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Electrocoagulation and electro-oxidation treatment for the leachate of oil-drilling mud

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ABSTRACT

The pollution caused by discharges of oil drilling is now a source of environmental degradation and raises currently a particular interest. We propose in this work the application of electrocoagulation (EC) and electro-oxidation (EO) treatment for the leachate of these drilling muds. The effect of pH, current density, the electrolysis time, and the amount electrolytic added were studied, and the effectiveness of the processes is evaluated by measuring the chemical oxygen demand (COD). The dissolution is the best way to mobilize pollutants from drilling mud so we conducted leaching before starting the electrochemical treatment. The processes were carried out in batch mode using a stainless steel anode and ruthenium cathode for the EO and aluminum electrodes materials for the EC. The preliminary results clearly demonstrate the compatibility of the two techniques used with the type of pollution studied. In fact, the EC allowed the COD removal of about 95% and a rebate rates above 78% for EO.

Keywords: Oil drilling fluid; Leaching; Electrocoagulation; Electro-oxidation

1. Introduction

The drilling fluid is a system composed of different liquid components (water and oil) and/or gas (air or gas) containing suspended minerals and other additives organic [1,2] added to the slurry to give it the desired properties (flocculant, emulsifying, clogging, and viscosifying). Composed of different natures and whose toxicity and biodegradability are incorrect settings; however, these muds are discharged into quagmires without prior pretreatment [1].

Hydrocarbons are considered hazardous pollutants soils. Their presence can significantly affect the ecosystem and human health [3]. Hydrocarbon toxicity toward the people and the environment depend on their structure and concentration. For example, benzene and its derivatives at low-dose have neurotropic and carcinogenic effects, at higher doses, they cause muscle tremors and convulsions, and a concentration of 65 mg/L in the atmosphere can be rapidly fatal. So many health effects may be associated with drilling fluids, namely dermal irritation, respiratory, and even carcinogenic effects [1].

To this end, we consider it essential to focus on the treatment of sludges stagnant in sloughs that they are wet or dry.

Electrocoagulation (EC) is a technique derived from chemical coagulation; it is one of the simplest electrochemical methods and effective for the

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purification of many types of water and wastewater. This technique is characterized by its simple and easy equipment; a small volume of mud, the coagulant is produced by electrochemical oxidation of an anode which leads at a suitable pH to metal hydroxides insolubles able to remove a wide variety of pollutants [4]. These species play the role of coagulant and lead to the formation of precipitates and flocks easily removable. Pablo [5] have developed a comparative study of EC and chemical coagulation of an oil/water emulsion with the products of hydrolysis of aluminum salt, it was obtained that the two technologies are highly dependent on aluminum concentration and pH. Gholamreza [6] studied the remediation of groundwater contaminated with hydrocarbons by the method of EC. The results showed a removal efficiency of TPH 95% at a pH close to 7 at a current density of 181 A/cm^2. Yang [7] tested the effectiveness of EC on an oil emulsion using iron electrodes. Weintraub et al. [8] applied the EC of oil wastewater by using iron electrodes, the rate of removal was more than 70%.

Treatment by electro-oxidation (EO) is based on the production of radical species, including hydroxyl radical (OH°), which are the most powerful oxidizing species for the treatment of wastewater whose redox potential of 2.8 Volts/NHE at pH 0 [9]. For example, the hydroxyl radicals can oxidize a large number of organic compounds with an oxidation rate substantially higher than that of ozone (109 times higher) [10]. Free radicals are highly active species able to react with substantially all of the organic molecules [11]. The treatment of industrial effluent containing organic matters by electrochemical oxidation is most convenient than the physical/chemical methods because the decomposition of dissolved organic matter by oxidation/reduction reactions are carried out on the surface of the electrode without the use of reagents, so minimizing the refusal of treatment frequently pose problems in processing or storage. The electro-oxidation was successfully applied for the treatment of wastewater [12], the treatment of water from a nuclear power factory [13] and for the treatment of industrial effluents [14]. In this study, we present the results of the application of EC and EO of leachate-drilling muds. Once the optimal conditions for each method identified, we conduct a comparison between the two methods.

