Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4793-4804

Application of Electro-Fenton Oxidation of Refractory Organic Pollution

AZRI YAMINA MOUNIA*, ZEROUALI DJILALI and A.H. AL-TAIAR
Laboratory of Electrochemical, Department of Chemistry, Faculty of Sciences, University of Sciences and Technology of Oran U.S.T.O. BP-1505 el M'naouer Oran 31000, Algeria
Tel/Fax: (213)(41)425763, E-mail: myazri@yahoo.fr

In order to eliminate organic pollution contained in waste water of refinery, Electro-Fenton technique is applied to incinerate lubricate additive biocide N,N-methylenebismorpholine ($C_9H_{18}N_2O_2$). This process is based on a continuous electrogeneration of hydrogen peroxide in acidic solution by reducing the dissolved oxygen using an industrial graphite cathode. The cathodic potential, the electrolysis time and the dissolved oxygen level were systematically studied. The results obtained indicate that the optimal electrochemical conditions to electrogenerate hydrogen peroxide are: cathodic potential of -500 mV/SCE and current density of 1.4 mA/cm^2. The production of hydrogen peroxide increased with the aeration and electrolysis time, then became stationary after approximately 2 h of electrolysis. Optimized parameters (potential, oxygen level and concentration of ferrous ions) were also applied to incinerate N,N-methylenebismorpholine. The incineration efficiency of the optimized parameters (potential, current density, COD/Fe^{2+} ratio and aeration) indicates that 97 % of COD was incinerated at 50 mA and the optimal concentration of catalyst is between 28 and 56 mg/L. The anode electro-activity of N,N-methylenebismorpholine offers other possibilities to oxidize directly this substance.

Key Words: Indirect oxidation, Electro-Fenton, Biocide, Hydrogen peroxide, Oxygen reduction.

INTRODUCTION

The oxidation of dissolved organic matter constituting pollution in waste water of petroleum industries is traditionally treated by a biological treatment process such as activated sludge, trickling filter and aerated lagoon. However, the use of biological treatment is limited by the biodegradability of same pollutants which did not occur systematically and sometimes this treatment needs chemical oxidation.

Advanced oxidation process (AOP) was developed in the last decade to solve degradation problems of refractory substances such as pesticides, phenols, dyes[1-4]. These techniques are fundamentally based on the oxidation power of hydroxyl radical ($OH^{\bullet}$) which is a non-selective powerful oxidant radicals $E_{.OH/OH-}$ = + 2.8V/SHE (standard hydrogen electrode) in acidic medium and a very reactive species. *In situ* generated hydroxyl radicals react with organic pollutants leading to their incineration, their transformation into CO_2, H_2O and inorganic ions.

The production of radical hydroxide is generated by redox reaction of hydrogen peroxide and ferrous ions.

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + Fe^{3+} + OH^- \quad (1)$$

Reaction (1) is called Fenton reaction and the process is called Fenton process.

In the classical Fenton process, the reactants H_2O_2 and Fe^{2+} are simultaneously added to the polluted solution. In the indirect electro-oxidation process (electro-Fenton) hydroxyl radicals are produced *via* Fenton's reaction in homogeneous medium *via* electrogenerated H_2O_2 in the presence of ferrous ions. However the use hydrogen peroxide could be dangerous[5].

According to Pourbaix diagrams, the oxidation/reduction of water and oxygen gives a possible electrochemical way to produce hydrogen peroxide using cathodic reduction of dissolved oxygen in aqueous medium[6].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2)$$

The electroreduction of dissolved oxygen is a multi-electron reaction associated with the formation of a large number of intermediates. Oxygen can be reduced directly to H_2O in a 4-electron transfer:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (3)$$

Or first reduced to H_2O_2 in a 2-electron transfer:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (4)$$

This 2-electron transfer is then followed by reduction of H_2O_2 to H_2O:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (5)$$

The reaction (4) can take place at different cathode such as mercury pool[7], gold[8] reticulate vitrous carbon[9,10], activated carbon fiber[11], carbon felt[12-15] and O_2-diffusion[16-18] cathodes.

The oxidative power of electrogenerated hydrogen peroxide is enhanced in the presence of Fe^{2+} ions[7,17]. Fe^{3+} ions formed by eqn. 1 are reduced at cathode at the potential of oxygen reduction[19]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (6)$$

In general, all reductions in aqueous medium are perturbed by hydrogen evolution, which depends on hydrogen overpotential of the cathodic materials.

