Energy saving by the intensification of the electro- Fenton process for water treatment using boron doped diamond electrode

Ilie Siminiceanu[1*], Carmen Ionela Alexandru[1], Eric Brillas[2]

[1]Gheorghe Asachi Technical University of Iasi, Department of Chemical Engineering, 73, Bd. Mangeron, 700050 Iasi

[2]University of Barcelona, Department of Physical Chemistry, Spain

Romania; isiminic@yahoo.com

The mineralization of Crystal Violet in acidic aqueous solution by the electro- Fenton process has been studied in an undivided electrolytic cell under galvanostatic conditions, using either a boron doped diamond (BDD) or a platinum (Pt) anode. The effectiveness of the process has been evaluated not only through the mineralization degree but also by means of the mineralization current efficiency (MCE) and the specific energy consumption (SEC). The results are presented for a relevant set of operating conditions: $C^o_{Fe^{2+}} = 1.0$ mM , $C^o_{Cu^{2+}} = 1.0$ mM, $TOC^o_{CV} = 100$ ppm, I = 300 mA, pH = 3, T= 308 K. The use of BDD anode instead of Pt is a major means to intensify the electro- Fenton process: the mineralization degree was 92.52 % with BDD, compared to 66.37% with Pt, under the same other conditions. In addition, the specific energy/ exergy consumption with BDD was 20% inferior to that with Pt.

1. Introduction

The *Crystal Violet* (hexamethyl pararosaniline chloride) also named Methyl Violet 10B, or Gentian Violet, is extensively used in textile dying, paper printing, as a biological stain, and as a dermatological agent (Saquib and Muneer, 2003). It is a mutagen, a mitotic poison, and has been used for many years in veterinary medicine, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus (Saquib and Muneer, 2003). Littlefield et al. (1985) found that CV is carcinogenic in mice at several different organ sites. They also reported the reduction of CV to leuco-CV by human, rat and chicken intestinal micro flora under anaerobic conditions. Because of its low cost, its effectiveness as an antifugal agent for commercial poultry feed, and its ready availability, the people may be exposed to this dye and its metabolites through the consumption of treated poultry products. On the other hand, it is estimated that over 15 % of the dyes produced are lost during synthesis and processing with wastewater (Sahoo et al., 2005).Therefore, there are both environmental and human health concerns regarding the bioaccumulation of CV in aquatic systems (CV water solubility is 1.68 %). The most effective methods to treat effluents containing CV or other dyes proved to be the advanced oxidation processes (AOPs), based on *in situ* generation of hydroxyl radical (Martinez-Huilte and Brillas , 2009). Unfortunately,

there are few published studies on the CV degradation in water by AOPs (Siminiceanu et al., 2008). All of these used heterogeneous photocatalytic degradation on TiO_2 in batch reactors with powdered catalyst in suspension. Despite the encouraging laboratory- scale results this process has unsolved problems regarding the scale- up.

The present paper reports a study performed to test the efficiency of the electro- Fenton (EF) method for the degradation of Crystal Violet (CV) in water. *Electro- Fenton (EF)* is a relatively new advanced electrochemical oxidation process (AEOP) for the purification of water containing organic pollutants. It has been already applied for the degradation of a number of organic pollutants in water (Panizza M.and Cerisola, 2003; Brillas et al., 2007). In the EF process one or both reactants of the Fenton reaction is/ are electro-generated.

2. Materials and method

The *Crystal Violet* (hexamethyl pararosaniline chloride, or methyl violet 10B), used as substrate in the degradation experiments, was purchased from Aldrich. It has the empirical formula $C_{12}H_{30}N_3Cl$ and the structure from the figure 1. The analytical grade sulfuric acid was purchased from Merck. Anhydrous sodium sulfate and heptahydrated ferrous sulfate, both of p.a. purity, were supplied by Fluka.All solutions were prepared with high purity water obtained from a Millipore Milli- Q system, with conductivity lower than $6x10^8$ S cm at 298 K.