2. Materials and methods

2.1. Wastewater samples

The mud used comes from the Hassi Messaoud field with physical/chemical characteristics shown in the Table 1.

Also, analysis by X-ray diffraction reveals a varied mineralogical composition as the presence of minerals such as quartz, calcite, anhydrite (Table 1).

Mineralogical analysis by X-ray crystallography (Fig. 1) showed that the sample 1 consists of: quartz (SiO_2), calcite ($CaCO_3$), dolomite $CaMg(CO_3)_2$ trace, gypsum $CaSO_4$, $CaSO_4$ anhydrite, barite $BaSO_4$, orthoclase $K(Si, Al)_4O_8$, albite $NaAlSi_3O_8$ and Illite clays in low concentration K ($AlSi_2O_9$ $(OH)_3$), kaolinite $Al_2Si_2O_5(OH)$.

2.2. Leach operation

The leaching operation is the dissolution of the metal or valuable metals for subsequent extraction [15]. The acid solution used for the leaching is an aqua regia, the system mud and aqua regia are put together with mechanical stirring for 2 h. Recovering the leachate will undergo electrochemical treatment is carried out after settling of two days.

2.3. The electrocoagulation

A batch of monopolar electrochemical reactor was constructed with two aluminum electrodes for the EC step. The installation was connected to a DC power supply PS-305D, each electrode was rectangular plates, separated from each with distance of 2 cm, the thickness was 1.1, and the width was 1.1 and 6 cm in length for an area of 6.6 cm^2. Stirring was provided by a magnetic stirrer type veb MLW PRUFGERATE-WERK.

2.4. Electro-oxidation process

The EO was carried out in batch mode (Fig. 1) using a stainless steel anode and ruthenium cathode. Both the electrodes are drilled hard of 2 mm pore diameter, the diameter of the anode (Fig. 2) equal to 5 cm and the thickness to 1 cm (active area = 1.96 cm^2) attached to a stainless steel rod and the cathode was with a diameter of 4 cm. A DC power source (PS-305D) supplied for the system the current density, the system worked with constant stirring speed of 400 rev/min, speed chosen to ensure good homogenization and that shear forces is not too important and do not break the solid formed. Stirring is provided by a magnetic stirrer type veb MLW PRUFGERATE-WERK.

2.5. Characteristics of effluent to be treated

Processes EC and EO are applied to masses of sludge equal to 20 and 40 g (Table 2).

Table 1
Characterization of drilling muds used

Physical/chemical analysis		Diffraction analysis (XRD)	
Parameters	Results	Crystalline substances	Chemical formula
pH	8.07	Barite	$BaSO_4$
Humidity (%)	4.8	Quartz	SiO_2
Nitrates (mg/L)	0.4	Calcite	$CaCO_3$
Nitrites (mg/L)	5	Anhydrite	$CaSO_4$
Phosphore (mg/L)	0.46	Halite	NaCl
Chlorides (g/L)	1.51	Galenq	PbS
Dried residues (mg/L)	10	Dolomite	$CaMg(CO_3)_2$
Conductivity (mS/cm)	4.66	Kaolinite	$Al_2Si_2O_5(OH)_4$
COD (mg/L)	303	Bassanite	$CaSO_4$
BOD_5 (mg/L)	16.9	–	–
Calcium (mg/L)	315.6	–	–
Magnesium (mg/L)	1.22	–	–
TPH (%)	27	–	–

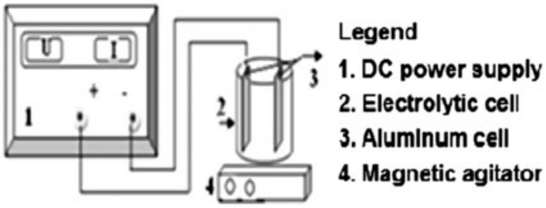

Fig. 1. Electrolytic cell.

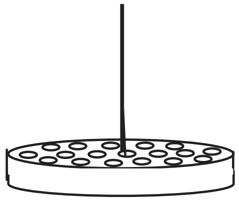

Fig. 2. Stainless steel anode. Active area = $1.96\,cm^2$.

