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Removal of N,N methylene-bis-morpholine pollutant in water by advanced oxidation process "electro-Fenton"

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ABSTRACT

This study discusses the degradation of biocide solution containing N,N Methylene-bis-morpholine by electro-Fenton process. Hydrogen peroxide (H_2O_2) was produced by electro-reduction of oxygen dissolved in a diluted acid solution containing the supporting electrolyte. This oxidation process allows the production of active intermediates, which react on the organic compounds, leading to their mineralization. The independent current parameters, Fe^{3+} concentration, in the range (0.3–2.77) mA/cm and (2.8–224) mg/L, respectively, were evaluated. Other parameters related to optimization of generation of hydrogen peroxide were explored, such as the optimal cathodic potential, electrolysis/aeration time, the concentration of supporting electrolyte, and effect of pH, and investigated to find the best experimental conditions for achieving generation of oxidant (H_2O_2) *in situ*. Results showed that potential of −500 mV/ECS, 0.05 M Na_2SO_4 electrolyte, O_2 sparging during 2 h, and pH 3 were the best conditions for production of the hydrogen peroxide. After optimizing the operational parameters such as Fe^{3+} concentration of 28 mg/L and current density of 1.4 mA/cm, the mineralization of N,N Methylene bismorpholine was of 97% efficiency after 6 h to treatment.

Keywords: Electro-Fenton process; Hydroxyl radicals; Biocides; Degradation

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1. Introduction

Petroleum refinery effluents (PRE) are primarily wastes derived from industries, such as crude oil refining, fuels manufacturing, lubricants, and petrochemical intermediates [1]. These effluents are composed of oil and grease along with many other toxic organic compounds. The refining crude oil process requires large amount of water. Consequently, significant volumes of wastewaters are generated [2,3] and discharged into the environment which causes a negative impact on ecosystems and human health, making their treatment necessary.

PRE treatment includes chemical and physical treatment methods such as coagulation [4,5], adsorption

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[6,7], chemical oxidation [8], and biological techniques [9–11]. These methods have many disadvantages concerning of efficiency, cost, regeneration, and secondary pollution production. Therefore, a new strategy for technological development should be applied.

Advanced oxidation processes (AOPs) are promising technologies that have received great attention during the last years [12], as these alternative treatments are effective and rapid for various contaminants, including hazardous organic pollutants present in wastewaters especially PRE [13]. The AOP mechanism principal is the generation of highly free radicals reactive [14] capable to degrade complex compounds into CO_2 and water [15,16].

A large variety of AOPs have been classified under the broad definition of AOPs: Ozonation, UV radiation, hydrogen peroxide, Fenton's reagent [17]. Among these methods, the electrochemical advanced oxidation process (EAOP), electro-Fenton (EF), seems to be a very attractive tool due to its high effectiveness [18–21], fast treatment rate, and its environmental compatibility [22].

In this process, H_2O_2 is produced electrochemically via oxygen reduction on cathode in acidic media using Eq. (1) [23] with the addition of ferrous ions into the system; the classical Fenton reaction takes place, in the solution via Eq. (2) [24]. Moreover, when the EF process is used, the amount of added ferrous ions is much smaller than in the classical Fenton because in this process, the ferrous ions are regenerated at the cathode by Eq. (3) [25,26].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

Then, the addition of ferrous ions allows an H_2O_2 oxidation power enhancement, according to the Fenton's reaction, through the formation of $OH^{\cdot}$ radicals

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\cdot} + Fe^{3+} + OH^- \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

The EF process is more environment-friendly since it involves the use of no toxic chemical reagents: Fe^{2+} ions, H_2O_2, and the hydroxyl radicals produced ($OH^{\cdot}$) [27], in addition, the overall process does not create secondary pollutants when the electricity is used as a clean energy source [28]. The EF process was successfully applied for degradation and removal of dyes [29–33], pesticides and herbicides [34–36], leachate [37,38], drugs [24,38,39], phenolic compounds [40–42], and petrochemical wastewater [43].

The objective of this study was to investigate the EF process efficiency to degrade "N,N Methylene-bis-morpholine" which is rejected by the Arzew refinery, and the effects of some parameters were explored such as: the cathodic potential, electro-generation of hydrogen peroxide, aeration time, and inert supporting electrolyte, pH of the solution and Fe^{3+} concentration effect also was examined.

2. Experimental

2.1. Chemicals

The biocide N,N Methylene-bis-morpholine was supplied by the Algerian petroleum refinery of Arzew. It is used as biocide to preserve lubricating oil from a biological oxidation, it is non-biodegradable and cannot be treated by biological techniques, therefore, it is necessary to incinerate this pollutant petrochemical before the biological treatment. The N,N Methylene-bis-morpholine 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), heptahydrate ferrous sulfate ($FeSO_4$ $7H_2O$), anhydrous ferric sulfate ($Fe_2(SO4)_3$), sulfate titanium (IV) ($Ti(SO4)_2$), potassium dichromate ($K_2Cr_2O_7$), ammonium iron(II) sulfate hexahydrate (Mohr salt) ($Fe(NH_4)$ $(SO4)_2{\cdot}6H_2O$), silver sulfate (Ag_2SO_4), and sulfate mercury ($HgSO_4$) were supplied from Aldrich. All aqueous solutions of biocide were prepared with deionized water.

