

Treatment of Leaden Sludge of Algiers Refinery by Electrooxidation

K. Ighilahriz, M. Taleb Ahmed, R. Maachi

Abstract—Oil industries are responsible for most cases of contamination of our ecosystem by oil and heavy metals. They are toxic and considered carcinogenic and dangerous even when they exist in trace amounts. At Algiers refinery, production, transportation, and refining of crude oil generate considerable waste in storage tanks; these residues result from the gravitational settling. The composition of these residues is essentially a mixture of hydrocarbon and lead. We propose in this work the application of electrooxidation treatment for the leachate of the leaden sludge. The effect of pH, current density and the electrolysis time were studied, the effectiveness of the processes is evaluated by measuring the chemical oxygen demand (COD). The dissolution is the best way to mobilize pollutants from leaden mud, so we conducted leaching before starting the electrochemical treatment. The process was carried out in batch mode using graphite anode and a stainless steel cathode. The results clearly demonstrate the compatibility of the technique used with the type of pollution studied. In fact, it allowed COD removal about 80%.

Keywords—Electrooxidation, leaching, leaden sludge, the oil industry.

I. INTRODUCTION

THE activities of oil industry generate discharges of extreme variability in quantity, nature and toxic degree. At Algiers refinery, production, transportation, and crude oil refining generate considerable residues at storage tanks; these residues are derived from the gravity settling. At the gasoline storage tanks, solid deposits are formed; called tanks bottom deposits or slop oil. The composition of these residues is essentially a mixture of hydrocarbon and lead. The use of metal drums at Algiers refinery can be a lower cost solution to store leaden sludge nevertheless when the storage drums are corroded or overload, the sludge is placed on surfaces. The presence of heavy metals in the environment lead in our case, it is not desirable. It is characterized by its acute toxicity, it is not biodegradable, once deposited on the soil, plants, and in water's surface, it may enter the food chain. Exposure to lead can cause serious adverse health issues and can even be fatal at high doses. The lead can accumulate in the body by its exposure to even very low doses. This led us to consider the treatment of leaden sludge by the electrooxidation. In the electrochemical technique, the main reagent is the electron a clean reagent, which degrades all the organics present in the effluent without generating any secondary pollutant or sludge.

The electrooxidation (EO) offers the advantage to react on pollutants by either a direct or an indirect oxidation process. In the direct anodic oxidation process, the pollutants are adsorbed on the anode surface and then destroyed by the generated hydroxyl radicals [1]. In the indirect oxidation process, strong oxidants (hypochlorite/chlorine, ozone, and hydrogen peroxide) are electrochemically generated to destroy the pollutants in a bulk solution. All the oxidants are generated in situ and utilized immediately [2]. This technique has been the subject of the number of users with attractive purifying yields such as the treatment of ammonia and phosphate wastewater [3], azo dyes [4], olive mills wastewater [5] and drilling mud [6]. The present work is intended to treat the leachate of leaden sludge to a level that meets the discharge standards of pollution control Board. The effect of a set of parameters has been studied; the current efficiency and energy consumption were also calculated.

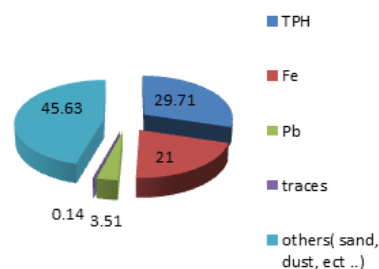


Fig. 1 Sludge composition

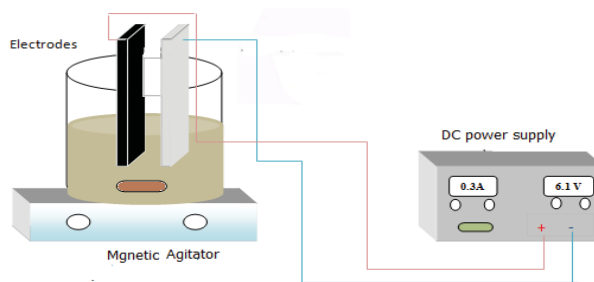


Fig. 2 Electrochemical cell

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II. MATERIALS AND METHODS

A. Sampling Leaden Sludge

Fig. 1 shows the composition of the leaden sludge; it is mainly contaminated by hydrocarbons and iron due to the corrosion of metal drums and lead whose concentration is of the order of 35140mg / kg.

B. Electrooxidation Treatment

The volume of solution to be treated equally to 200 ml, extracted from a leaching operation. The leaching operation consists of the dissolution of the metal or valuable metals for subsequent extraction. The acid solution used for the leaching is nitric acid, the mass of sludge is 20 g, and the mixture is mechanically stirred for 2 hours. Recovering the leachate from undergoing electrochemical treatment is carried out after settling of 2 days. The solution obtained has a COD of 324 and pH equal to 8. The experiments were run in batch mode (Fig. 2) using a graphite anode and stainless steel cathode. A DC power source supplied the system, worked with the constant stirring speed of 400 rev/min, speed chosen to ensure good homogenization. A magnetic stirrer type N0690 / 1 provides stirring. COD was measured by using ECO/thermo-reactor closed titrimetric reflux method per the standard NF T90-101.