Table 2
Leachate samples

Sludge mass (g)	pH	Conductivity (mS/cm)	COD (mg O_2/L)
20	1.4	19.08	384
40	1.3	14.04	468

The operative effect of several parameters (pH, current density, electrolysis time) on the effectiveness of these two operations was evaluated. The volume of the treated solution is 200 mL.

To investigate the feasibility of electro-oxidation process, we performed dilutions of the leaching solution with a the chemical oxygen demand (COD) of about 384 mg O_2/L.

2.6. Analytical techniques used

On all treated samples, we performed before and after treatment the physical/chemical properties:

- Mineralogical analysis by X-ray with an X'Pert PRO diffractometer.
- pH measured by a pH meter (HANNA Ph210).
- The electrical conductivity was measured by a conductivity meter (type HANNA/EC214).
- COD was measured by using ECO/thermoreactor closed reflux titrimetric method according to the standard NF T90-101.

3. Results and discussion

3.1. Electrocoagulation results

The effect of various operating parameters on the efficiency of this operation was evaluated. It has been established that the pH initial play an important role on the performance of eletcrocoagulation process. Pablo et al. [6] achieved 80% removal efficiency to the treatment of oil-in-water emulsion in the pH range from 5 to 9 using aluminum electrodes.

In our study, the pH of the leachate was adjusted to the desired values by adding aliquots of sodium hydroxide from the range of 1.31–5. The current density was fixed at 0.0496 A/cm ^{2} during 1 h. The results are shown in Fig. 3, the highest rate of COD was recorded at a value of pH=5 corresponds to a maximum reduction (95%) in the case of leaching 20 g of sludge. Highest removal efficiency can be achieved near acidic pH; it can be explained by amphoteric behavior of metal hydroxides that lead to soluble cations and to monomeric anions [16]. The process of formation of coagulant is made through the reactions during the process for EC, the electrochemical reactions brought into play for electrodes subjected to a continuous flow [17] are:

Half-reaction of oxidation: The reaction that occurs at the anode is the in situ production of cations and the oxidation of water.

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \tag{1}$$

Catonné [18] states that if the current density is sufficient and if the environmental conditions are favorable, the anode may also be the seat of a water oxidation.

$$2H_2O \rightarrow 4H^{+} + O_2 + 4e^{-} \tag{2}$$

Reduction half-reaction: The main reaction listed in the bibliography leads to the reduction of water.

$$H_2O + e^{-} \rightarrow 1/2H_2 + OH^{-} \tag{3}$$

All Al^{3+} and OH^{-} generated in solution react to form various species such as Al $(OH)^{2+}$, $Al_2(OH)_2$, $Al_{13}OH)^{5+}_{34}$, which eventually transform into $Al(OH)_3$ complexes according precipitation kinetics [19,20]. This species acts as a coagulant by neutralizing the negative charges on the surface of the colloids.

The current density is judged to be an essential parameter that controls the performance of the EC process, because it determines the coagulant dosage rate. Kaliniichuck et al. [21] studied the application of elecrocoagulation to treat oil refinery wastewater, the electrolysis was carried out using a range of current density of 2–35 A/m^{2} the results showed that it was possible to obtain a rate removal of 99.5%.

Four current densities were tested; the pH initial was fixed at the value of 3 during 1 h of reaction. Fig. 4 shows the effect of current density as a function of COD reduction is about 95% obtained for a current density of about 0.0286 A/cm^{2}. For a current density less than 0.0286 A/cm^{2}, the rate of reduction is 75%. This is attributed that a low current density will produce a small amount of aluminum oxide, resulting in a small amount of precipitate to remove colloidal particles. For higher current density at 0.0286 A/cm^{2}, the rate of reduction is lower which means that the amount of the coagulating agent is in excess. Amirtharajah et al. [22] showed that in the case of an overdose of coagulant, source of cations, can result an important adsorption of cations and reversing the charge of the particles which becomes positive, so the particles are destabilized. Also in Fig. 4 shows an increase in the pH of the solution after EC treatment according to the current density. This is mainly due to the OH-ions produced by the electrolysis of water with evolution of hydrogen at the cathode according to the redox reaction (3) and this has been observed by other researchers [23].