The electrochemical processes and measurements were performed with an Amel 2049 potentiostat- galvanostat. The solution pH was measured with a Crison 2000 pH- meter. The total organic carbon (TOC) for the treated solutions was determined with a Shimadzu 5050 TOC analyzer, using the standard non- purgeable organic carbon method.

All electrolyses were conducted in an open, undivided and thermostated cylindrical cell containing 100 mL solution stirred with a magnetic bar. A 3.0 cm^2 Pt sheet of 99.99 % purity, supplied by SEMPSA, was used as anode in the first run. Then the Pt anode was replaced by a BDD anode with the same exposed area. The preparation of the BDD anode by the method of Christos Comninellis is described elsewhere (Paniza et al., 2001). The cathode was a 3.0 cm^2 carbon- PTFE electrode fed with an oxygen flow rate of 20 mL min^{-1} for the electro-generation of H_2O_2 from the reaction (2).
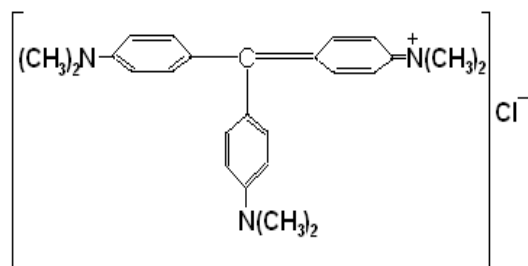

Figure 1: Structure of crystal violet (methyl violet 10B).

Crystal Violet aqueous solutions (100 mL) were prepared at TOC concentrations of 50 ppm, 100 ppm, 200 ppm and 400 ppm. All solutions contained 50 mM Na_2SO_4 as background electrolyte. Sulfuric acid was added to adjust pH to 2.0, 3.0 and 4.0.

Suitable quantities of heptahydrated ferrous sulfate have been also added to have initial $FeSO_4$ concentrations of 0.25, 1.0, and 2.0 mM for the electro- Fenton process. The electrolyses were conducted at constant current of 100, 300 and 450 mA for each treatment. In most cases the solution temperature was maintained at 298 K. Separate measurements have been done at 308 K and 318 K in order to find in temperature influence. Six different operation factors have been finally investigated: (1) anode material, (2) solution pH, (3) temperature, (4) current intensity, (5) Fe (II) concentration, (6) initial TOC concentration of the CV solution.

The degradation of CV was monitored by measuring the total organic carbon (TOC) of the treated solution on a Shimadzu 5050 TOC analyzer. The electrolyses were conducted in an open, undivided and thermostated cylindrical cell containing 100 mL CV aqueous solution. The anode was a 10 cm^2 Pt sheet of 99.99 % purity and the cathode was a 3.1 cm^2 carbon- PTFE electrode fed with an O_2 flow of 20 mL min^{-1} to electro generate H_2O_2 from the reaction (1):

$$O_{2\,(g)} + 2\,H^+ + 2\,e^- = H_2O_2 \qquad (1)$$

The oxidizing power of hydrogen peroxide was enhanced in the presence of catalytic Fe^{2+}, added as ferrous sulphate, due to the formation of hydroxyl radical from the Fenton's reaction (2):

$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO^{\cdot} + HO^- \qquad (2)$$

The EF process was also intensified by replacing the Pt anode with a boron doped diamond (BDD) one, prepared according the Comninellis' method (Paniza et al., 2001).

