

ELECTROCHEMICAL INCINERATION OF REFRACTORY ORGANIC POLLUTION BY ELECTROCHEMICALLY GENERATED FENTON'S REAGENT

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(Received: June 28, 2012 - Accepted: July 20, 2012)

ABSTRACT

The electro-Fenton process is an electrochemical method for waste water treatment based on the production of hydroxyl radicals via H₂O₂ generation in the presence of ferrous ions. The aim of this work is of applied Electro-Fenton technique to incinerate lubricate additive biocide N,N-methylenebismorpholine (C₉H₁₈N₂O₂). the effect of some operational parameters such as applied cathodic potential, the electrolysis time and aeration, concentration of supporting electrolyte on the generation of H₂O₂ was investigated. The optimal cathodic potential on the generation of H₂O₂ production was -500mV/SCE corresponding to a density current of 1.4 mA/cm², the production of hydrogen peroxide with the aeration and electrolysis time, then became stationary after 2h of electrolysis, the low pH favorite production of H₂O₂ electro generated. Whereas the

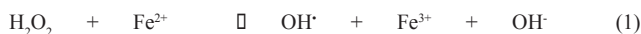
Concentrations of supporting electrolyte of the solution have a slight affect. The degradation and incineration of N,N-methylenebismorpholine in the optimized parameters was also investigated (potential, current density, COD/Fe²⁺ ratio) the result indicates that 97% of COD was incinerated at 50mA and the optimal concentration of catalyst is between 28 and 58mg/l.

Keywords: indirect oxidation, Electro-Fenton, biocide, hydrogen peroxide, oxygen reduction

INTRODUCTION

Recently advanced oxidation process (AOP) have attracted more and more attention because they can be used to degrade pollutants in water by generating plenty of hydroxyl radical (OH•). hydroxyl radicals (OH•) are non selective, very powerful oxidants E_{OH/OH•} = + 2.8V/SHE³ (standard hydrogen electrode) in acidic medium. They are able to react with organic pollutants to mineralize these pollutants into CO₂, water and inorganic ions.

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



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

In traditional Fenton process, the reactants H₂O₂ and Fe²⁺ are simultaneously added to the polluted solution and it is employed to efficiently treat a variety of industrial pollution.⁴ Waste water containing a range of organic compounds like phenol, pesticides, plastic additives and rubber chemicals with low cost and relatively easy operation and maintenance^{5,6} however despite its high efficiency the wide of application of traditional Fenton process is limited by its acidic pH requirement (pH 2-4) and the formation of ion sludge in the coagulation step as well as high cost of hydrogen peroxide.

In order to avoid the use of expensive hydrogen peroxide electro-Fenton process was established in this process hydroxyl radicals are produced via Fenton's reaction in homogeneous medium via electro-generated H₂O₂ and dissolved iron ions

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 medium⁷ Pourbaix .



The electro-reduction of dissolved oxygen is a multi-electron reaction associated with the formation of a large number of intermediates. Oxygen can be reduced directly to H₂O in a 4-electron transfer:



Or, first reduced to H₂O₂ in a 2-electron transfer:



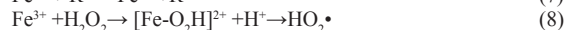
This 2-electron transfer is then followed by reduction of H₂O₂ to H₂O



The reaction (4) can take place at different cathode such as mercury pool⁸, gold⁹ reticulate vitrous carbon^{10,11}, activated carbon fiber¹², carbon felt^{13,14,15} and O₂-diffusion cathodes^{16,17,18}.

The oxidative power of electrogenerated hydrogen peroxide is enhanced in the presence of Fe²⁺ ions^{8,17} to produce OH• through a Fenton process (reaction 1).

The regeneration of Fe²⁺ can occur either direct cathodic reaction (reaction 6) by the oxidation of an organic (reaction 7) or by the reaction with H₂O₂ (reaction 8)¹⁹.