Mercury, lead and graphite exhibit large overpotentials for hydrogen evolution, however, mercury and lead are not compatible with the environment and their use in industrial application is not recommended. Actual research on adapted materials focused on boron doped diamond (BDD) which provides a high O_2-overvoltage anode. In this case, hydroxyl radicals are formed in the medium from Fenton's reaction eqn. 1[20,21]. However, industrial applications need electrodes with specific large surfaces, high availability and a minimum cost.

This study is focus on use an industrial graphite for cathodic incineration of N,N-methylene bismorpholine by electro generating hydrogen peroxide in the reactor.

N,N-Methylenebismorpholine is used as biocide to preserve lubricating oil from a biological oxidation. Thus, it is likely a non biodegradable and cannot be treated by conventional techniques. It is not compatible with biological process for the treatment of waste water issued from petrochemical industries. Therefore, it is necessary to incinerate this petrochemical pollutant before the biological treatment.

All electrochemical characterization work is done on the graphite electrode by potentiodynamic polarizations in an acid solution of sodium sulfate.

EXPERIMENTAL

Electrochemical device (Fig. 1): Electrolyses were carried out in double compartment cells, Potentiostat Tacussel 40-1X was used in both potentiodynamic and potentiostatic experiments. The working electrode was industrial graphite with tubular form and an area of 36 cm^2 (Fig. 1). A saturated calomel electrode (SCE) was used as a reference electrode. The counter electrode was platinum grid of 2 cm^2. Potentiodynamic curves were plotted using an X-T Potentiometric Leybold-Herareus Enregistrer.

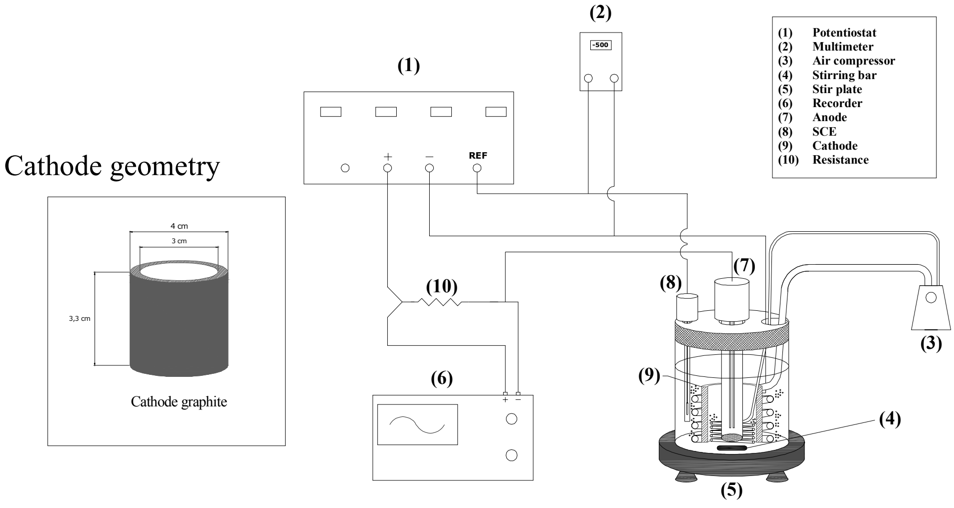

Fig. 1. Experimental device for potentiodynamic test

The anodic compartment consists of a glass tube with a glass-frit bottom which allows its separation of the cathodic compartment. Anodic compartment was filled with a solution of 0.5 M Na_2SO_4 as an electrolyte and the cathodic compartment was filled with an acidified solution of H_2SO_4 (pH 3). Oxygen was bubbled through the cathodic compartment during the experiment with a flow rate of 1 L/min. The resulting oxygen concentration was measured by oxymeter (Model 97-08-99, Orion Research INC). Experimental solutions were magnetically stirred.

All reagents were from Merck or Prolabo products grade analysis. The biocide N,N-methylenebismorpholine was supplied by Algerian petroleum refinery in Arzew. The industrial graphite was from Algerian Electrical and Gas company.

Analytical procedures

Hydrogen peroxide analysis: Concentration of hydrogen peroxide produced in the cell was analyzed by titanium(IV) sulfate method[22]. Spectrophotometer SAFAS 320 G was used to measure the light absorbance of the Ti^{4+}-H_2O_2 orange complex at 410 nm.

Chemical oxygen demand (COD) analysis: Chemical oxygen demand (COD) was measured according to French AFNOR norm. Samples withdrawn during electro Fenton processing were filtered through a Millex-GV Millipore hydrophilic membrane with 0.22 µm pore diameter.

The organic matter was oxidized by potassium dichromate in the presence of silver sulfate (catalyst) and mercury sulfate for 2 h at 170 ºC. COD was calculated from the following equation:

$$\text{COD (mg } O_2 \text{ } L^{-1}) = 8000\ (V_{MS\ blank} - V_{MS\ sample}) \times N_{MS} / V_0$$

where $V_{MS\ blank}$ and $V_{MS\ sample}$ are the volumes of standard Mohr salt solution using the blank and sample respectively, N_{MS} is the normality of the Mohr salt and V_0 is the volume of the sample.