The aim of this work was to determine the influence of the anode material on two important performance criteria: the mineralization current effectiveness (MCE, η_{MIN}) defined by the equation (3), and the specific electrical energy consumption (SEC, ε) defined by the equation (4):

$$\eta_{MIN} = \frac{(\Delta_{TOC})_{\exp} \cdot z \cdot F \cdot V_L}{I \cdot M_C \cdot n_C \cdot \tau \cdot 10^3} \qquad (3)$$

$$\varepsilon = \frac{U_{cel} \cdot I \cdot \tau}{(\Delta_{TOC})_{\exp} \cdot V_L} \qquad (4)$$

where: I= current intensity (A); M_C = atomic weight (12 g/mol); n_C = number of carbon atoms in the CV molecule (25 for CV); z= number of transferred electrons in the mineralization; F= Faraday number (96 487 C/mol); τ = time of mineralization (h); $(\Delta_{TOC})_{\exp t}$ = experimental TOC variation (mg/ L) from the beginning to the reaction time τ ; V_L= liquid volume.

3. Results and discussion

The experimental results, for the other factors fixed at their optimal values, are presented in the Table 1. The calculated performance criteria MCE and SEC are presented in the Figures 1 and 2.

Table 1: TOC(ppm) decreasing with time for the two anodes at constant factors:
$C^o_{Fe}{}^{2+} = 1,0\ mM$, $C^o_{Cu}{}^{2+} = 1,0\ mM$, $TOC^o_{CV} = 100\ ppm$, $I = 300\ mA$, $pH = 3$, $T = 308\ K$.

Time, minutes	Platinum anode	BDD anode
0	100.00	100.00
10	64.03	55.31
20	45.16	46.11
40	38.63	38.17
60	36.86	35.58
120	35.53	28.85
180	35.51	23.50
240	34.94	18.18
300	34.92	12.08
360	33.63	7.48

The replacement of Pt with BDD results in better performances: the MCE becomes 1.53 to 3.25 times higher, whereas SEC is 1.43 to 2.81 times lower. The values of SEC obtained in this work are of the same order of magnitude as those found (Hamza et al., 2009) for the mineralization of Methyl Violet by EF in similar conditions.
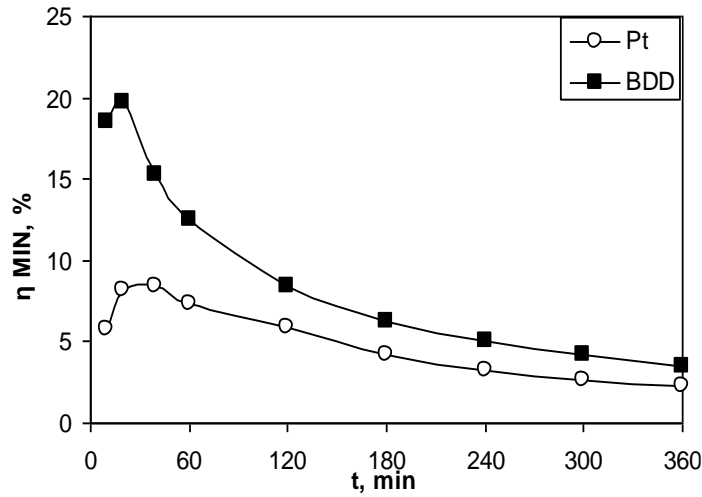

Figure 2: The influence of the anode material on the MCE($C^o_{Fe}{}^{2+} = 1.0\ mM$, $C^o_{Cu}{}^{2+} = 1.0\ mM$, $C^o_{CV} = 100\ ppm$, $I = 300\ mA$, $pH = 3$, $T = 308\ K$, $Na_2SO_4\ 50\ mM$)
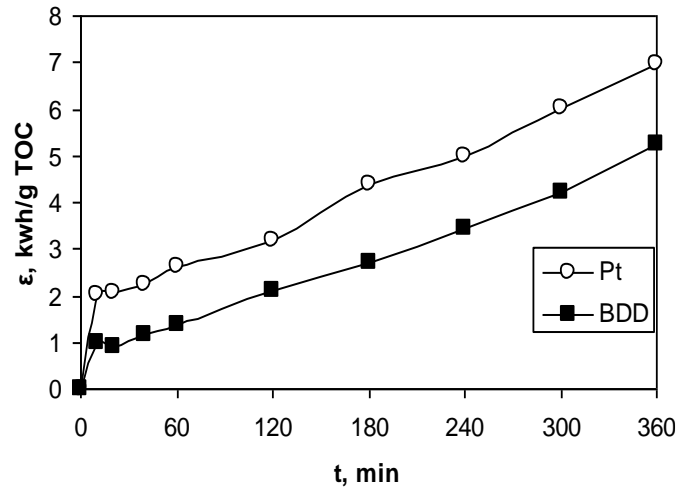
Figure 3: The influence of the anode material on the SEC ($C^o_{Fe}{}^{2+}= 1,0$ mM , $C^o_{Cu}{}^{2+}=$ 1,0 mM, $C^o_{CV} = 100$ ppm, I = 300 mA, pH = 3, T= 308 K)