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 O₂-overvoltage anode. In this case, hydroxyl radicals are formed in the medium from Fenton's reaction (reaction 1)^{20,21}. However, industrial applications need electrodes with specific large surfaces, high availability and a minimum cost.

In this paper, we studied the performance of the graphite cathode for H₂O₂ electrogeneration, and investigated the degradation of N,N Methylenebismorpholine in the Electro-Fenton process using the graphite cathode. The influence of the different operational parameters on the H₂O₂ electrogeneration (cathodic potential, time of aeration and electrolysis, concentration of supporting electrolyte) and the incineration and mineralization of N,N-methylenebismorpholine (ratio COD/Fe²⁺, current) which affect the efficiency of electro-Fenton process in biocide oxidation in acidic solutions.

EXPERIMENTAL

Reagent and material:

The graphite electrode was supplied by Algerian Electrical and Gas Company. The surface of electrode was polished using 600 and 1600SiC papers. After polishing the electrode were rinsed, sonicated for 15min, and rinsed with deionized water.

The biocide N,N Methylenebismorpholine was supplied by Algerian

petroleum refinery of Arzew the 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. The N,N Methylenebismorpholine was used without further purification and its structure is shown in fig 1. All other chemicals including sulfuric acid H_2SO_4 , sodium hydroxide NaOH, anhydrous sodium sulfate Na_2SO_4 , hydrogen tetrachlorate $HAuClO_4$ 99%; heptahydrate ferrous sulfate $FeSO_4 \cdot 7H_2O$, anhydrous ferric sulfate $Fe_2(SO_4)_3$, sulfate titanium (IV) $Ti(SO_4)_2$, potassium dichromate $K_2Cr_2O_7$ and ammonium iron(II) sulfate hexahydrate (Mohr salt) $Fe(NH_4)(SO_4)_2 \cdot 6H_2O$, silver sulfate Ag_2SO_4 , sulfate mercury $HgSO_4$ were of analytical grade, deionized water was used.

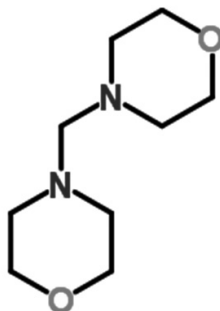


Figure 1. Structure of N,N-Methylenebismorpholine.

Electrochemical device (figure 2):

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 (Figure 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.

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 Na_2SO_4 0.5M 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 liter/ min. The resulting oxygen concentration was measured by oxymeter (Model 97-08-99, Orion Research INC).

Experimental solutions were magnetically stirred.

Analytical procedures:

Hydrogen peroxide analysis:

Concentration of hydrogen peroxide produced in the cell was analyzed by titanic sulfate, $Ti(SO_4)_2$ method Eisenberg²². Spectrophotometer SAFAS 320G 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 $0.22 \mu\text{m}$ pore diameter.

The organic matter was oxidized by potassium dichromate $K_2Cr_2O_7$ in the presence of silver sulfate (catalyst) and mercury sulfate for 2h at 170°C . COD was calculated from the following equation:

$$\text{COD (mg O}_2 \text{ l}^{-1}) = 8000 (V_{\text{MS blank}} - V_{\text{MS sample}}) \times N_{\text{MS}} / V_0$$

Where $V_{\text{MS blank}}$ and $V_{\text{MS sample}}$ 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.

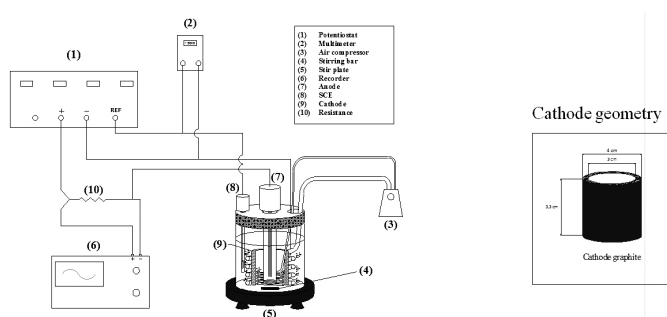


Figure 2. Experimental device for potentiodynamic test

RESULTS AND DISCUSSION

In this part of study, the factors significantly affecting the limiting current of H_2O_2 generation, including cathodic potential, time of electrolysis and aeration, pH and concentration of supporting electrolyte were investigated using potential mode, under this mode, the electrical current was monitored on line by digital multimeter.

