Automated System for Study of the Crystal Violet Mineralization in Water by the Electro-Fenton Method

C.I. Alexandru[1], M.C.Branzila[2], I.Siminiceanu[1]

[1]Technical University “Gh. Asachi” Iasi Faculty of Chemical Engineering,
Blvd.D.Mangeron 71, 700050, Iasi, Romania
[2]Technical University “Gh. Asachi” Iasi. Faculty of Electrical Engineering.,
Blvd.D.Mangeron 53, 700050, Iasi, Romania

Abstract-The mineralization of acidic aqueous solutions with 0.166 to 1.333 mM Crystal Violet (CV) in 50 mM Na_2SO_4, as background electrolyte has been studied by the electro- Fenton method, where the oxidizing hydroxyl radicals were produced from the Fenton reaction between added ferrous ions and hydrogen peroxide generated at a oxygen- diffusion cathode. The influence of six operating factors on the mineralization degree has been investigated: anode material (platinum versus boron doped diamond), pH, Fe (II) dose, current intensity, temperature and initial concentration of CV. The mineralization degree had a maximum (91.18 %) after 420 minutes of electrolysis, under the following optimal conditions: boron doped diamond (BDD) anode, pH3, 1mMFe (II), 300 mA, 308 K, and 100 ppm initial total organic carbon (TOC).

Keywords*:* crystal violet, mineralization degree, BDD anode, experimental study

I. Introduction

Electro- Fenton (EF) is a 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 such as aniline [1-3]; 2,4-dichlorophenoxyacetic acid[4], the herbicide 3,6-dichloro-2-methoxybenzoic acid [5], the azo dye Acid Red 14 [6] and the Reactive Black 5 azo dye [7] in aqueous media.

The present paper reports a study performed to test the efficiency of the EF method for the degradation ot Crystal Violet (CV) in water using an automated system. This substance is largely used in textile dyeing and paper printing, as well as a highly effective antifungal agent for commercial poultry food J Several papers reported on the carcinogenic effects of CV in mice [8-10]. Therefore, waters containing CV must be treated by advanced oxidation processes, based on hydroxyl radical generation [11].

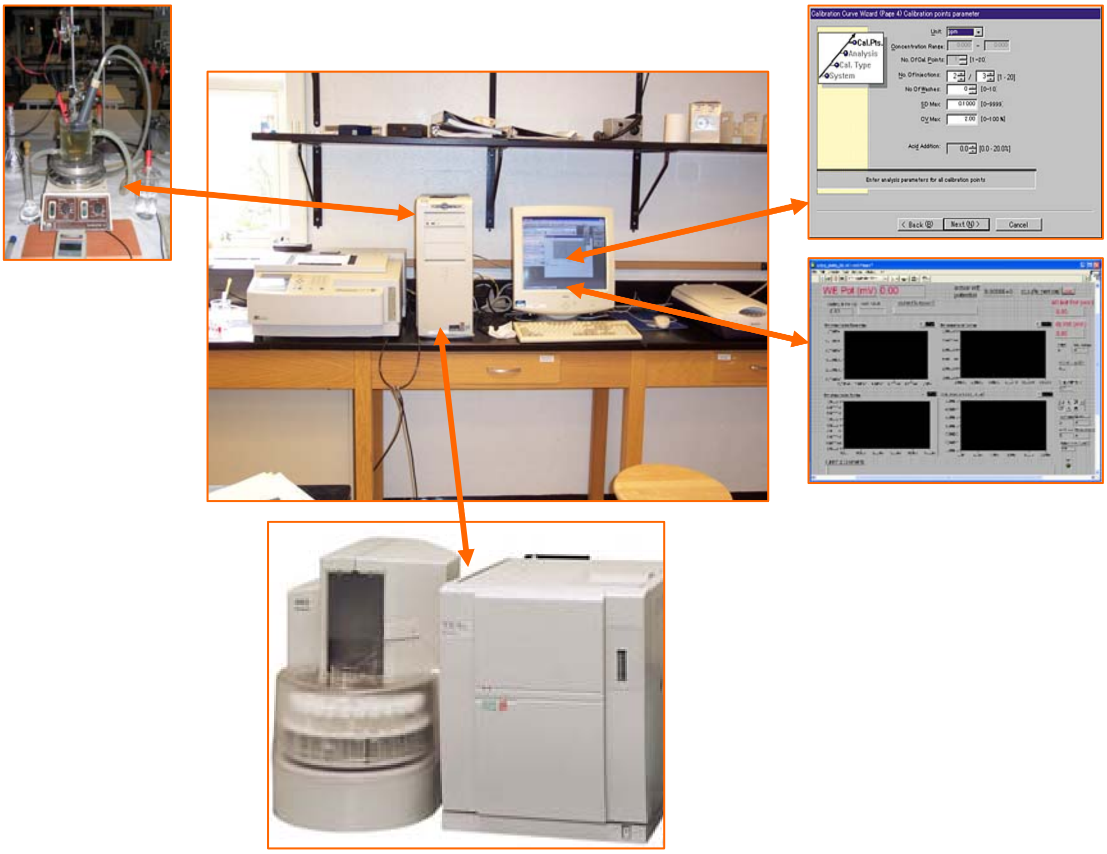
This study compares the performance of platinum to those of BDD in the EF degradation of CV in water. Once the advantage of BDD a has been proved, the influence of other five operation *m* parameters has been investigated: pH, Fe (II) dose, current intensity, temperature and the initial CV concentration in water.