2.2. Electrolytic system

The experiments were performed using the "Potensiostat/galvanostat" model (TACUSSEL), equipped

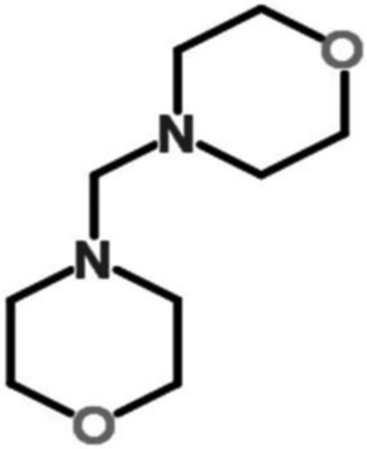

Fig. 1. N,N-Methylene-bis-morpholine structure.

with conventional three-electrode cell. The electrode used is graphite made, a platinum wire is used as counter electrode, and SCE is used as a reference electrode. The distance between the working electrode and the counter electrode is 2 cm. The H_2O_2 production experiments were performed in a divided cell 200 mL capacity, using a constant magnetic stirring. The Na_2SO_4 solution is used as supporting electrolyte and the pH is adjusted with NaOH and H_2SO_4 before electrolysis. Oxygen has been provided by a compressor near the cathode .The catalyst $Fe_2(SO_4)_3$ was added to achieve the Fenton reaction. All experiments were performed at room temperature (20° ± 1℃).

In this study, the factors significantly affecting the limit current of H_2O_2 generation, including cathodic potential, effect of aeration time, and inert supporting electrolyte, were investigated using the constant potential mode. The pH effect was studied using constant potential mode and transient current response was systematically recorded by HEWLETT PACKARD X-Y recorder (Model 7001 A).

2.3. Analytical method

The linear sweep voltammetry (LSV) was used to confirm the generation of H_2O_2 under specific conditions. The LSV was obtained using the Potensiostat/galvanostat TACUSSEL controlled computer, at the scanning speed of 2 mVs^{-1} in the electrochemical cell as described above. The H_2O_2 concentration was determined spectrophotometrically (SAFAS) using titanium chloride (IV) with the Heisenberg method at 410 nm wave length. The current efficiency (CE) of H_2O_2 generated is defined by the equation given below:

$$E_C = \frac{nFC_{H_2O_2}V}{\int_0^t I dt} \times 100\% \tag{4}$$

where C_{H2O2} is the concentration of H_2O_2 in solution (M), V is the volume of the electrolyte (L), n is the number of electrons transferred to the oxygen reduction in H_2O_2, F is the Faraday constant, 96,500 C mol^{-1}. The biocide solution mineralization (N,N methylene bis-morpholone) was assessed using the COD of the semi-micro closed reflux method.

In this study, we present an electrochemical “EF process” study and its characteristics by seeking the optimum conditions for pollutant degradation. Our study is divided into three main lines:

(1) Electrochemical experimental conditions searching “optimal cathodic potential”.
(2) Hydrogen peroxide production.
(3) Organic molecules degradation.

3. Results and discussion

3.1. Operational system parameters effect on the H_2O_2 production

The EF system performance in the organic pollutants degradation is related to the hydroxyl radical amount produced in the medium. This is affected by the H_2O_2 production rate, obtained by the reduction of two electrons of O_2 on the cathode surface. Therefore, the H_2O_2 production rate on graphite electrode is very important for recalcitrant compounds degradation.

3.1.1. Optimal cathodic potential

In order to choose the correct potential at which the electrochemical H_2O_2 generation efficiency is optimum and based on the current-potential curves [44], Panizza and Cerisol have reported that −1 V/SCE is the potential optimal, however, Daneshver and Oturan et al. [45,46] have used −0.5 V/SCE potential for production H_2O_2. The aim of this part was to search the cathodic field for H_2O_2 generation in our electrochemically operating conditions. Fig. 2 shows these experiments results performed in the electrolyte Na_2SO_4 at pH 3 and without catalyst Fe^{3+}.

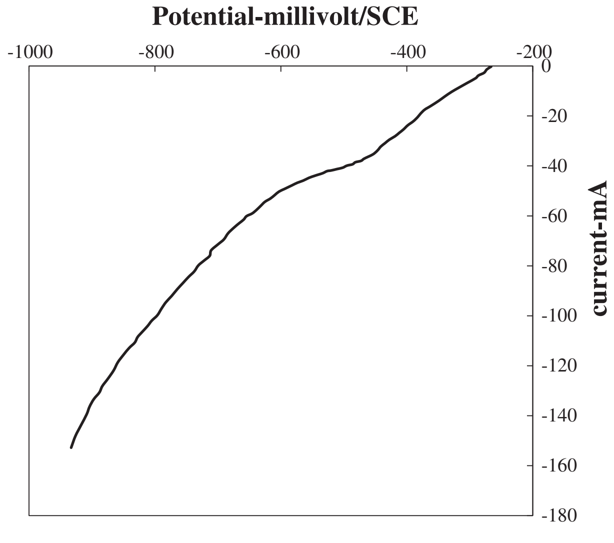

Fig. 2. Current-potential curve of O_2 saturated solution. $[Na_2SO_4]$ = 0.5 M, pH 3.0.

