all the investigated electrodes (reduction: BDD, GC, Hg; oxidation: BDD, GC, Au), in KCl 0,1M and Na_2SO_4 0.1 M solutions, from 50-400 mV.sec^{-1}. When the direction of sweep was reversed, one small anodic peak was observed in the entire pH range, for both (P) and (T). When the sweep direction was again changed, two new small reduction quasi-reversible peaks were noticed at pH > 4.0. The peak currents of the first peak was more or less constantly below pH 7.0 and showed a decrease at higher pH. It was concluded that supplementary peaks were due to reduction of the products generated in oxidation.

The reduction (T) and (P) on Hg takes place easier (ε_{red}= 400mV for T) and (ε_{red}=254mV for P), due to the adsorptive interactions of azo dye with the mercury surface, but the use of Hg for the discoloration of the dyes aqueous solution could be a polluting alternative. For this reason our interest in the future will be the preparative reduction of (P) and (T) in boron doped diamond batch cell.

The cumulative data on the redox processes of azo linkage in (MO), (T) and (P), on different electrodes and at different pH, in Na_2SO_4 0.1M and Britton-Robinson buffers (BR) are presented in Table 1.

Table 1.

Peak potentials for the investigated compounds depending on pH and the electrode nature

Potential (V/ vs. Ag/AgCl,KCl)									
pH	~2.51			~7.1			~12.7		
Dye	GC	Au	BDD	GC	Au	BDD	GC	Au	BDD
$(T)_{red}$	- 0.72	-	-1.01	-1.1	-	-1.11	-	-	-1.52
$(P)_{red}$	-0.65	-	-1.02	-0.88	-	-1.32	-0.92	-	-1.58
$(MO)_{ox}$	0.80	0.81	0.86	0.77	0.76	0.74	0.70	0.69	0.75

The data concerning the influence of pH over the electroreduction potential of the alimentary dye (P) and (T) has been achieved on Hg electrode.

The dependence of *E*p on pH for (T) and (P) can be represented by the following equations:

for (T) pK_a= 6.8*:*

$$Ep_{(pH\ 2.0-6.8)} = [79.96 + 97.38\ pH]\ mV\ vs.\ Ag/AgCl;\ R^2=0.95$$

$$Ep_{(pH\ 6.8-12.0)} = [28.88 + 607.74\ pH]\ mV\ vs.\ Ag/AgC;l\ R^2=0.99$$

for (P) pK_a= 5.9:

$$Ep_{(pH\ 2.0-5.9)} = [174.1pH - 222.22]\ mV\ vs.\ Ag/AgCl;\ R^2=0.95$$

$$Ep_{(pH\ 5,9-12.0)} = [579.83 + 34.16\ pH\ ]\ mV\ vs.\ Ag/AgC;\ R^2=0.99$$

Discoloration of synthetic solution by electrochemical oxidation - preliminary results

The preliminary experiments on electrochemical oxidation of (MO) were carried out in a 1L reactor on BDD electrode, pH neuter (0.1M Na_2SO_4), at 0.5 A.

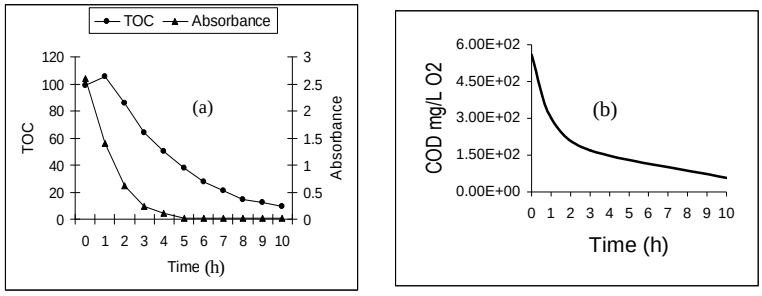


Figure 6. The variation of Absorbance, TOC and COD during the 10 hours electrolyses. pH=7.1 (0.1M Na_2SO_4); I= 0.5 A; D=168 L/h

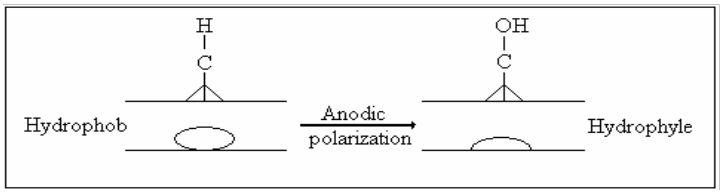
The electrode diameter was 10 cm with an area of 63.6 cm^2.

During the electrolyze samples were taken each hour and UV-VIS, TOC and COD determinations were made.

Figure 6 shows the evolution of absorbance, TOC (a) and COD (b).

CONCLUSIONS

Electrochemical oxidation of (MO), (T) and (P) on BDD electrodes can be used for treating and removal of azo dyes waste waters, in the accessible potential range, on BDD and GC electrodes. The good results obtained on BDD could be explained by the electrocatalytic activity of modified surface during the polarization.



The data on the dependence of peak potential on pH - pK_a= 6.8 for (T), pK_a= 5.9 for (P) and pK_a= 5.9 and pK_a= 5.1 for (MO), nature of electrode and electrolyte were reported.

During the electro-oxidation of (MO) on BDD electrode, after 10 hours the absorbance records a decreasing of 99.5%, the COT 90.3% and COD with 89.6%.

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