3.2. Electro-oxidation results

The effect of a number of operating factors on electro-oxidation of leachate has been investigated, pH, current density, as well as electrolytes added. These factors variously influence pollutant removal efficiency. Experiments were conducted under three

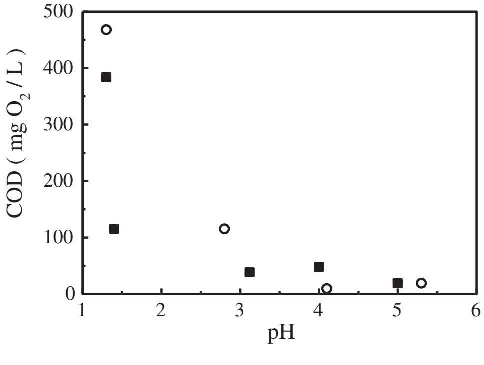

Fig. 3. Effect of initial pH on COD. Current density = 0.0496 A/cm^{2}; mass leaching mud: ■ 20 g, ○ 40 g.

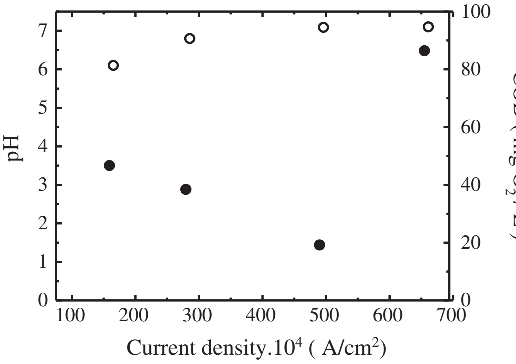

Fig. 4. Effect of current density on COD and pH supernatant; mass leaching mud: 20 g; initial pH: 3, ◆ COD, ○ supernatant pH.

pH conditions covering acid, alkaline and neutral, the electrolysis time was fixed at 1 h and NaCl mass equal at 2 g. As shown in Fig. 5, low range of pH is not desirable. It was observed during the present investigations that under alkaline conditions we obtained maximum removal efficiency, the results show that at pH=8, the purification of the solution reached a level maximum of abatement. In fact, acidic and alkaline conditions during electrochemical oxidation could help organics removal. Acidic conditions significantly decrease the concentration of CO_3^{2-} and HCO_3^-, both well-known scavengers of $^{\circ}OH$ generated on anodes, and so enhances oxidation [24], while alkaline condition boosts the Cl^- redox circulation to enhance indirect oxidation [25]. The sample is mineralized according to the electrochemical mechanism.

EO of pollutants in wastewater is fulfilled through two different approaches, as shown in Fig. 7, either directly or indirectly.

Direct anodic oxidation, where pollutants are destroyed on the anode surface [24], the exchange of electrons takes place only on the electrode. Insoluble electrodes called high oxygen overvoltage (Pt, Ti/IrO_2; Ti/RuO_2; Ti/SnO_2, PbO_2, Gr, etc.) are commonly used [25,26]. Used at the anode, these electrodes allow the complete oxidation of a large number of organic molecules contained in the wastewater. By-products resulting from the anodic oxidation are carbonic acid, ammonia and water and other products. In many cases, the anodic oxidation of organic [28] or inorganic pollutants leads to the formation of simple compounds, less toxic and biodegradable [29]. For example, the anode phenols are oxidized to maleic acid, cyanides into cyanates, and sulfides into sulfates [27,30]. It is important to note that these electrodes called high oxygen overvoltage can oxidize compounds not chemically oxidizable or difficult to oxidize [31].

Step 1: anodic discharge of water: production of radicals on the electrode M

$$H_2O + M \rightarrow M[OH^{\circ}] + H^+e^- \tag{4}$$

Step 2: Oxidation of organic substances by the radicals OH°

$$R + M[OH^{\circ}] \rightarrow M + RO + H^+ + e^- \tag{5}$$

(M) is an active site of the electrode on which the radicals can adsorb and (RO) the oxidized organic product.