Fig. 2 shows current-potential curve of air-saturated solution in the experimental conditions. At $E_c > -300$ mV, the current increases rapidly with E_c increasing, in this area, the potential regime is under mixed control. However, a plateau appears in the range of −300 to −600 mV, attributed to the limiting current-region for the dissolved oxygen reduction to H_2O_2, according to reaction (1). When the E_c continues to increase above −800 mV, the current I quickly rises, implying a significant reduction of H_2O to H_2. Generally, hydrogen gas evolution simultaneously occurs at the cathode according to reaction 5:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (5)$$

Qiang et al. [47] have reported that H_2O_2 accumulation in the potential range of −0.5 V to −1 V is approximately constants, but more the electricity is consumed at high E_c, more the CE is reduced. Thus, the optimal cathodic potential is −0.5 V/SCE.

3.1.2. Electro-generation of hydrogen peroxide

An important study in the EF process is the production and CE for the formation of hydrogen peroxide on site [48]. The potential effects on H_2O_2 production at the graphite cathode are shown in Fig. 3. The H_2O_2 yield at the potentials ranging between −100 and −900 mV were 1, 3, 7, 13, 21, 26, 25, 19, 16, 12, 7, 4, and 2 mg/L, respectively.

This indicates that the highest H_2O_2 accumulation was achieved at the potential −500 mV. When the potential exceeded the optimum, the H_2O_2 accumulation declined. As shown in Fig. (3(b)), the current efficiencies of H_2O_2 production at the applied cathode potential ranging from −100 to −900 mV were 12, 18, 21, 23, 29, 16, 2, and 2 1%, respectively. The current in the system has obviously increased with potentials increased, as a result, the CE decreased considerably when the cathodic potential became more negative than −500 mV. The side reactions corresponding to the H_2O_2 decomposition became dominant, which resulted in a decreased yield and the efficiencies of current to produce H_2O_2. By plotting the CE and E shown in Fig. (3(a) and (b)), the optimal cathodic potential is −500 mV/ECS.

3.1.3. Effect of electrolysis and aeration time

In the cathodic reduction of dissolved oxygen, it is transferred from the gaseous phase to the aqueous phase, and then it is transferred from the bulk aqueous solution to the cathodic surface. The oxygen, which is adsorbed on active cathodic sites, is reduced to hydrogen peroxide. Hence, the mass transfer rate of oxygen from the gaseous to the aqueous phase is enhanced and the removal efficiency increased when the aeration oxygen time increased [45,49]. Effect of aeration before and during the electrolysis on hydrogen peroxide production was experimented in this part with a potential of −500 mV/SCE. A solution of Na_2SO_4 (0.5 M), magnetically stirred at pH 3, was used in this experiment.

The results in Fig. 4 indicate two parts: a rapid increase of hydrogen peroxide production before approximately 2 h, after, it became stable may be due to equilibrium between the hydrogen peroxide production and its decomposition [50]. Pourbaix shows the hydrogen peroxide instability domain which can be oxidized to oxygen or reduced to form H_2O. The

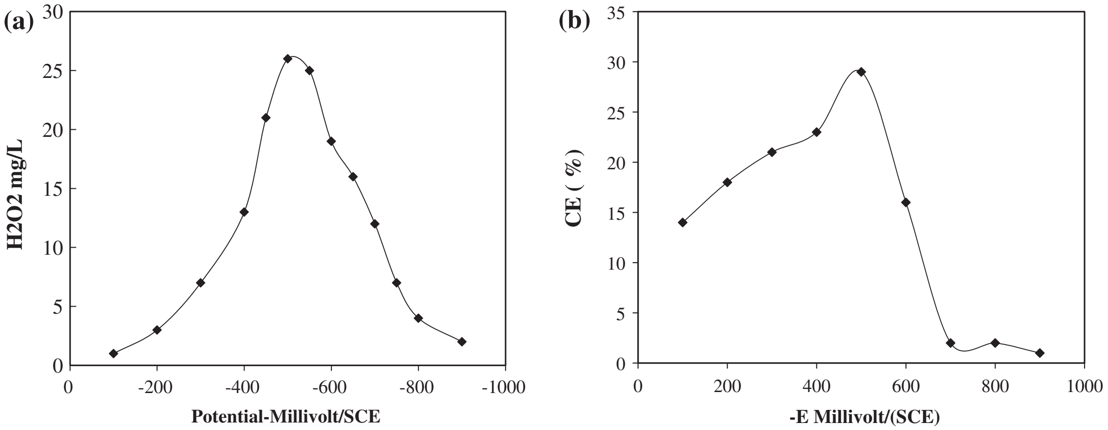

Fig. 3. Potential-imposed effect on H_2O_2 accumulation: (a) current efficiency at various applied potential imposed and (b) $[Na_2SO_4] = 0.5$ M, pH 3.

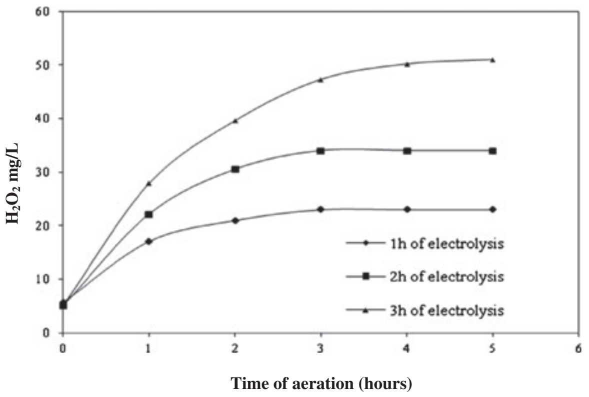

Fig. 4. Aeration time effect.

plateau in Fig. 4 indicates that the production and decomposition occur simultaneously after 2 h of electrolysis, the decomposition became higher and the production increased slightly.