4. Conclusions

It has been demonstrated that acidic wastewaters with Crystal Violet can be almost completely purified by the electro- Fenton method where oxidizing hydroxyl radicals (HO˙) are generated from Fenton' s reaction between added ferrous ions and hydrogen peroxide produced by two- electron reduction of oxygen on a O_2- diffusion carbon-PTFE cathode. The influence of six major operating factors (anode material, pH, temperature, current intensity, Fe (II) dose and initial TOC) on the mineralization degree has been investigated in order to find the optimal conditions.

The mineralization was significantly enhanced by using a new boron doped diamond (BDD) anode instead of the conventional platinum electrode. This may be due to the additional hydroxyl radicals generated by water discharge on the BDD anode through the reaction (3).

The use of BDD anode instead of Pt is a major means to intensify the electro- Fenton process: the mineralization degree was 92.52% with BDD, compared to 66.37% with Pt, under the same other conditions. In addition, the specific energy/ exergy consumption with BDD was 20% inferior to that with Pt.

Notation

$C^o_{Cu}{}^{2+}$, initial dose of cupric ion, mM;

$C^o_{Fe}{}^{2+}$, initial dose of ferrous ion, mM;

CV, crystal violet acronyme;

TOC^o_{CV}, initial total organic carbon of CV solution, ppm;

$\eta_{MIN,}$ mineralization current efficency (MCE);

ε, specific electrical energy consumption (SEC).

References

Brillas E., Baños M.A., Skoumal M., Cabot P.L., Garrido J. A., Rodriguez R.M., 2007, Degradation of the herbicide 2, 4- DP by anodic oxidation, electro- Fenton and photoelectro- Fenton using platinum and BDD anodes, Chemosphere, 68, 199- 209.

Hamza M., Abdelhedi R., Brillas E. and Sires I., 2009, Comparative electrochemical degradation of the triphenylmethane dye Methyl Violet with boron- doped diamond and Pt anodes, Journal of Electroanalytical Chemistry, 627, 41- 50.

Littlefield N.A., Blockwell B.N., Hewitt C.C. and Gaylor D.W., 1985, Chronic toxicity and carcinogenicity studies of gentian violet in mice, Fundamental and Applied Toxicology, 5, 902- 912.

Martinez- Huilte C.A., Brillas E., 2009, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. A General Review, Applied Catalysis B: Environmental, 87, 105- 145.

Paniza M., Michaud, P.A., Cerisola, G., and Comninellis, Ch., J. 2001, Journal of Electroanalytical Chemistry., 507, 206- 211

Sahoo C., Gupta A.K. and Pal A., 2005, Photocatalytic degradation of Crystal Violet on silver ion doped TiO_2, Dyes and Pigments, 66(3), 189- 196.

Saquib M. and Muneer M., 2003, TiO_2- mediated photocatalytic degradation of a triphenylmethane dye in aqueous suspensions, Dyes and Pigments, 56, 37- 49.

Siminiceanu I., Alexandru C.I. and Brillas E., 2008, A kinetic model for the Crystal Violet mineralization in water by the electro- Fenton process, Environmental Engineering and Management Journal, 7(1), 9- 12.