RESULTS AND DISCUSSION

Cathodic potential for hydrogen peroxide electrogeneration: A solution of 0.5 M Na_2SO_4, pH 3 and saturated air (oxygen level = 7 mg/L) were used for cathodic polarizations, air was bubbled during all experiment with a rate of 1 L/min.

A range of potentials of -100 mV/SCE to -900 mV/SCE were investigated with a scan rate of 2 mV/s.

The cathodic I-E curve Fig. 2 shows that, two cathodic limiting current for oxygen and hydrogen peroxide reductions, respectively according to reaction (2) and (3).

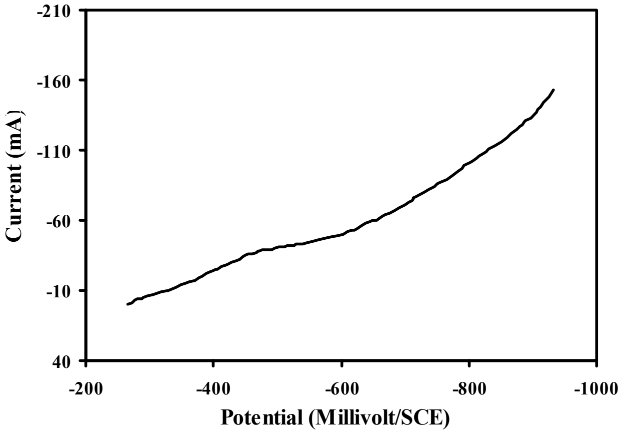

Fig. 2. Potentiodynamic polarization of industrial graphite, Experimental conditions: Scan rate = 2 mV/s; pH = 3; CO_2 = 7 mg/L, Electrolyte = 0.5 M Na_2SO_4

The reduction of oxygen to give peroxide occurs in the potential range of E = -300 mV/SCE to -500 mV/SCE and the hydrogen peroxide reduction in the range of -500 mV/SCE to -650 mV/SCE. For more negative values of potential, cathodic current increases strongly exhibiting hydrogen evolution.

These results are in accordance with Qiang[23] and Oturan and Pinson[24]. Potentials of -600 mV/SCE was obtained by Chu[25] and -550 mV/SCE by Hsioa and Nobe[26]. The use of industrial graphite gives a good concordance in the range of reduction potential of reduction of oxygen to hydrogen peroxide with laboratory graphite.

Potentiostatic electro generation of hydrogen peroxide: Potensiostatic electro generation of hydrogen peroxide was performed in a two compartments cell. Effect of applied potentials, time of electrolysis and time of pre-aeration before the start of electrolysis were experimented for Na_2SO_4 (0.5 M) and (pH 3) solution was magnetically stirred. Hydrogen peroxide was analyzed every hour.

Effect of applied potential: Fig. 4 shows the effect of applied potential on hydrogen peroxide electro generation in the range of -100 mV to -900 mV/SCE. The curve represents a maxima in the potential range from E = -500 to E = - 550 mV/SCE, corresponding to the limiting current as in Fig. 2.

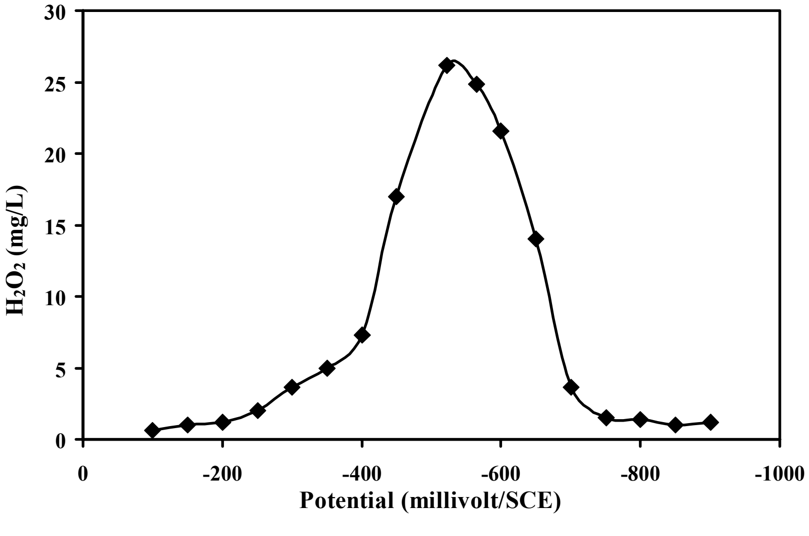

Fig. 3. Effect of cathodic potential on hydrogen peroxide production, Electrolyte: Na_2SO_4 (0.5 M), pH 3, time of electrolysis: 2 h

A maximum rate of hydrogen peroxide (26 mg/L) was electrogenerated at a potential of -500 mV/SCE after 2 h of electrolysis. The best potential for oxygen to hydrogen peroxide reduction (-500 mV/SCE) is in accordance with the results of previous workers[23,24,27] and with the potentiodynamic results.