3.1.4. Effect of pH on solution

The pH of the solution is one of the most important factors for EF technology. Usually, the EF reaction has highest efficiency when the pH is between 2 and 4 [51], a low pH is favorable for the dissolved oxygen conversion to hydrogen peroxide which consumes protons from the acidic solution according to Eq. (1). However, low pH also promotes hydrogen evolution, according to Eq. (5), reducing the number of active sites available for hydrogen peroxide generation [50]. Here, we only investigated the pH affect on the H_2O_2 electro-generation using graphite cathode in a Na_2SO_4 (0.5 M) acidic solution with adjusting pH between 1 and 4 by adding H_2SO_4 or NaOH in the absence of ferric or ferrous ions. Fig. (5(a)) indicates that there is a maximum value of the H_2O_2 concentration, when pH reaches 3 after 120 min of electrolysis, however, below pH value of 2, the maximum value of H_2O_2 concentration was 16 mg/L, this could be explained by the oxonium ion ($H_3O_2^+$) formation [48], which improved the H_2O_2 enhanced the stability Eq. (6).

Fig. (5(b)) shows that the current stabilizes quickly after the electrolysis initiation. Steady state is rapidly reached because a constant oxygen dissolved concentration (DO) is maintained in the solution, at same time, a high proton concentration may promote H_2 evolution and reduce the CE.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (6)$$

3.1.5. Support electrolyte concentration effect

Electro-generation of H_2O_2 was examined at different supporting electrolyte concentration (0.05–0.9 M of Na_2SO_4) at pH 3 and cathodic potential of −500 mV/SCE. From Fig. 6, it can be concluded that the H_2O_2 electro-generation is weakly affected by the supporting electrolyte concentration variation, whose role is to decrease the solution ohmic resistance and eliminate the migration of current I_m, the overall current is $I = I_m + I_d$. We suppose that this current is eliminated by the highly acidic solution and transport phenomenon in electrical mobility are much higher than that of sodium ions, however, the addition of supporting electrolyte helps to improve the conductive solution characteristics.

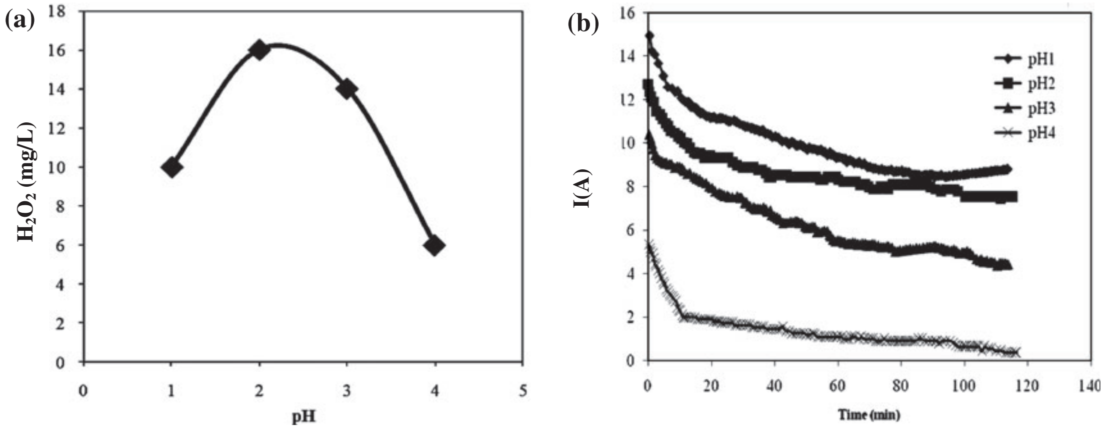

Fig. 5. Generation of H_2O_2 at various applied pH: (a) accumulated concentration and (b) current. Experimental conditions: time of aeration 1 h, time of electrolysis 120 min, and $E = -500$ mV/SCE.

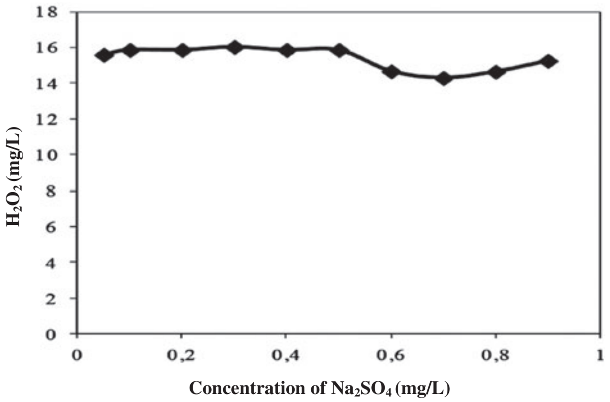

Fig. 6. Effect of Na_2SO_4 concentration in electro-generation of H_2O_2. Experimental conditions: time of aeration 60 min, time of electrolysis 120 min, and $E = -500$ mV/SCE.