Optimal cathodic potential:

A solution of 0.5M 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 liter /mn. A range of potentials of -100mV/SCE to -900mV/SCE were investigated with a scan rate of 2mV/s.

Polarization curve reflect current response with the cathodic potential applied I-E, the figure (3) shows that, two cathodic limiting current for oxygen and hydrogen peroxide reductions respectively according to reaction (2) and (3).

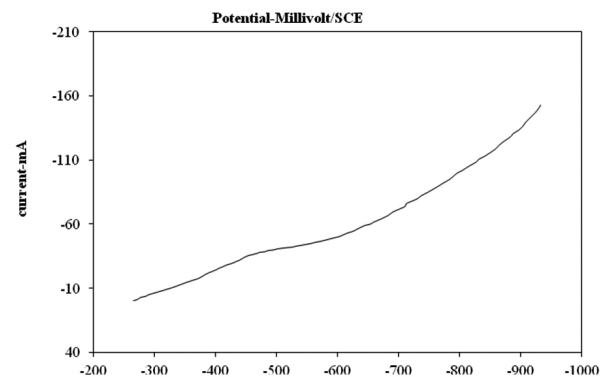


Figure 3. Potentiodynamic polarization of industrial graphite.

Experimental conditions: Scan rate = 2mV/s; pH=3; C_{O_2} = 7mg/l, Electrolyte = 0.5M Na_2SO_4

The reduction of oxygen to give peroxide occurs in the potential range of $E = -300 \text{ mV/SCE}$ 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 (eq 9).



These results are in accordance with Qiang (2002) and Oturan and Pinson (1992).^{23,24} Potentials of -600 mV/SCE was obtained by Chu (1995) and -550 mV/SCE by Hsiao and Nobe (1993)^{25,26}. The use of industrial graphite gives a good concordance in the range of reduction potential of reduction of oxygen to hydrogen peroxide.

At the anode, the oxidation of H_2O releases oxygen gas and protons



The protons so generated will be driven to the catholyte electro-statically and partially supplement the protons consumption during the synthesis of H_2O_2 .

Potentiostatic electro generation of hydrogen peroxide

Potentiostatic 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 Na₂SO₄ (0.05M) and (pH 3) solution was magnetically stirred. Hydrogen peroxide was analyzed every hour.

Effect of applied potential:

Figure 4 shows the effect of applied potential on hydrogen peroxide electro generation in the range of -100mV to -900mV/SCE. The curve represents a maxima in the potential range from E= -500 to E= -550mV/SCE, corresponding to the limiting current as in Figure 3.

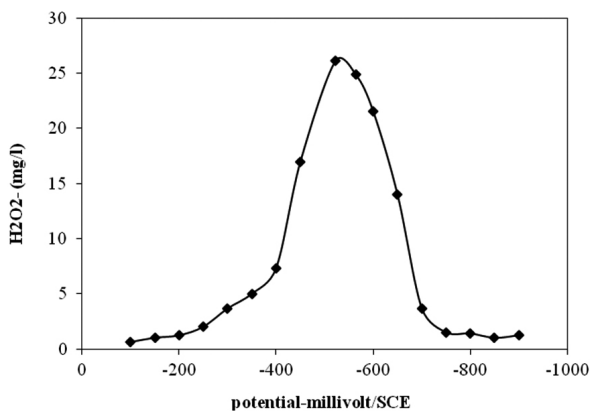


Figure 4. Effect of cathodic potential on Hydrogen Peroxide production Electrolyte: Na₂SO₄ (0.5M), p H 3, time of electrolysis: 2h