In some cases, electrolysis can be inefficient or slow. It is then necessary to generate an oxidant that reacts electrochemically with pollutants. In the case of indirect oxidation, a mediator is electrochemically generated to carry out the oxidation [26]. During indirect oxidation, the agents generated anodically, which are responsible for the oxidation of inorganic and organic pollutants, may be chlorine and hypochlorite [33,34], hydrogen peroxide [35,36], ozone [37,38], and metal mediators such as Ag^{2+} [39].

Current density, the current per unit area of electrode, may be the most frequently referred term in an electrochemical process because it controls the reaction rate [40]. Fig. 6 shows the evolution of the COD as a function of the current density, the rate of maximum reduction is observed for a current density equal to 0.01892 A/cm^2, higher current densities decrease the removal efficiency.

The variation of COD with electrolysis time is presented in Fig. 8. The rate of reduction of COD is very sharp at the beginning of the process and reached a higher rate after 15 min (leachate dilution 10 mL), and after 60 min (leachate dilution 20 mL), this can be explained for the first case that the bulk is less charged than the second dilution.

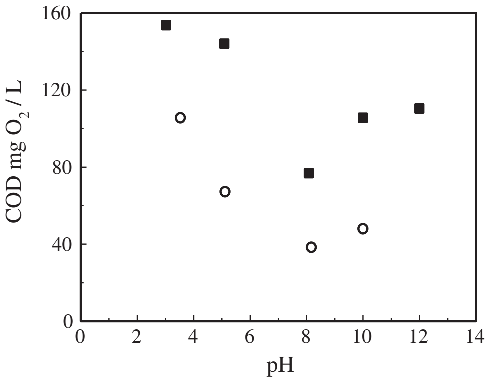

Fig. 5. Effect of pH on COD. Current density = 0.01892 A/cm2. Lixiviat dilution: ■ 10 mL, ○ 20 mL.

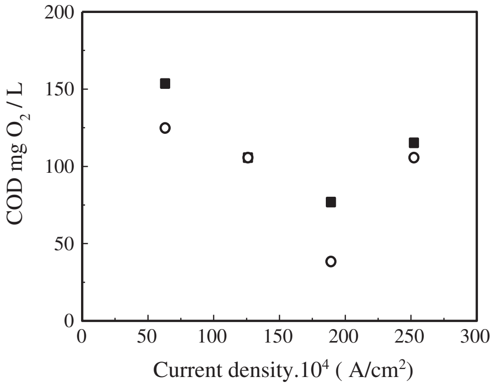

Fig. 6. Current density effect on COD pH=8. Lixiviat dilution: ■ 10 mL, ○ 20 mL.

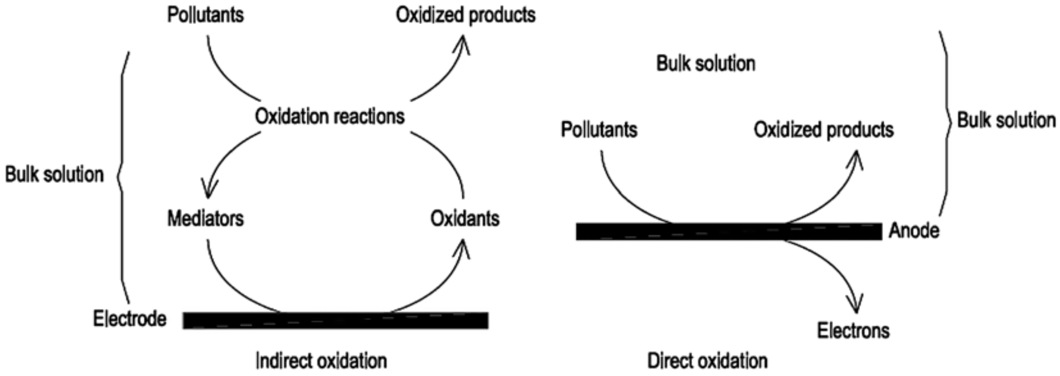

Fig. 7. Pollutant removal pathways in electrochemical oxidation (indirect and direct oxidation). Data from [32].