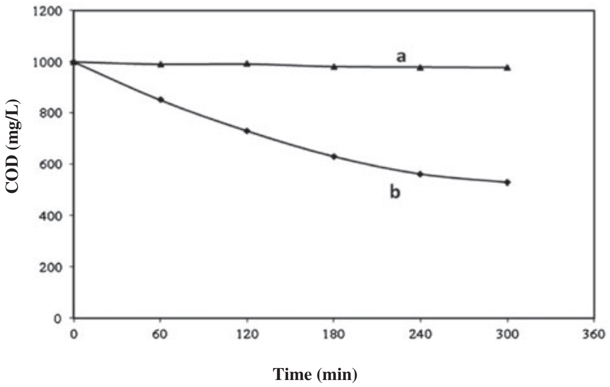

Fig. 7. COD abatement with time (a: without catalyst b: with a catalyst), $[Fe^{3+}] = 12$ mg/L, 0.05 M Na_2SO_4, pH 3, $COD_i = 1{,}000$ mg/L, and $I = 30$ mA.

We chose a 0.05 M concentration for the remaining of the study, this value has been used by several researchers [52,53].

3.2. Incineration parameters optimization

Indirect incineration of N,N-Methylene-bis-morpholine was performed using a galvanostatic experimental device.

A generator D.C, LEYBOLDS 15 V/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.

An Na_2SO_4 (0.05 M) solution and 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. Ferric sulfate was added as Fenton catalyst 5 min before starting the electrolysis. pH was adjusted between 2.5 and 3 by the adding sulfuric acid.

The incineration performance was controlled by COD analysis every hour, effect of applied current, and ratio COD/Fe^{3+} were experimented.

3.2.1. The ferric sulfate effect

A 200 mL sodium sulfate solution containing a pure biocide (COD: 1,000 mg/L) was firstly, electrolyzed to galvanostatical mode ($I = 30$ mA) during 6 h without ferric ions, and the residual COD was analyzed every hour. Fig. (7(a)) shows different changes on COD concentration. The addition of 12 mg/L of ferric ions corresponding to an approximate ratio of $[H_2O_2]/[\text{iron III}] = 2$ [54] indicates a residual COD decrease in Fig. (7(b)); a residual concentration of 580 mg/L was registered after 5 h of electrolysis representing an efficiency of 42%.

3.2.2. Applied current effect

The current is the most important parameter to influence the reaction rate of electrochemical processes. The applied current influence on biocide COD removal was examined by electrolyzing a ≈ 1,000 mg/L of N,N-Methylene-bis-morpholine solution at pH 3 with different current values. The obtained results are shown in Fig. 8, where the kinetics appear more rapid during the first 2 h then the residual COD decreases weakly.

The increase in current from 12 to 100 mA offer a faster biocide COD removal, which can contributed to

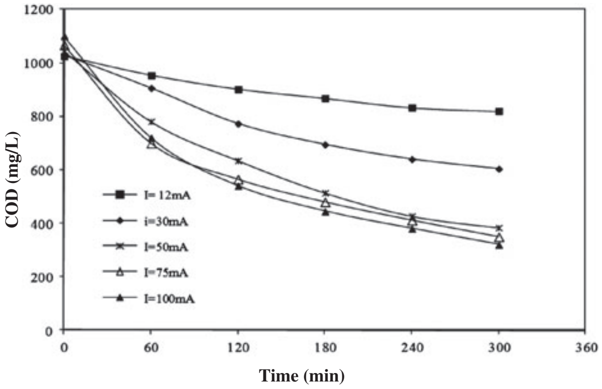

Fig. 8. Applied current effect on the incineration of biocide. 0, 05 M Na_2SO_4 pH 3, $COD_i = 1{,}000$ mg/L ± 100, and $[Fe^{2+}] = 12$ mg/L.

the H_2O_2 formation (Eq. (1)) and the Fe^{2+} regeneration (Eq. (3)), including the higher generation amount of hydroxyl radicals (Eq. (2)). The observed results are similar to those reported in literature [55–57]. However the current and the applied potential increase proportionately, then, it is advisable to limit the current to avoid adverse effects such as heat generation and higher power consumption with H_2 evolution.

The results indicate that the increase in current beyond 50 mA decreases the COD removal rate, due to the increase in COD intermediate products of biocide mineralization, and parasite reactions increase like reduction of H_2O_2 to H_2O and reduction of H^+ proton.

In the Fig. 9, the result shows two parts of different applied currents. For the current less than − 50 mA (−1.4 mA/cm), the biocide incineration rate increases with the applied current, and for the current higher than 50 mA, the rate of incineration stabilizes and becomes independent. The current density value of −1.4 mA/cm for N,N Methylene-bis-morpholine incineration is optimal.

3.2.3. Ratio COD/(FeIII) effect

The COD/(FeIII) ratio effect on incineration efficiency was experimented for 2 h on galvanostatic electrolysis at 50 mA.

A Na_2SO_4 (0.05 M) solution at pH 3 saturated with air and magnetically stirred was used in all experiments, an aqueous solution having initial concentration of N,N Methylene-bis-morpholine 1,000 mg/L was treated for 1 h with Fe^{3+} at dosage ranging from 12 to 224 mg/L and at pH 3. The equivalent of COD was systematically analyzed.