A maximum rate of hydrogen peroxide (26 mg/l) was electrogenerated at a potential of -500mV/SCE after 2 hours of electrolysis. The best potential for oxygen to Hydrogen peroxide reduction (-500 mV/SCE) is in accordance with the theorist results of ^{23,24,27}(Qiang et al 2002; Oturan et al 1992; Tzedakis et al 1989) 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 -500mV/SCE. A solution of Na₂SO₄ (0.5M) pH 3, magnetically stirred was used in the experiment.

The results of figure 5 showed two parts: a rapid increase of hydrogen peroxide production for times less than approximately 2h, 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's⁷ diagram of hydrogen peroxide Pourbaix shows instability domains of hydrogen peroxide which can be oxidized to form oxygen or reduced to form H₂O. The plateau of Figure 5 indicates that the production and decomposition occur simultaneously after two hours of electrolysis. The decomposition becomes higher and the production increases slightly.

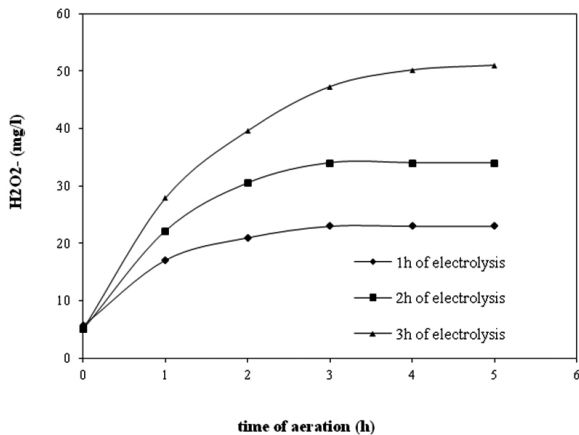


Figure 5. effect of time of aeration

Effect of pH

Electro-Fenton reaction is generally performed in acidic conditions pH values between 2 and 4. The optimum pH value was 2.8 for hydroxyl radical production ²⁸, Ferric species begin to precipitate as ferric hydroxides at higher pH values. On the other hand, ferric species form stable complexes with H₂O₂ at lower pH values. Here, we only investigated the effect of pH on the electrogeneration of H₂O₂ using graphite cathode in a solution of Na₂SO₄ 0.5M in acidic region between the pH values of 1 to 4 by addition of H₂SO₄ or NaOH in the absence of ferric or ferrous ions, it can be seen from figure 6. That there is a maximum value, of the H₂O₂ concentration is pH3 after 120min of electrolysis. However below pH2 the maximum value of H₂O₂ concentration was of 16mg/l. this could be explained by the formation of oxonium ion (H₃O₂⁺)^{29,30}, which enhanced the stability of H₂O₂ (eq 10). At same time, a low pH also promotes hydrogen evolution according to (eq 9), and then reduces the number of active sites for generating hydrogen peroxide ³¹.



Above pH2, the values of H₂O₂ concentration decreases due to insufficient protons.

This result indicates that pH2 is the optimal condition which is an agreement with ²³. A fig.6b show that *i* stabilize quickly after the electrolysis is initiated. A steady-state condition is rapidly reached because a constant dissolved oxygen concentration is maintained in solution.