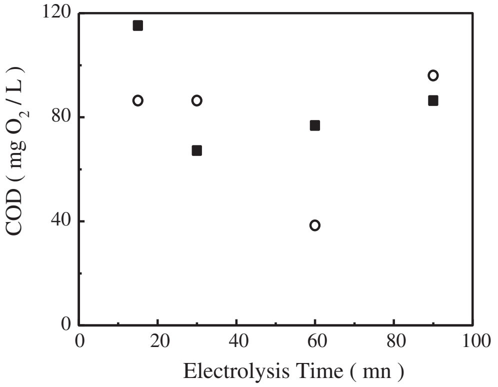

Fig. 8. Electrolysis time effect on COD; pH = 8; NaCl mass = 2 g. Lixiviat dilution: ■ 10 mL, ○ 20 mL.

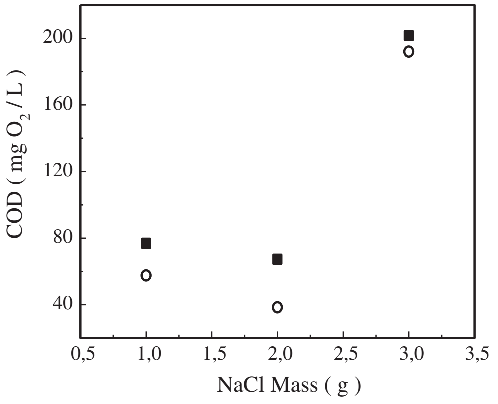

Fig. 9. Effect of NaCl mass on COD pH = 8; electrolysis time = 30 min Lixiviat dilution: ■ 10 mL, ○ 20 mL.

After 60 min, we observe an increase in COD. The possible reason is that during a long time of electrolysis an important amount of hazard of chlorinated organic is formed in the effluent because of the adding of NaCl, and this leads to the presence of another type of pollutant in the solution and as a result of growth of the COD.

Electrolyte is a substance which is responsible for increasing the conductivity of the solution, and a medium that provides the ion transport mechanism between the anode and the cathode necessary sustain electrochemical process. Hence, we can have more variety of electrolytes we choose to work with NaCl because of its availability in a low cost. In our study, we selected range of different amount of NaCl (1–3 g), from Fig. 9, it can be ascertained that the adding of electrolyte enhances the destruction of organics present in the wastewater, the amount of NaCl needed to reach a maximum removal of COD is 2 g; beyond this amount, there is a higher pollution load.

4. Conclusion

The EC and EO each has advantages and disadvantages, EC reduces the processing time [39] and does not require addition of chemicals [40], which is very effective in removing fine colloidal [41]; however, this method is ineffective for the removal of organic matter, unlike the EO which is very effective in reducing organic compounds but requires a long reaction time in the presence of colloids in suspensions [14], the decrease in the current efficiency during the reaction and the formation of products parasite [42] makes this process a disadvantaged, it is interesting to note that these two methods are complementary and their coupling will induce to a synergistic process that will be able to mineralize organic matter in a reasonable time.

In this paper, we propose EC and EO for the treatment of the leachate of oil-drilling mud. Indeed, we have reached abatement rate for the EC of the order of 95% for an electrolysis time of 1 h and we have obtained a reduction of COD for the same time of the order of 78% in the case of the EO. The comparison between various techniques shows an important contribution of each method. However, these methods are often criticized regarding feasibility, cost, precision, and conditions used.

References

[1] M. Khodja, J.P. Canselier, F. Bergaya, K. Fourar, M. Khodja, N. Cohaut, A. Benmounah, Shale problems and water-based drilling fluid optimisation in the Hassi Messaoud Algerian oil field, Appl. Clay Sci. 49 (2010) 383–393.

[2] H.C.H. Darley, G.R. Gray, Composition and Properties of Drilling and Completion Fluids, 5th ed., Gulf Professional Publishing, Houston, TX, 1988, p. 630.