The Fig. 10 shows a maximum COD/FeIII ratio efficiency range of 20–30, which decreases with the catalyst Fe^{3+} concentration increase, indeed, as expected, biocide efficiency degradation increase was observed with Fe^{3+} concentration increase, which may be due to the hydroxyl radicals and Fe^{2+} produced by electrolysis.

The degradation rate decrease of biocide for a higher concentration of Fe^{3+} is due to the trapping of $OH^{\cdot}$ as shown in Eq. (7) [23].

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \quad k = 3.2 \times 10^{8} \text{L/Ms} \tag{7}$$

Eq. (6) becomes a competitive reaction for the consumption of hydroxyl radicals, which affects the rate of biocide degradation.

The optimal ferric ion concentration for the "N,N Methylene-bis-morpholine degradation" is in the range of 28–56 mg/L for an applied current of 50 mA and a COD level to mineralize of 900–1,000 mg/L.

3.3. Organic molecule N,N-Methylene bis-morpholine degradation

The molecule that we tested is N,N-Methylene-bis-morpholine is a lubricating oil component manufactured in the Arzew refinery (Algeria).

This compound is a necessary additive for the oil's preservation during storage, as it has a biocide function and by its nature it is non-biodegradable. This molecule seems very suitable for application of EF process, and we present, in this study, the result of biocide degradation by EF after optimization of experimental parameters: the aeration effect, ferric sulfate addition, and the applied current. According to the optimized parameters (current 50 mA, concentration of iron(III) 28 mg/L) the biocide has been incinerated by EF process in a divided cell.

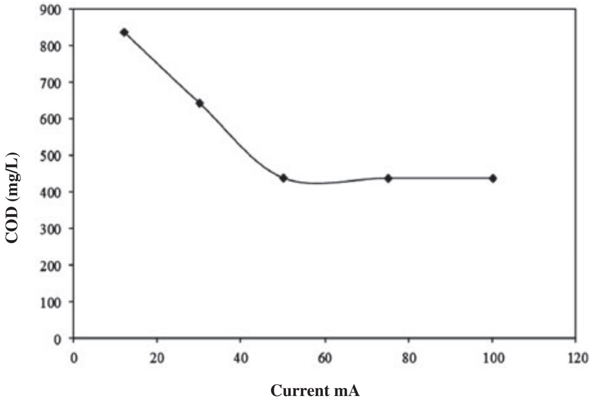

Fig. 9. COD residual concentration variation with current.

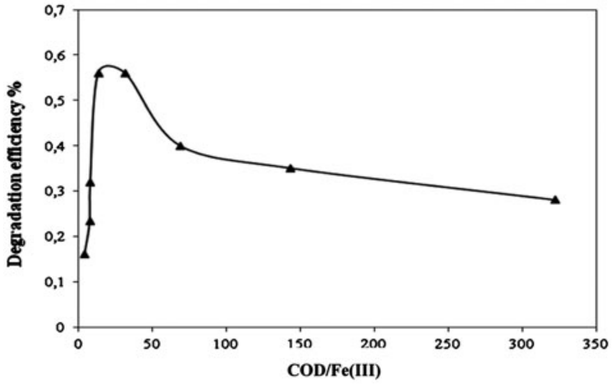

Fig. 10. Effect of the ratio COD/Fe^{3+} on incineration efficiency.

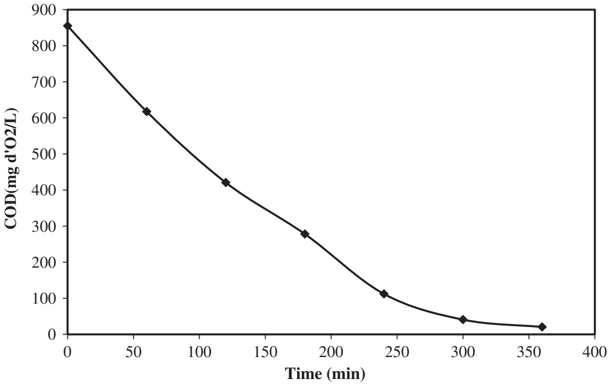

Fig. 11. Biocide incineration by electro-Fenton. $I = 50$ mA, [Fe(III)] = 28 m.

The biocide mineralization evolution with time of the electrolysis during the EF treatment is shown in Fig. 11. The mineralization kinetic curve is characterized by a steady and rapid decline of COD values acceptable by the Algerian standard (20 mg/L) with a yield of 97% after 6 h of treatment.

4. Conclusion

This study is within the framework of industrial wastewater decontamination. Its aim is to investigate an electrochemical advanced oxidation method (EF method) for recalcitrant molecule degradation, from the petrochemical industry. This technique is based on the hydroxyl radical generation *in situ* by Fenton reaction applied electrochemically, on the biocide degradation (N,N-Methylene bis-morpholine). The application of EF process for incineration of (N,N-Methylene-bis-morpholine) allowed a COD reduction of 97%, which is very promising and generalized the EF method to other resistant biodegradation molecules, such as the pesticides, dye, and antibiotics.