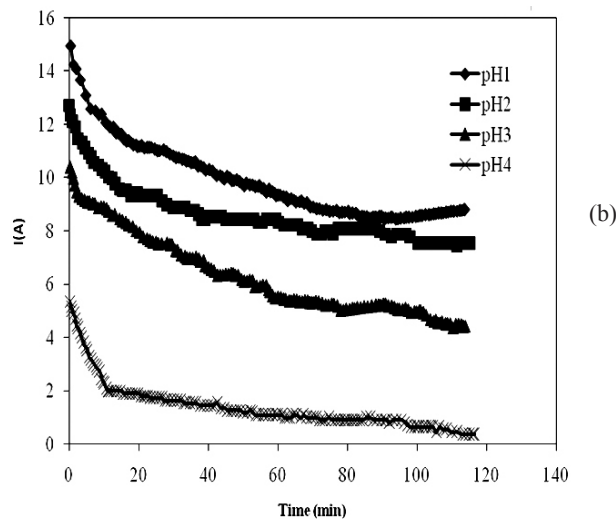
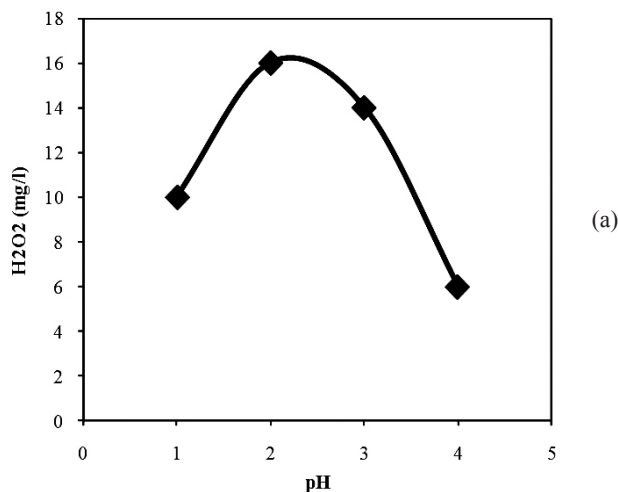


Figure6. Generation of H₂O₂ at various applied pH: (a) accumulated concentration; (b) current. Experimental conditions: time of aeration 1 H time of electrolysis 120min and E=-500mV/SCE

Effect of the concentration of support electrolyte

Electro-generation of H_2O_2 was examined in different concentration of supporting electrolyte (0.05 to 0.9 mole/l of Na_2SO_4) of pH 3 and cathodic potential of -500mV/SCE. From fig 7, it could be conclude that the electro-generation of H_2O_2 is weakly affected by change in the concentration of supporting electrolyte whose role is to decrease the ohmic resistance of the solution and eliminate the migration current I_m , the overall current is $I=I_m+I_d$. We believe that this current is eliminated by the highly acidic solution and transport phenomena in electrical mobility are much higher than that of sodium ions. However the addition of supporting electrolyte helps to improve the characteristics of conductive solution.

We chose a concentration 0.05 mole/l for the rest of this part of study. This value has been used by several researchers^{32,33}.

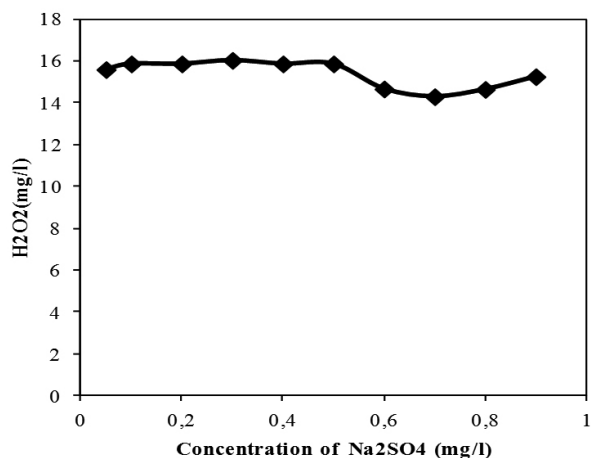


Figure 7. Effect of the concentration of Na_2SO_4 in electro-generation of H_2O_2 . Experimental conditions: time of aeration 1 H time of electrolysis 120min and $E=-500mV/SCE$.

Electrochemical characterization of N, N Methylenebismorpholine:

The electrochemical behavior of the biocide N, N Methylenebismorpholine was analyzed using cathodic and anodic potentiodynamic polarizations. A solution of Na_2SO_4 (0.05M) (p H 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 -1300mV/SCE with a scan rate of 2mV/s.