Effect of time of electrolysis and time of aeration: Effect of aeration before and during the electrolysis on hydrogen peroxide production was experimented for a potential of -500 mV/SCE. A solution of Na_2SO_4 (0.5 M) pH 3, magnetically stirred was used in the experiment.

The results of Fig. 4 showed two parts: a rapid increase of hydrogen peroxide production for times less than *ca.* 2 h, then the production of hydrogen peroxide stabilizes.

The stabilized production of hydrogen peroxide is probably due to equilibrium between the production and decomposition of hydrogen peroxide. Pourbaix's diagram of hydrogen peroxide[6] shows instability domains of hydrogen peroxide which can be oxidized to form oxygen or reduced to form H_2O. The plateau of Fig. 4 indicates that the production and decomposition occur simultaneously after 2 h of electrolysis. The decomposition becomes higher and the production increases slightly.

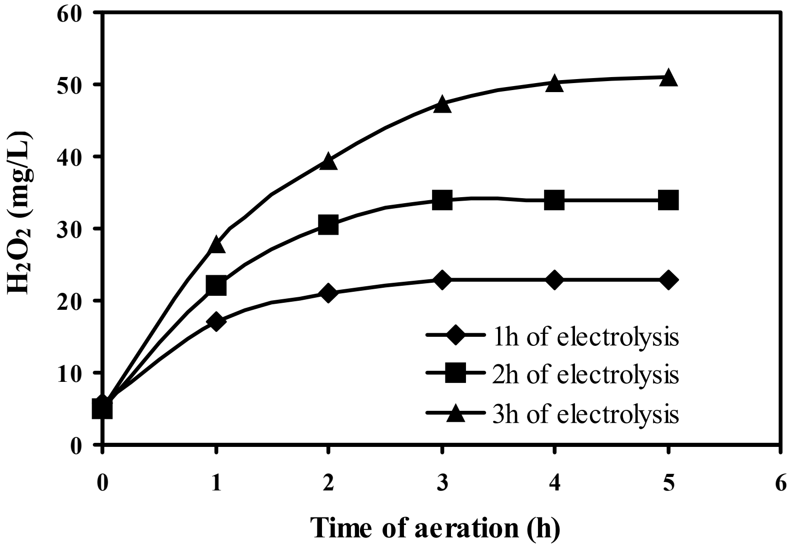

Fig. 4. Effect of time of aeration

Electrochemical characterization of N,N-methylenebismorpholine: The electrochemical behaviour of the biocide N,N-methylenebismorpholine was analyzed using cathodic and anodic potentiodynamic polarizations. A solution of Na_2SO_4 (0.05 M) (pH 3) added with 1 mL of N,N-methylenebismorpholine was experimented on graphite electrode. The pH was systematically controlled during all experiment.

Cathodic polarization: The graphite electrode was cathodically polarized in the potential range of 0 to -1300 mV/SCE with a scan rate of 2 mV/s.

The result in Fig. (5b) shows the effect of biocide on the electrochemical behaviour of the system. The potentials of oxygen and hydrogen reduction moved to larger negative values and the limiting current of oxygen becomes higher.

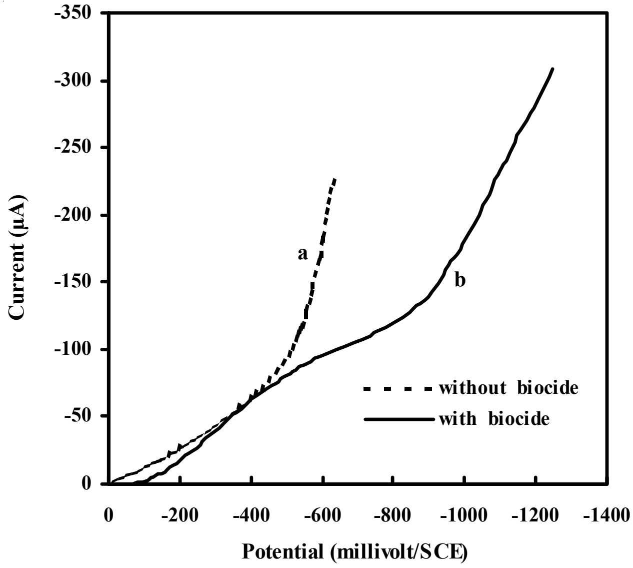

Fig. 5. Influence of biocide on the cathodic polarization, Na_2SO_4 0.05 M, H_2SO_4 pH = 3, Sr = 2 mV/s, Nr = 4000 rds/min, (a) without biocide, (b) with biocide pure 1 mL

The addition of biocide increases the pH from 3 to 7 moving the potentials of hydrogen evolution to more negative values in accordance with thermodynamics data.