[3] S. Semrany, L. Favier, H. Djelal, S. Taha, A. Amrane, Bioaugmentation, possible solution in the treatment of bio-refractory organic compounds (Bio-ROCs), J. Biochem. Eng. 69 (2012) 75–86.

[4] F. Ilhan, U. Kurt, O. Apaydin, M. Talha Gonullu, Treatment of leachate by electrocoagulation using aluminium and iron electrodes, J. Hazard. Mater. 154 (2008) 381–389.

[5] C. Pablo, Coagulation and electrocoagulation of oil-in-water emulsions, J. Hazard. Mater. 151 (2008) 44–51.

[6] M. Gholamreza, Removal of petroleum hydrocarbons from contaminated groundwater using an electrocoagulation process: Batch and continuous experiments, Desalination 278 (2011) 288–294.

[7] C.-L.Yang, Electrochemical coagulation for oily water demulsification, Sep. Purif. Technol. 54 (2007) 388–395.

[8] M.H. Weintraub, R.L Golovoy, M.A Dzieciuch, Development of electrolytic treatment of oily wastewater, Environ. Prog. 2 (1) (1983) 32–37.

[9] H. Suty, C.D.E. Traversay, M. Coste, Application of advanced oxidation processes: Present and future, in: Dans: Proceedings of the Third Conference on Oxidation Technologies for Water and Wastewater Treatment, Goslar, Allemagne, 2003, p. 8.

[10] S. Parsons, Advanced Oxidation Processes for Water and Wastewater Treatment, IWA. Publishing, Alliance House, London, England, 2004, p. 356.

[11] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[12] C. Feng, N. Sugiura, S. Shimada, T. Maekawa, Development of high performance electrochemical wastewater treatment system, J. Hazard. Mater. B 103 (2003) 65–78.

[13] K.H. Yeon, J.H. Song, J. Shim, S.H. Moon, Y.U. Jeong, H.Y. Joo, Integrating electrochemical processes with electrodialysis reversal and electro-oxidation to minimize COD and T–N at wastewater treatment facilities of power plants, Desalination 202 (2007) 400–410.

[14] I. Linares-Hernándeza, C. Barrera-Díaza, B. Bilyeub, P. Juárez, G. Rojasa, E. Campos- Medinac, A combined electrocoagulation–electrooxidation treatment for industrial wastewater, J. Hazard Mater. 175 (2010) 688–694.

[15] R.M.M. Abed, N.M.D. Safi, J.R. Köster, D. de Beer, Y. El-Nahhal, J. Rullkotter, F. Gareia-Picliel, Microbial diversity of a heavily polluted microbial mat and its community changes following degradation of petroleum compounds, Appl. Environ. Microbiol. (2002).

[16] V.A. Glembotskii, A.A. Mamakov, A.M. Ramanov, V.E. Nenno, in: Proceedings of the 11th International Mineral Processing Congress, Cagliari, Italy, 1975, pp. 562–581.

[17] J.G. Ibanez, M.M. Singh, Z. Szafran, Laboratory experiments on eletcromechemical remediation of the environment. Part 4: Color removal of simulated wastewater by electrocoagulation-electroflotation, J. Chem. Edu. 75(8) (1998) 1040–1041.

[18] J.C. Catonné, Traitements de surface par voie humide: Introduction, Techniques de l'Ingénieur, M 1428 (1996) 1–16.

[19] J.Q. Jiang, N. Graham, C. Andre, G.H. Kelsall, N. Brandon, Laboratory study of electrocoagulation–flottation for water treatment, Water Res. 365 (2002) 4064–4078.

[20] J. Qu, H. Liu, Optimum conditions for Al13 polymer formation in PACL preparation by electrolysis process, Chemosphere 55 (2004) 51–56.

[21] E.M. Kaliniichuk, I.I. Vasilenko, V.Y. Shchepanyuk, N.A. Sukhoverkhova, I.A. Makarov, Treating refinery wastewaters to remove emulsified oils by electrocoagulation and electroflotation, Int. Chem. Eng. 16(3) (1976) 434–435.