The result in figure (8b) shows the effect of biocide on the electrochemical behavior of the system. The potentials of oxygen and hydrogen reduction moved to larger negative values and the limiting current of oxygen becomes higher.

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:

Figure 9, shows the result of anodic polarization of graphite at the potential range of 0 to 1400mV/SCE. The curve (9a), 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:



The addition 1mL of Biocide, exhibits two limiting currents in the potential range of 70mV/SCE to 400mV/SCE for the first one and 400mV/SCE 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.

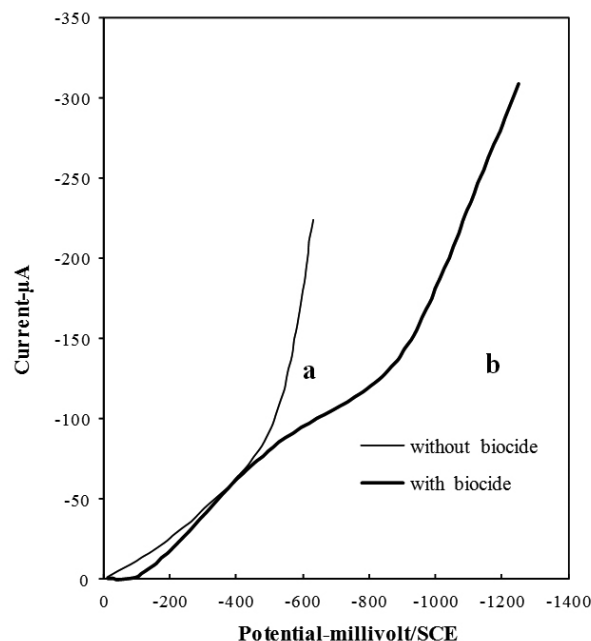


Figure 8. Influence of biocide on the cathodic polarization Na_2SO_4 0.05M, H_2SO_4 pH=3, $S_r= 2mV/s$, $N_r= 4000$ rds/min **a:** without biocide, **b:** with biocide pure 1ml.

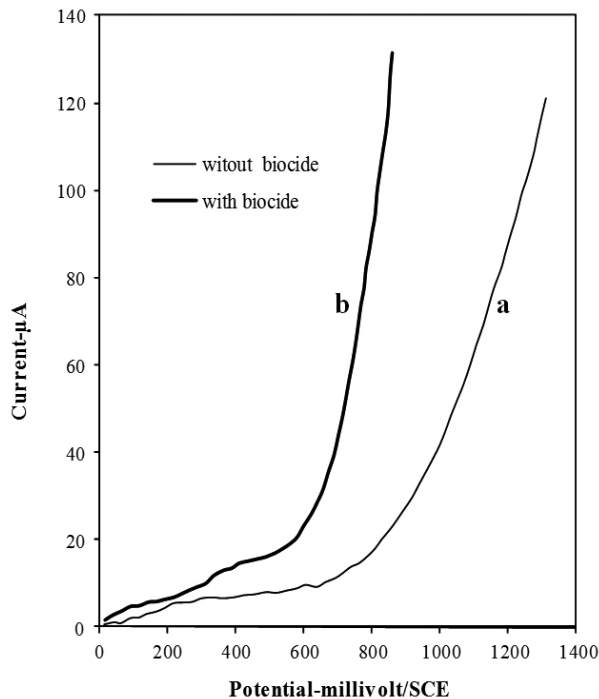


Figure 9. Influence of biocide on the anodic polarization Na_2SO_4 0.05M, H_2SO_4 pH=3, $S_r= 2mV/s$, $N_r= 4000$ rds/min **a:** without biocide, **b:** with biocide pure 1ml.

The electrochemical behavior 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: $E = 400 \text{ mV/SCE}$ to $E = 600 \text{ mV/SCE}$ with a controlled diffusion kinetics.

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 millivoltmeter were used for current and potential measurements.