Anodic polarization: Fig. 6, shows the result of anodic polarization of graphite at the potential range of 0 to 1400 mV/SCE. The curve (7a), without biocide, shows one anodic limiting current relative to the oxidation of water to hydrogen peroxide in the potential range of: E = 150 to 700 mV/SCE:

$$H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \qquad \text{[Ref. 6]} \qquad (7)$$

The addition of 1 mL of biocide, exhibits two limiting currents in the potential range of 70 to 400 mV/SCE for the first one and 400 to 600mV/SCE for the second. Oxygen gas evolution occurs for anodic potential more positively for the solution containing biocide.

The second limiting current corresponds to an oxidation process controlled by a mass transfer.

The electrochemical behaviour of N,N-methylenebismorpholine depends on the applied potential and its polarity. In the cathodic regions, the potentials of reduction of oxygen and hydrogen moved to the higher negative values. This result can be attributed to the alkaline nature of N,N-methylenebismorpholine.

The neutralizing effect of biocide must be considered for the application of electro-Fenton process and the pH was systematically controlled.

In the anodic regions, N,N-methylenebismorpholine oxidizes in a potential range of: E = 400 mV/SCE to E = 600 mV/SCE with a controlled diffusion kinetics.

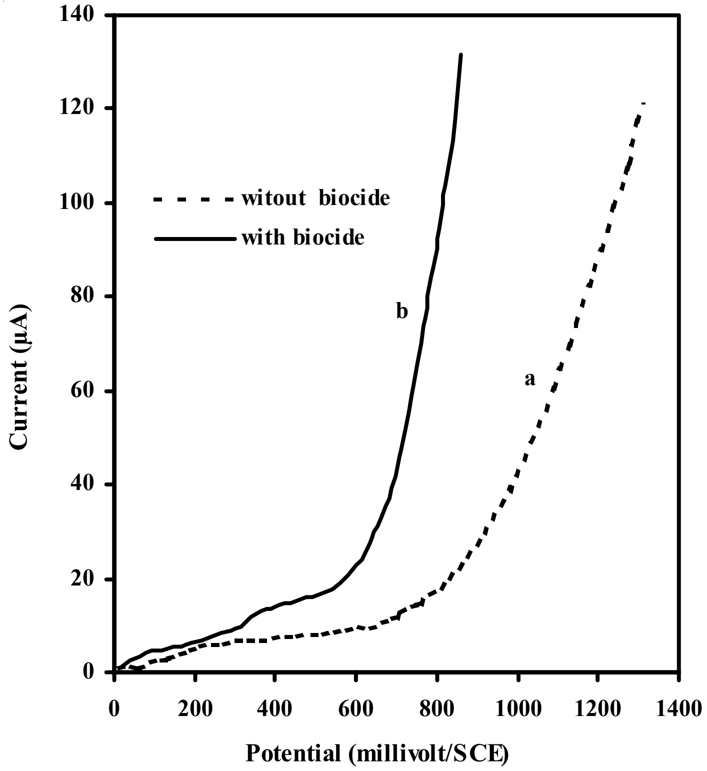

Fig. 6. Influence of biocide on the anodic polarization, Na_2SO_4 0.05 M, H_2SO_4 pH = 3, Sr = 2 mV/s, Nr = 4000 rds/min, (a) without biocide, (b) with biocide pure 1 mL

This result appears interesting because it represents an opportunity for a direct incineration of the biocide.

Optimization of incineration parameters: Indirect incineration of N,N-methylenebismorpholine was performed using an galvanostatic experimental device.

A DC generator Leybolds 15V/20A was used as a current source, industrial graphite and platinum were used as cathode and anode, respectively. The digital ammeter and millivotmeter were used for current and potential measurements.

A solution of 0.05 M Na_2SO_4, air saturated (7 mg/L) at pH 3 were used for all experiments. The solution was magnetically stirred and air was bubbled during all the experiment. Ferrous sulfate was added as Fenton catalyst, 5 min before starting the electrolysis. pH was adjusted in the range of 2.5 to 3 by the adding of sulfuric acid. The performance of incineration was controlled by COD analysis every hour. Effect of applied current and ratio COD/ Fe^{2+} were experimented.