III. RESULTS AND DISCUSSION

A. Effect of Current Density

The current density has a significant influence on the rate of reduction of organic matter; it is the driving force of the migration of the charge [7].

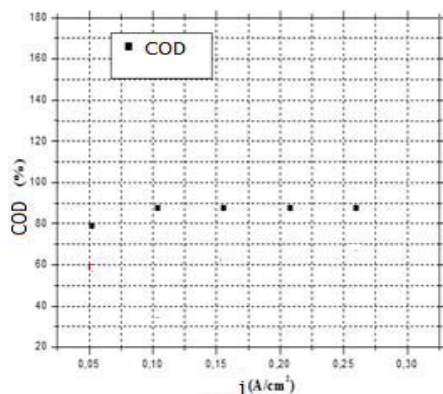


Fig. 3 Effect of current density on COD Removal ($t=2h$, $pH=8$, $mNaCl=0.5g$)

From the results, when the current density increases the oxidation rate increases (the oxidation rate increases as well/too). The percentage reduction of COD passes from 80% at a current density of 0.05 A / cm² to 89% for a 0.1 A/cm² beyond this value the effectiveness of the treatment remains constant. Indeed, the use of high current densities may imply a remarkable formation of OH[•] radicals, which contribute to the electrochemical oxidation of organic compounds, thus reducing the COD [8]. We have calculated the current efficiency using:

$$ICE = \left(\frac{(\Delta COD)V}{\frac{16 I \Delta t}{2F}} \right) \times 100 \quad (1)$$

where (COD)_t and (COD)_{t + Δt} respectively represent the chemical oxygen demand (g / L) at time t and $t + \Delta t$, I : intensity of electric current (A), F : Faraday's constant (96500 C / mol), V : the volume of the solution (L).

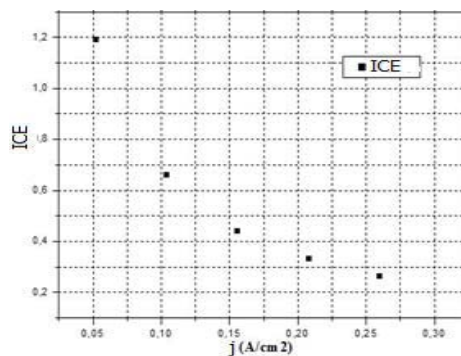


Fig. 4 Current efficiency as function of current density ($t=2h$, $pH=8$, $mNaCl=0.5g$)

The increase of current density causes a decrease in current efficiency (ICE). We conclude that electro-oxidation with lower current density is advantageous, according to [9] when the current applied density exceeds the current density limit this means that the oxidation is performed at a higher current density than the minimum required stoichiometrically. Secondary reactions will also take place, resulting in a decrease of ICE [10].

B. Effect of Electrolysis Time

We evaluated the influence of time on the effectiveness of treatment, under the following conditions ($j = 0.1$ A/cm²; $pH = 8$, $mNaCl=0.5g$). Increasing the time induces an increase in the reduction efficiency of the COD to reach a plateau after 3h wherein the percentage reduction is of the order of 85%. Fig. 6 shows the same manners obtained for the current density.

C. Effect of pH

The electrochemical oxidation of organic compounds can be highly dependent on pH of the solution to be treated. To study the effect of pH on the reduction of COD, it is adjusted to values ranging from 3 to 12. We set the current density at 0.1 A/cm², an electrolysis time of 3h with an amount of NaCl of 0.5g.

It is evident that the rate of COD reduction was considered negligible at pH 3 and pH 5 but raising the pH leads to increasing the degree of COD reduction. At pH 8 the percentage reduction was 85%, at pH = 9 and pH = 12, the removal rate remains constant. A review of previous experiments cannot conclude whether the increase or decrease in pH favors the elimination of COD. The alkaline conditions enhance redox circulation of $Cl^- \rightarrow Cl_2 \rightarrow ClO^- \rightarrow Cl^-$ to improve indirect oxidation [4]. Further at higher pH active chlorine is present in form of hypochlorite which is a weaker oxidizing towards organic species relative to hypochlorous acid which is the major species present at lower pH. Fig. 8 shows an increase of ICE as

function a of pH to reach an ICE of 88%. Therefore, the alkaline conditions favor the reduction of pollution, which is also stated in the literature [8].