References

[1] M.F. Harry, Industrial Pollution Handbook, McGraw Hill. Inc., New York, NY, 1995.
[2] A. Coelho, A.V. Castro, M. Dezotti, G.L. Sant'Anna Jr., Treatment of petroleum refinery sourwater by advanced oxidation processes, J. Hazard. Mater. 137 (2006) 178–184.
[3] B.H. Diya'uddeen, W.M.A. Daud, A.R. Abdul Aziz, Treatment technologies for petroleum refinery effluents: A review, Process Saf. Environ. Prot. 89 (2011) 95–105.
[4] S. Demirci, B. Erdogan, R. Ozcimder, Wastewater treatment at the petroleum refinery Kirikkale Turkey using some coagulant and Turkiskh clays as coagulant aids, Water Res. 32 (1997) 3495–3499.
[5] M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney, S. Makhlouf, Assessment of electrocoagulation for the treatment of petroleum refinery wastewater, J. Environ. Manage. 91 (2009) 180–185.
[6] M.H. El-Naas, S. Al-Zuhair, M.A. Alhaija, Reduction of COD in refinery wastewater through adsorption on date-pit activated carbon, J. Hazard. Mater. 173 (2009) 750–757.
[7] A.J. Serafim, Solid retention time on carbon adsorption of organics in secondary effluents from treatment of petroleum refinery waste, PhD Thesis, Texas A&M University, 1979.
[8] O. Abdelwahab, N.K. Amin, E.-S.Z. El-Ashtoukhy, Electrochemical removal of phenol from oil refinery wastewater, J. Hazard. Mater. 163 (2009) 711–716.
[9] C.G. Jou, G. Huang, A pilot study for oil refinery wastewater treatment using a fixed-film bioreactor, Adv. Environ. Res. 7 (2003) 463–469.
[10] M.M. Rahman, M.H. Al-Malack, Performance of a crossflow membrane bioreactor (CF–MBR) when treating refinery wastewater, Desalination 191 (2006) 16–26.
[11] F. Ma, J.-B. Guo, L.-J. Zhao, C.-C. Chang, D. Cui, Application of bioaugmentation to improve the activated sludge system into the contact oxidation system treating petrochemical wastewater, Bioresour. Technol. 100 (2009) 597–602.
[12] A.S. Stasinakis, Use of selected advanced oxidation processes (AOPs) for wastewater treatment—A mini review, Global NEST J. 10 (2008) 376–385.
[13] S. Hammami, A. Ouejhani, N. Bellakhal, M. Dachraoui, Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents, J. Hazard. Mater. 163 (2009) 251–258.
[14] E. Rosales, M.A. Sanromán, M. Pazos, Application of central composite face-centered design and response surface methodology for the optimization of electro-Fenton decolorization of Azure B dye, Environ. Sci. Pollut. Res. 19 (2012) 1738–1746.
[15] S. Garcia-Segura, E. Brillas, Mineralization of the recalcitrant oxalic and oxamic acids by electrochemical advanced oxidation processes using a boron-doped diamond anode, Water Res. 45 (2011) 2975–2984.
[16] S. Hammami, N. Bellakhal, N. Oturan, M.A. Oturan, M. Dachraoui, Degradation of Acid Orange 7 by electrochemically generated ·OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: A mechanistic study, Chemosphere 73 (2008) 678–684.
[17] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F.J. Rubio, Chemical decomposition of 2,4,6-trichlorophenol by ozone, Fenton's reagent, and UV radiation. Ind. Eng. Chem. Res. 38 (1999) 1341–1349.
[18] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, Advanced oxidation processes for the treatment of wastes polluted with azoic dyes, Electrochim. Acta 52 (2006) 325–331.

[19] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm. 71 (2006) 236–244.

[20] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[21] C.A. Martínez-Huitle, E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed. 47 (2008) 1998–2005.

[22] L.C. Almeida, S. Garcia-Segura, C. Arias, N. Bocchi, E. Brillas, Electrochemical mineralization of the azo dye Acid Red 29 (Chromotrope 2R) by photoelectro-Fenton process, Chemosphere 89 (2012) 751–758.

[23] P.V. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination 299 (2012) 1–15.

[24] A. Dirany, I. Sirés, N. Oturan, M.A. Oturan, Electrochemical abatement of the antibiotic sulfamethoxazole from water, Chemosphere 81 (2010) 594–602.

[25] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631.

[26] A. Da Pozzo, E. Petrucci, Sequential use of Fenton and electro-Fenton process for the oxidation of an effluent-containing hypophosphite and phosphite, Desalin. Water Treat. 53 (2015) 1352–1360.

[27] O. Iglesias, M.A. Fernández de Dios, M. Pazos, M.A. Sanromán, Using iron-loaded sepiolite obtained by adsorption as a catalyst in the electro-Fenton oxidation of Reactive Black 5, Environ. Sci. Pollut. Res. 20 (2013) 5983–5993.

[28] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta 45 (2000) 2575–2594.

[29] B. Gözmen, B. Kayan, A.M. Gizir, A. Hesenov, Oxidative degradations of reactive blue 4 dye by different advanced oxidation methods, J. Hazard. Mater. 168 (2009) 129–136.

[30] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, Oxidative degradation of direct orange 61 by electro-Fenton process using a carbon felt electrode: Application of the experimental design methodology, J. Electroanal. Chem. 610 (2007) 75–84.