Effect of ferrous sulfate: A solution of 200 mL of 0.05 M sodium sulfate containing pure biocide (COD: 1000 mg/L) was first galvanostatically (I = 30 mA) electrolyzed during 6 h without addition of ferrous ions, the residual COD was analyzed every hour. Fig. 7a shows different changes on COD concentration.

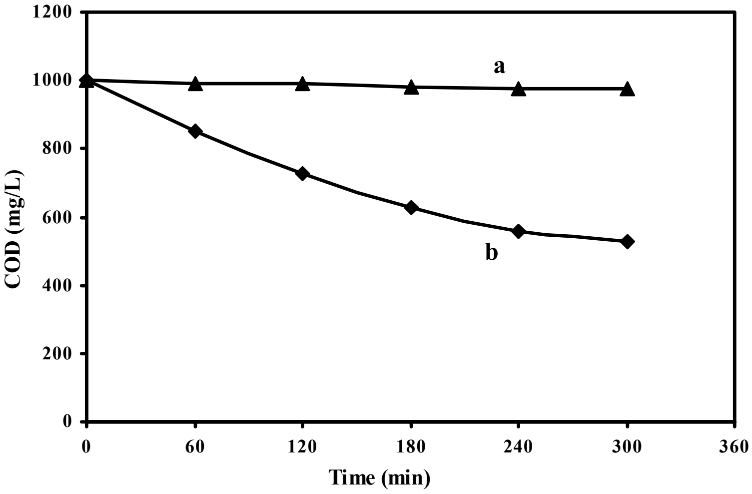

Fig. 7. Abatement of COD as a function of time, (a) not catalyst (b) with a catalyst, $[Fe^{2+}]$ = 12 mg/L. I = 30 mA

The addition of 12 mg/L of ferrous ions corresponding to an approximate ratio of $[H_2O_2]$/[iron(II)] = 2^{28} shows a decrease in residual COD Fig. 7b. A residual concentration of 580 mg/L was unregistered after 5 h of electrolysis representing to an efficiency of 42 %.

Applied current effect: Applied current of 12, 30.50, 75 and 100 mA were used in similar conditions of previous experiment. Fig. 8 shows time evolution of the residual COD.

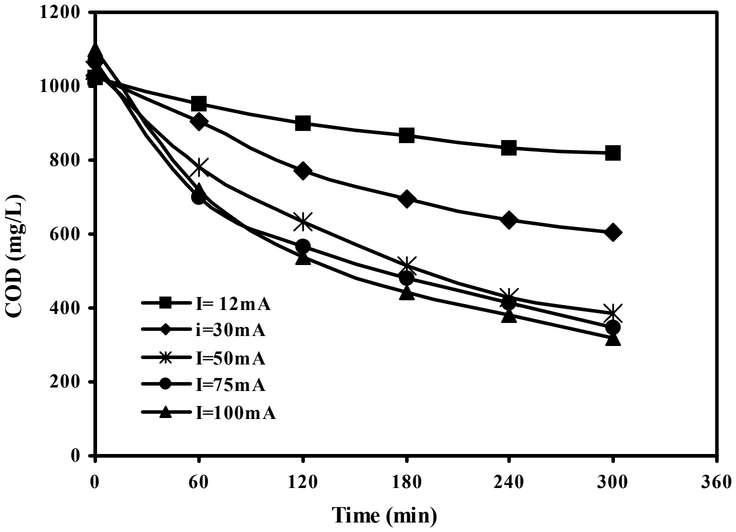

Fig. 8. Effect of applied current on the incineration of biocide, 0.05 M Na_2SO_4 pH = 3, CODi = 1000 mg/L ± 100, $[Fe^{2+}]$ = 12 mg/L, CO_2 = 7 mg/L

The kinetics appears more rapid during the first 2 h then the decrease of residual COD becomes lower. The residual values of COD for 6 h of electrolysis and for different applied currents are shown in Fig. 9.

The result shows two parts of different applied currents. For the current less than - 50 mA (-1.4 mA/cm^2), the rate of incineration of the biocide increase with the applied current, for the current higher than 50 mA the rate of incineration stabilizes and becomes independent. The current density of -1.4 mA/cm^2 for N,N-methylenebismorpholine incineration represents an optimum, the potential of the cathode was unregistered each 0.5 h and showed a variation in the values range of :- 480 mV/SCE at starting of electrolysis to - 620 mV/SCE at the end of electrolysis.

Ratio COD/Fe(II) effect: The effect ratio of COD/Fe(II) on efficiency of the incineration was experimented for 2 h of galvanostatic electrolysis (50 mA).