[22] A. Amirtharajah, C.R. O'Mella, Coagulation Processes: Destabilization, Mixing, and Flocculation, Chapter 4, Water Quality and Treatment, Handbook of Commzinity Water Supplies, 4th ed., A WWA, 1999, pp. 269–365.

[23] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.

[24] J. Grimm, D. Bessarabov, R. Sanderson, Review of electroassisted methods for water purification, Desalination 115(3) (1998) 285–294.

[25] P. Wang, W.C.I. Lau, H.P.H. Fang, Landfill leachate treatment by anaerobic process and electrochemical oxidation, Environ. Sci. 22(5) (2001) 70–73.

[26] D. Gandini, C. Comninellis, N.B. Tahar, A. Savall, Électrodépollution: Traitement électrochimique des eaux résiduaires chargées en matières organiques toxiques, Actualité Chimique 10 (1998) 68–73.

[27] K. Rajeshwar, J.G. Ibanez, Environmental Electrochemistry. Fundamentals and Applications in Pollution Abatement, Academic Press, Londres, Angleterre, 1997, p. 776.

[28] C. Comninellis, P. Seignez, P. Peringer, E. Plattner, Dégradation des polluants organiques industriels : Traitement électrochimique, biologique et leur couplage, Swiss Chem. 14 (1992) 25–30.

[29] P. Calvin, C. Poon, Electroflotation for groundwater decontamination, J. Hazard. Mater. 55 (1997) 159–170.

[30] C. Pulgarin, N. Adler, P. Peringer, C. Comninellis, Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment, Water Res. 28 (1994) 887–893.

[31] Y. Deng, J.-D. Englehards, Electrochemcial oxidation for landfill leachate treatment, memorial Dr, University of Miami, Coral globes, FL 33164, USA.

[32] J. Naumczyk, L. Szpyrkowicz, F. Zilio-Grandi, Electrochemical treatment of textile wastewater, Water Sci. Technol. 34(17) (1996) 17–24.

[33] A.G. Vlyssides, C.J. Israilides, M. Loizidou, G. Karvouni, V. Mourafeti, Electrochemical treatment of vinasse from beet molasses, Water Sci. Technol. 36(2–3) (1997) 271–278.

[34] E. Brillas, R.M. Bastida, E. Llosa, J. Casado, Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O2-fed cathode, J. Electrochem. Soc. 142(6) (1995) 1733–1741.

[35] E. Brillas, E. Mur, J. Casado, Iron(II) catalysis of the mineralization of aniline using a carbon-PTFE O2-fed cathode, J. Electrochem. Soc. 143(3) (1996) L49–L53.

[36] S. Stucki, H. Baumann, H.J. Christen, R. Kotz, Performance of a pressurized electrochemical ozone generator, J. Appl. Electrochem. 17(4) (1987) 773–778.

[37] W. El-Shal, H. Khordagui, O. El-Sebaie, F. El-Sharkawi, G.H. Sedahmed, Electrochemical generation of ozone for water treatment using a cell operating under natural convection, Desalination 99(1) (1994) 149–157.

[38] J.C. Farmer, F.T. Wang, R.A. Hawley-Fedder, P.R. Lewis, L. J. Summers, L. Foiles, Electrochemical treatment of mixed and hazardous wastes: Oxidation of ethylene glycol and benzene by silver (II), J. Electrochem. Soc. 139(3) (1992) 654–662.

[39] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38(1) (2004) 11–41.

[40] E.V. Cenkin, N.A. Belevstev, Electrochemical treatment of industrial wastewater, Eff. Water Treat. J. 25 (1985) 243–247.

[41] A.H. Essadki, M. Bennajah, B. Gourich, Ch. Vial, M. Azzi, H. Delmas, Electrocoagulation/electroflotation in an external-loop airlift reactor-application to the decolorization of textile dye wastewater: A case study, Chem. Eng. Proc. April (in press).

[42] N. Kannan, G. Karthikeyan, N. Tamilselvan, Comparison of treatment potential of electrocoagulation of distillery effluent with and without activated Areca catechu nut carbon, J. Hazard. Mater. 137 (2006) 1803–1809.