A solution of 0.05M 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 minutes 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.

The effect of ferrous Sulfate:

A solution of 200 ml of 0.05M sodium sulfate containing pure biocide (COD: 1000 mg/l) was first galvanostatically ($I = 30 \text{ mA}$) electrolyzed during six hours without addition of ferrous ions, the residual COD was analyzed every hour. Figure (10a) shows different changes on COD concentration.

The addition of 12 mg/l of ferrous ions corresponding to an approximate ratio of $[\text{H}_2\text{O}_2] / [\text{ironII}] = 2^{34}$ shows a decrease in residual COD Figure (10b); a residual concentration of 580 mg/l was unregistered after 5h of electrolysis representing to an efficiency of 42%.

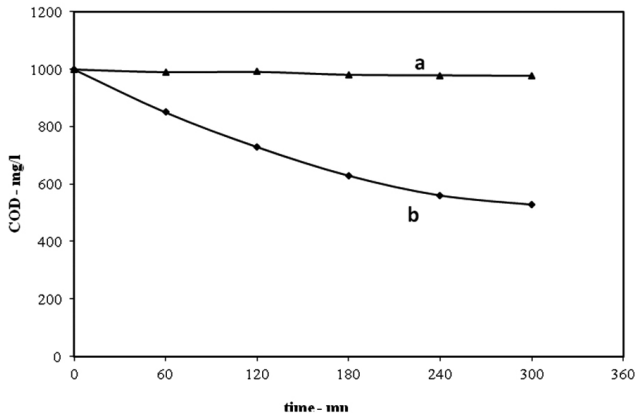


Figure 10. Abatement of COD as a function of time. a: not catalyst b: with a catalyst , $[\text{Fe}^{2+}] = 12 \text{ mg/l}$. $I = 30\text{mA}$.

Applied current effect

Applied current of 12, 30, 50, 75 and 100mA were used in similar conditions of previous experiment; figure 11 shows time evolution of the residual COD.

The kinetics appears more rapid during the first two hours then the decrease of residual COD becomes lower.

The residual values of COD for six hours of electrolysis and for different applied currents are shown in Figure (12).

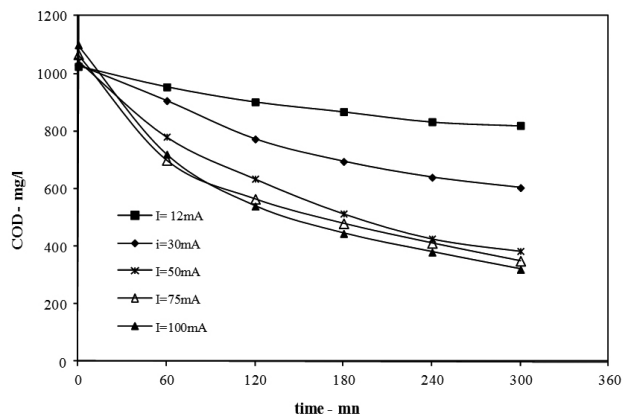


Figure 11. Effect of applied current on the incineration of biocide. 0, 05M Na_2SO_4 pH =3, CODi = 1000mg/l ± 100 , $[\text{Fe}^{2+}] = 12 \text{ mg/l}$, $C_{\text{O}_2} = 7\text{mg/l}$.

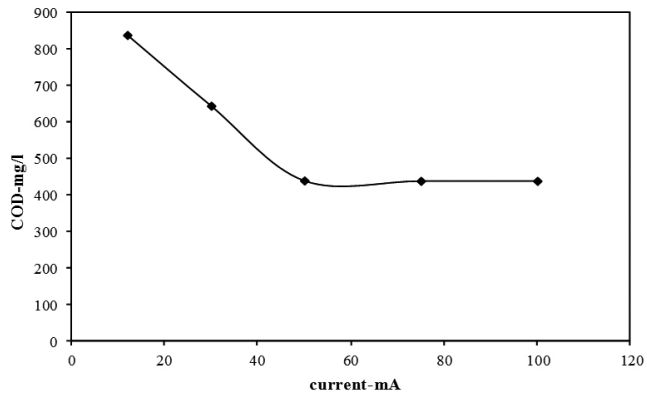


Figure 12. Variation of residual concentration of COD as a function of current

The result shows two parts of different applied currents. For the current less than - 50 mA (-1.4 mA/cm²), the rate of incineration of the biocide increase with the applied current, for the current higher than 50 mA the rate of incineration stabilises and becomes independent.