II. Experimental system

The *Crystal Violet* (hexamethyl pararosaniline chloride, or methyl violet 10B), used as substrate in the degradation experiments, was purchased from Aldrich. 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 6xl0^{8}Scm at 298K.

The electrochemical processes and measurements were performed with an Amel potentiostat-galvanostat with a fully automatic function allowing the instrument to search and adjust itself for the optimum current range from 1μA to 1A in few milliseconds, a continuous control of the positive feedback allowing compensation for the iR drop signal. Both current and potential are permanently available as low-impedance replicas at the front-panel along with all digital I/O for current ranges and cell control, thus greatly simplifying the connection with a standard acquisition board to be fitted into a PC. The solution pH was measured with a pH-meter with PC interfacing capability. The total organic carbon (TOC) for the treated solutions was determined with a Shimadzu TOC analyzer, using the standard non-purgeable orgaraaj carbon method. Total TOC analyzer operation, control, and data collection are handled by personal computer running enhanced software. Wizards allow simple input of measurement and calibration settings.

All information is stored as files in the personal computer for reference and re-use. The measurement conditions and results can be output to EXCEL or other application software or input from other application software like LabVIEW.


Calibration Curve Wizard (Page 4) Calibration points parameter

Unit: ppm

Concentration Range: 0.000 - 0.000

No. Of Cal. Points: 1 [1-20]

No. Of Injections: 2 / 3 [1 - 20]

No Of Washes: 0 [0-10]

SD Max: 0.1000 [0-9999]

CV Max: 2.00 [0-100 %]

Acid Addition: 0.0 [0.0 - 20.0%]

Enter analysis parameters for all calibration points

Fig.1. Automated system for study of the Crystal Violet Mineralization in Water by the Electro-Fenton Method.

All electrolyses were conducted in an open, undivided and thermostated cylindrical cell containing 100mL 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 cathode was a 3.0cm^2 carbon-PTFE electrode fed with an oxygen flow rate of 20$mLmin^{-1}$ for the electro-generation of H_2O_2.

III. Results and discussions

The anode material has a great influence on the mineralization of CV. After 420 min of electrolysis, the mineralization degree was 91.18 % with BDD anode compared to only 46.08 % with platinum. This great difference can be explained by the additional hydroxyl radicals formed on the surface of BDD anode during the water discharge.

The pH influence According to experimental data the optimal pH is 3.0.

The iron dose influence. The mineralization degree, at a given time, increases with the quantity of added iron until a concentration of 1 mM $FeSO_4$. The typical range for the iron dose in the “chemical” Fenton process is one part of Fe per 5-25 parts of H_2O_2.