A solution of Na_2SO_4 0.05M (pH 3) saturated with air and magnetically stirred was used in all experiments. N,N-Methylenebismorpholine was added in the saturated air sulphate solution and the equivalent of COD was systematically analyzed. Concentrations of 12-224 mg/L of Fe^{2+} were experimented, Fig. 10 shown the results.

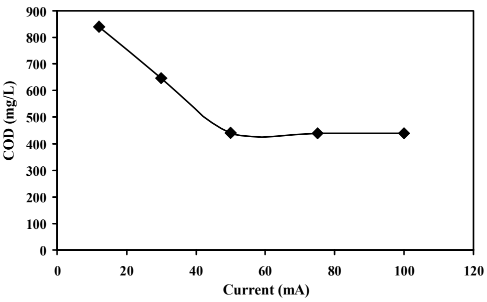

Fig. 9. Variation of residual concentration of COD as a function of current

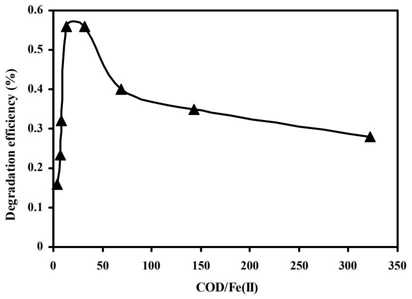

Fig. 10. Effect of the ratio COD/Fe^{2+} on efficiency of incineration

Fig. 10, shows a maximum efficiency for a COD/Fe(II) ratio of 20 to 30, then a decrease in efficiency with an increasing concentration of catalyst Fe^{2+}.

The decrease in the rate of degradation of biocide for a higher concentration of Fe^{2+} is due to the reduction in hydroxyl radicals.

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad k = 3.2 \times 10^{8}\ M^{-1}\ s^{-1}$$ [Ref. 29]

The optimal concentration of Fe^{2+} for the degradation of N,N-methylenebismorpholine is in the range of 30 to 50 mg/L for an applied current of 50 mA and a level of COD to mineralize of 900 to 1000 mg/L.

Incineration of N,N-methylenebismorpholine: This experiment represents the application of the optimized parameters of indirect incineration of N,N- methylenebismorpholine contained in an aqueous acidified sulphate solution saturated with air. The solution was first aerated by air insufflations for 2 h and then electrolyzed during 1 h to produce and accumulate hydrogen peroxide. The solution was magnetically stirred and air was introduced with a rate of 1 L/min during all experiments. The biocide and Fe^{2+} were then introduced after the electro generation of hydrogen peroxide. At each hour, we analyzed the residual COD. This result is represented in Fig. 11.

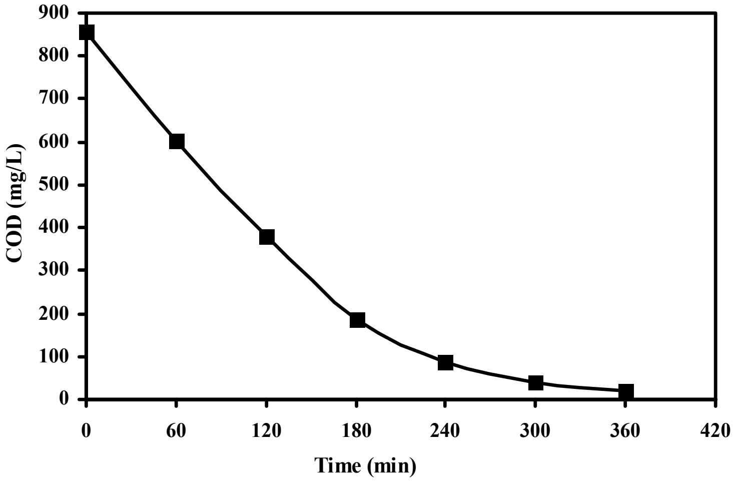

Fig. 11. Evolution of residual COD with time of electrolysis, Na_2SO_4 (0.05 M), pH 3, I = 50 mA, Fe(II) = 30 mg/L, C_{O2}: 7 mg/L, Initial COD : 880 mg/L

Fig. 11 shows a complete mineralization of the biocide after 6 h of electrolysis. The residual COD is 22 mg/L and the efficiency is 97 %.

Conclusion

Cathodic incineration catalyzed by ferrous/ferric redox ion pair (Electro-Fenton) of the N,N-methylenebismorpholine showed a very good efficiency, more than 97 % of the associated COD was oxidized after 5 h of electrolysis.

Industrial graphite, largely used in electrical and electrochemical industries was used as cathode in this study. It exhibits a good electrochemical behaviour with high hydrogen overpotential and a good availability.