The current density of -1.4 mA/cm² for N,N Methylenebismorpholine incineration represents an optimum, the potential of the cathode was unregistered each 30 mn 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/ (FeII) effect

The effect ratio of COD/ (FeII) on efficiency of the incineration was experimented for two hours 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 to 224 mg/l of Fe^{2+} were experimented, figure (13) shown the results.

Figure (13), 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.



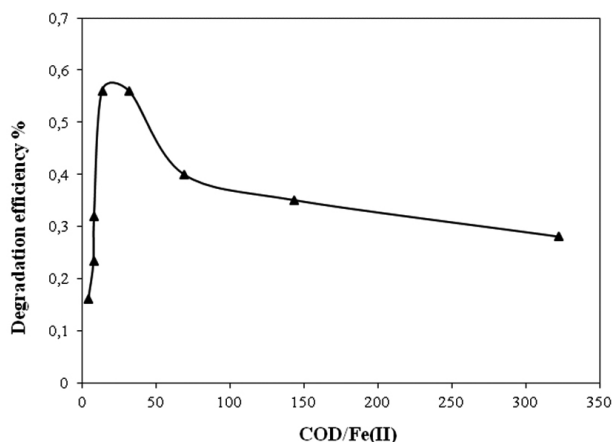


Figure 13. Effect of the ratio COD/Fe⁺⁺ on efficiency of incineration.

The optimal concentration of ferrous ions for the degradation of N,N-Methylenebismorpholine is in the range of 30 to 50 mg/l for an applied current of 50mA 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 two hours and then electrolyzed during 1 hour to produce and accumulate hydrogen peroxide.

The solution was magnetically stirred and air was introduced with a rate of 1 litre per minute during all experiments.

The biocide and Fe II were then introduced after the electro generation of hydrogen peroxide. At each hour, we analyzed the residual COD. This result is represented in Figure (14).

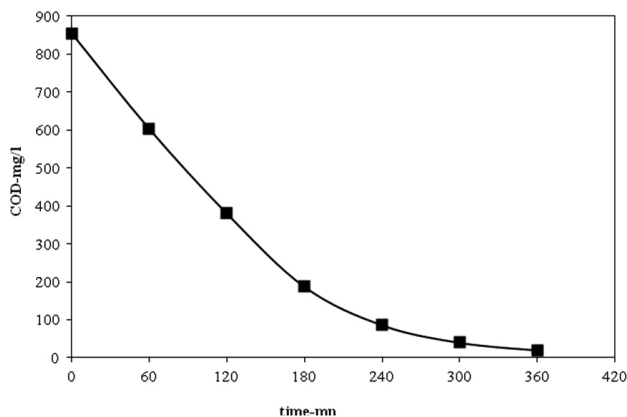


Figure14. Evolution of residual COD with time of electrolysis Na₂SO₄ (0,05M), p H 3, I= 50mA, Fe II= 30 mg/l, C_{O₂}: 7mg/l Initial COD: 880 mg/l

The Figure 14 shows a complete mineralization of the biocide after six hours 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 five hours of electrolysis.

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

A potential range of -500 mV/SCE 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⁺⁺ ratio of approximately 30 represented the best ratio in this study, 97% of COD was incinerated after two hours of saturated aeration and five hours 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.

ACKNOWLEDGMENTS

The author gratefully acknowledges Dr. Zerouali Djilali for his helpful discussion.

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