The current intensity is a very important kinetic factor. The quantity of H_2O_2 generated is proportional to the applied current until 450mA. Although, currents greater than 300mA bring little growth of the mineralization degree.

The temperature influence. The conversion steadily increased with the temperature in the 298-318 range. The results will be theoretically exploited in the kinetic study and modelling. A temperature greater than 308 K is not interesting from a practical point of view because of the economic reasons.

The initial concentration of CV in water, calculated in ppm of TOC, has an important influence on the TOC conversion. The corresponding CV molar concentration of 50, 100 and 400 ppm TOC are 0.1666, 0.3333 and 1.3333 mM respectively. The results will be useful for the kinetic equation identification. Practically, aqueous CV solutions up to 10,000 ppm TOC could be investigated (the solubility of CV in water at 298K is 1.68%). Nevertheless, such concentrated waste water is rarely encountered in the industrial practice.

IV. Conclusions

Using this complex automated system, 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 an O_2-diffusion carbon-PTFE cathode. 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.

All PC interfaced apparatus used for studying the influence of six major operating factors investigated, in order to find the optimal conditions (anode material, pH, temperature, current intensity, Fe (II) dose and initial TOC) improve the quality of measurements.

The presented system has the capability to perform tasks that diminish the work quantity of a specialized person and is capable to communicate with other computers. This system can be well integrated in a distributed measurement system in the electrochemical field and especially in the water treatment field. Using LabVIEW software we assure the flexibility and the portability of the system.

The proposed system is not quite simple, but is flexible, include data acquisition systems that combined with LabVIEW software, become a very useful measurement instrument.

References

1. Br1llas, £., Casado, J., Chemosphere, 47,2002, p. 241
2. Brillas, E., Mur, Eva, and J. CASADO, J, J. Electrochem. Soc, 143,1996, p. 49
3. Brillas, E., Mur, Eva, Sauleda, R, Sanchez, Laura, PEROL, J,DOMENECH, X., CASADO, J., Applied Catalysis B: Environmental, 16,1998, p. 31
4. Brillas, E, Calpe, J.C., Casado, J., Wat. Res., 34,2000, p. 2253
5. Brillas, E., Banos, Ma., Garrido, J.A., ElectrochimicaActa, 48,2003, p. 1697
6. Wang, A., Qu, J., Ru, J., Liu, H., Ge, J., Dyes and Pigments, 65,2005, p. 227
7. Kusvuran, E, 1rmak, S., Yavuz, H.I., Sam1l, A..Erbatur, O.,Journal of Hazardous Materials, 119,2005, p. 109
8. L1ttlef1eld, N.A., Blackwell, B.N, Hewitt, K.K., Gaylor, D.W.,Fundam. Appl. Toxicol., 5,1985, p. 902
9. Dacampo, R., Moreno, S.N., Drug Metab. Rev., 22,1990, p. 161
10. Hu, C, Tang, Y., You, J.C., Wong, P.K., Applied Catalysis B: Environmental, 40,2003, p. 131
11. Sahoo, C, Gupta, A.K., Pal, A, Dyes and Pigments, 66,2005,p. 189
12. Comninellis, Christos, Electrochemical Hydroxylation Using boron Doped Diamond Anodes, 7lh International Mini- Symposium on Diamond Electrochemistry, Keio University, Japan, March 30,2004, p. 125
13. Comninellis, Christos, Application of Synthetic BDD Electrodes in Electrooxidation, in: Diamond Electrochemistry (A. Fujishima, editor), Elsevier, Amsterdam, 2005, p. 477
14. Zhang, H., Choi, H.J., And Huang, C.P., J. Hazard. Mater, in print February 6,2006
15. C.I. Alexandru, I. Siminiceanu, Scientific Annals of the „Al.I.Cuza”University of Iassy, XIV, 21-26 (2006)
16. M.C. Brinzila, M.Temneanu, M.Crețu, M.D.Pereira, C.Donciu, *System for environmental monitoring using a data acquisition board by parallel port*, Buletinul Institutului Politehnic din Iasi, Tomul L(LIV), Fasc.5, 2004, pp.737-742, ISSN 1223-8139.