A potential range of -500 to -550 mV/SCE are optimal for the electrogeneration of hydrogen peroxide and the incineration of N,N-methylenebismorpholine in the Electro-Fenton process.

A COD/Fe(II) ratio of approximately 30 represent the best ratio in this study, 97 % of COD was incinerated after 2 h of saturated aeration and 5 h of electrolysis. The electro Fenton process exhibits, large possibilities for incineration or pre-incineration of refractory substances to biological treatments. The N,N-methylenebismorpholine presents an anodic electroactivity and offers other electrochemical possibilities for the treatment of aqueous waste containing this substance.

REFERENCES

1. J.J. Pignatello and K. Baehr, *J. Environ. Qual.*, **23**, 365 (1994).
2. M.A. Oturan, *J. Appl. Electrochem.*, **30**, 475 (2000).
3. C. Flox, S. Ammar, C. Arias and E. Brillas, *Appl. Catal. B: Environ.*, **67**, 93 (2006).
4. Chih-Ta Wang, Jen-Lu Hu, Wei-Lung Chou, Yi-Ming Kuo, *J. Hazard. Mater.*, **152**, 601 (2008).
5. M. Sudoh, H. Kitaguchi and K. Koide, *J. Chem. Eng. (Japan)*, **18**, 409 (1985).
6. M. Pourbaix, Atlas d'équilibres électrochimiques, Edition Gauthier-Villars, Paris (1963).
7. M.A. Oturan and J. Pinson, *J. Phys. Chem.*, **99**, 13948 (1995).
8. M.S. El-Deab, T. Okajima and T. Ohsaka, *J. Electrochem. Soc.*, **150**, A851 (2003).
9. A. Alvarez-Gallegos and D. Pletcher, *Electrochim. Acta*, **44**, 2483 (1999).
10. Y.B. Xie and X.Z. Li, *Mater. Chem. Phys.*, **95**, 39 (2006).
11. A. Wang, J. Qu, J. Ru, H. Liu and J. Ge, *J. Zhejiang Univ. Sci. A*, **65**, 227 (2005).
12. M.A. Oturan, *J. Appl. Electrochem.*, **30**, 475 (2000).
13. M.A. Oturan, J. Peiroten, P. Chartrin and A.J. Acher, *Environ. Sci. Technol.*, **34**, 3474 (2000).
14. K. Hanna, S. Chiron and M.A. Oturan, *Water Res.*, **39**, 2763 (2005).
15. J.J. Aaron and M.A. Oturan, *Turk. J. Chem.*, **25**, 509 (2001).
16. E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domènech and J. Casado, *J. Appl. Catal. B-Environ.*, **16**, 31 (1998).
17. B. Boye, M.M. Dieng and E. Brillas, *J. Environ. Sci. Technol.*, **36**, 3030 (2002).
18. E. Brillas, B. Boye, I. Sirès, J.A. Garrido, R.M. Rodriguez, C. Arias, P.L. Cabot and C. Comninellis, *Electrochim. Acta*, **49**, 4487 (2004).
19. S. Ammar, N. Oturan and M. Oturan, *J. Environ. Eng. Manage.*, **17**, 89 (2007).
20. C. Flox, P.L. Cabot, F. Centellas, J.A Garrido, R.M. Rodríguez, C. Arias and E. Brillas, *Chemosphere*, **64**, 892 (2006).
21. A. Morão, A. Lopes, M.T. Pessoa de Amorim and I.C. Gonçalves, *Electrochim. Acta*, **49**, 1587 (2004).
22. G.M. Eisenberg, *Ind. Eng. Chem.*, **15**, 327 (1943).
23. Z. Qiang J.H. Chang and C.P. Huang, *Water Res.*, **36**, 85 (2002).
24. M.A. Oturan and J. Pinson, *New J. Chem.*, **16**, 705 (1992).
25. C.H. Chu, The Electrochemical Oxidation of Recalcitrant Organic Compounds, Ph.D. Dissertation, University of Delaware, Newark, DE (1995).
26. Y.H. Hsiao and K. Nobe, *J. Appl. Electrochem.*, **23**, 943 (1993).
27. T. Tzedakis, A. Savall and M.J. Clifton, *J. Appl. Electrochem.*, **19**, 911 (1989).
28. E. Petrucci, A. Da Pozzo, P. Ferrantelli and C. Merli, *J. Appl. Electrochem.*, **35**, 391 (2005).
29. M.C. Edelhi, Ph.D. Dissertation, Université de Marne-La-Vallée (2004).

(*Received*: 22 October 2008; *Accepted*: 4 April 2009) AJC-7396