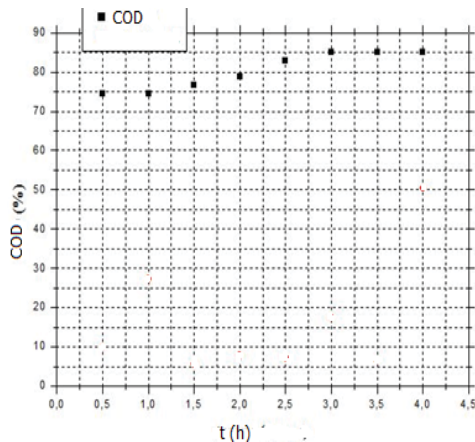


Fig. 5 Effect of electrolysis time on COD ($J=0.1 \text{ A/cm}^2$, $\text{pH}=8$, $\text{mNaCl}=0.5\text{g}$)

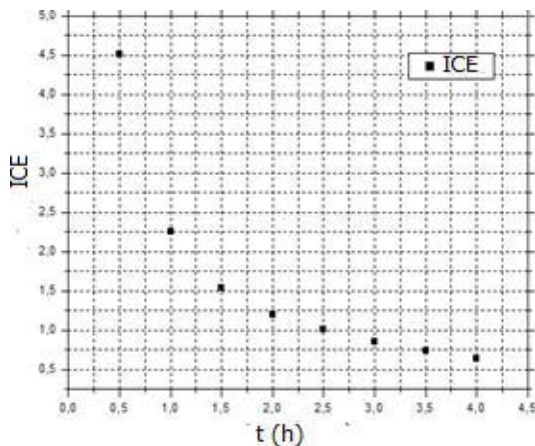


Fig. 6 Current efficiency as function of time ($J=0.1 \text{ A/cm}^2$, $\text{pH}=8$, $\text{mNaCl}=0.5\text{g}$)

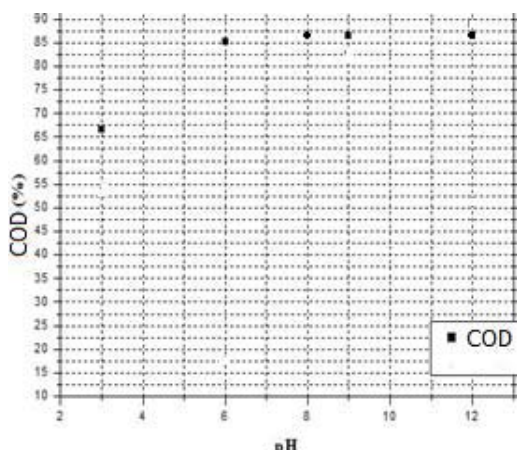


Fig. 7 Effect of pH on COD removal ($J=0.1 \text{ A/cm}^2$, $\text{mNaCl}=0.5\text{g}$, $t=3\text{h}$)

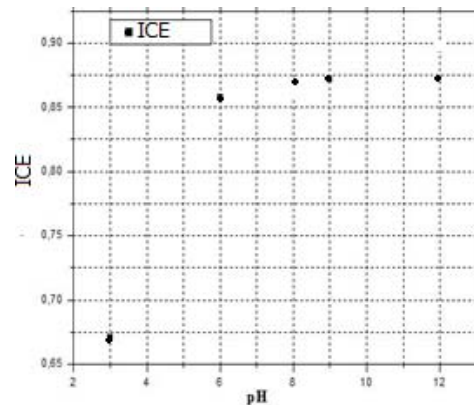


Fig. 8 Current efficiency as function of pH ($J=0.1 \text{ A/cm}^2$, $\text{mNaCl}=0.5\text{g}$, $t=3\text{h}$)

D. Electrochemical Energetic Consumption

The electrical energy consumption was calculated in terms of kWh/kg COD, using:

$$E = \frac{U \times I \times t}{1000 \times \Delta \text{COD} \times V} \quad (2)$$

where U is cell voltage (V), I is current (A), t is the electrolysis time (h), V the volume of solution and ΔCOD is the subtraction of COD before and after treatment. The emery consumption under optimal conditions found ($I=0.1 \text{ A}$, $t=3\text{h}$, $\text{pH}=8$, $\text{mNaCl}=0.5\text{g}$) equal to 22.5 kWh/kgCOD , similar results were found by Gotsi et al., 2005 for the Electrochemical oxidation of olive oil mill wastewaters [11].

IV. CONCLUSION

These series of experiments revealed the potential of pollution of EO. Experiments were carried out in a batch electrochemical cell for COD reduction. The COD reduction is significantly affected by the pH, time and current density. Abatement rates exceeding 80% have been obtained under the optimal conditions ($t=3 \text{ h}$, $\text{pH}=8$, $J=0.1 \text{ A/cm}^2$). This work has helped to expand the applications of electrochemistry, clean, economically viable technology in the environmental technology industry.

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