[31] B. Kayan, B. Gözmen, M. Demirel, A. Gizir, Degradation of acid red 97 dye in aqueous medium using wet oxidation and electro-Fenton techniques, J. Hazard. Mater. 177 (2010) 95–102.

[32] A. Özcan, Y. Şahin, A.S. Koparal, M.A. Oturan, A comparative study on the efficiency of electro-Fenton process in the removal of propham from water, Appl. Catal., B Environ. 89 (2009) 620–626.

[33] M. Zhou, Q. Yu, L. Lei, The preparation and characterization of a graphite–PTFE cathode system for the decolorization of C.I. Acid Red 2, Dyes Pigm. 77 (2008) 129–136.

[34] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for *in Situ* destruction of organic pollutants: Application to herbicide 2,4-D, J. Appl. Electrochem. 30 (2000) 475–482.

[35] M.C. Edelahi, N. Oturan, M.A. Oturan, Y. Padellec, A. Bermond, K. El Kacemi, Degradation of diuron by the electro-Fenton process, Environ. Chem. Lett. 1 (2004) 233–236.

[36] A.D. Da Pozzo, C. Merli, I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, Removal of the herbicide amitrole from water by anodic oxidation and electro-Fenton, Environ. Chem. Lett. 3 (2005) 7–11.

[37] E. Atmaca, Treatment of landfill leachate by using electro-Fenton method, J. Hazard. Mater. 163 (2009) 109–114.

[38] K.W. Pi, Z. Li, D.J. Wan, L.X. Gao, Pretreatment of municipal landfill leachate by a combined process, Process Saf. Environ. Prot. 87 (2009) 191–196.

[39] I. Sires, N. Oturan, M.A. Oturan, Electrochemical degradation of b-blockers studies on single and multicomponent synthetic aqueous solutions, Water Res. 44 (2010) 3109–3120.

[40] N. Oturan, M. Panizza, M.A. Oturan, Cold incineration of chlorophenols in aqueous solution by advanced electrochemical process electro-Fenton. Effect of number and position of chlorine atoms on the degradation kinetics, J. Phys. Chem. A 113 (2009) 10988–10993.

[41] T.S.N. Sankara Narayanan, G. Magesh, N. Rajendran, Degradation of chlorophenol from aqueous solution by Electro-Fenton process, Fresenius Environ. Bull. 12 (7) (2003) 776–780.

[42] M.A. Oturan, J. Peiroten, P. Chartrin, A.J. Acher, Complete destruction of p -nitrophenol in aqueous medium by electro-Fenton method, Environ. Sci. Technol. 34 (2000) 3474–3479.

[43] W.P. Ting, Y.H. Huang, M.C. Lu, Catalytic treatment of petrochemical wastewater by electroassisted Fenton technologies, React. Kinet. Catal. Lett 92(1) (2007) 41–48.

[44] M. Panizza, G. Ceriosola, Rmoval of organic polluants from industrial wastewater by electrogenerated Fenton's reagent, Water Res. 35 (2001) 3887–3992.

[45] N. Daneshvar, S. Aber, V. Vatanpour, M.H. Rasoulifard, Electro-Fenton treatment of dye solution containing orange II: Influence of operational parameters, J. Appl. Electrochem. 615 (2008) 165–174.

[46] M.A. Oturan, M.C. Edelahi, N. Oturan, K. El kacemi, J.J. Aaron, Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process, Appl. Catal., B Environ. 97 (2010) 82–89.

[47] Z. Qiang, J.H. Chang, C.P. Huang, Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions, Water Res. 36 (2002) 85–94.

[48] M. Zhou, Q. Yu, L. Lei, G. Barton, Electro-Fenton method for the removal of methyl red in an efficient electrochemical system, Sep. Purif. Technol. 57 (2007) 380–387.

[49] N. Masomboon, C. Ratanatamskul, M.C. Lu, Chemical oxidation of 2,6 dimethylaniline by electrochemically generated Fenton's reagent, J. Hazard. Mater 176 (2010) 92–98.

[50] M.Pourbaix, Gauthier- Villars, ed., Atlas d'équilibres électrochimiques (Atlas electrochemical equilibrium), Paris, 1963, pp. 167–169.

[51] H. Zhang, J.C. Heug, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater 615 (2005) 165–174.

[52] W. He, X. Yan, H. Ma, J. Yu, J. Wang, X. Huang. Degradation of methyl orange by electro-Fenton-like process in the presence of chloride ion. Desalin. Water Treat. 51 (2013) 6562–6571.

[53] L. Zhou, Z. Hu, C. Zhang, Z. Bi, T. Jin, M. Zhou, Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode, Sep. Purif. Technol. 111 (2013) 131–136.

[54] A. Pozza, P. Ferrantelli, C. Merli, E. Petrucci, Oxidation efficiency in the electro-Fenton process, J. Appl. Electrochem. 35 (2005) 391–398.

[55] S.H. Lin, C.T. Shyu, M.C. Sun, Saline wastewater treatment by electrochemical method, Water Res. 32(4) (1998) 1059–1066.

[56] A. Dimoglo, H.Y. Akbulut, F. Cihan, M. Karpuzcu, Petrochemical wastewater treatment by means of clean electrochemical technologies, Clean Technol. Environ. Policy 6 (2004) 288–295.

[57] L.C. Chiang, J.E. Chang, T.C. Wen, Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate, Water Res. 29(2) (1995) 671–678.