A Study of Electrocoagulation for Treatment of Wastewater from Oil Change Applying of Iron Electrodes

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Abstract: The liquid organic oil manufacturing content a high quantity of organic matter. Electrolytic degradation of organic matter in wastewater was conducted by electrocoagulation (EC) reagents. This process using iron electrodes were carried out in a batch electrolytic reactor. During the electrochemical process, hydroxide of iron was in situ generated by oxidation of iron from anodes and cathodic reduction of water. Effects of operating conditions such as current density, initial pH, intensity of current, quantity of electricity. The EC process on removal efficiencies of total organic matter (OM), mass of iron, energy consumed were investigated. Removal efficiency of 96,22% for MO, 0,167mg for consumption of iron, with 0.901kWh/kg for energy consumed from the EC process at the optimum operating conditions (15,92A/mm², 30 min, pH 7, 0,4A), were obtained.

Keywords: Electrocoagulation wastewater, oil change, Iron Electrode.

1. Introduction

In recent years, the use of oil motor (MO) containing humic matters in modern hydrocarbure industries has been increased considerably [1,2]. After their applications, the MOs producing of high-yielding waste present in soil and water. They contain growth promoting macronutrients, micronutrients, fulvic and humic acids [3,4]. These compound Chemical decrease fertility of plant and pollution water [7]. Effluents from mineral oil may include dark brown color, chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) [5]. The presence of the above pollutants in MO manufacturing wastewater leads to serious damage when discharged directly into the environment. These pollution factors have all been responsible for encouraging the rapid growth of algae (eutrophicication). Owing to the toxicity and plausible carcinogenicity caused by this effluent, the wastewater from manufacturing of oil motor should be properly disposed prior to release into the environment. Hence, MO must be treated before being discharged into the environment due to the legal restrictions and conservation of natural life in world (mainly in

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Several methods are used to treat pollutant (adsorption, coagulation, fenton, etc…) but their present a secondary pollution. Recent researches have shown that electrochemical techniques can offer a good opportunity to prevent and remedy pollution problems due to strict environmental regulations. Electrocoagulation (EC) processes is simple and efficient methods that have attracted a great deal of attention for the treatments of various industrial wastewaters such as olive mill wastewater [12, 6] alcohol distillery wastewater [13], paper pulp treatment effluent [14], agro-industry wastewater [15], baker’s yeast wastewater [16], potato chips manufacturing wastewater [17], chemical mechanical polishing wastewater [18], poultry slaughterhouse wastewater [19], tannery wastewater [20,21], electroplating rinse water [22] and textile wastewaters [23,24] and so on. The EC processes is environmentally friendly and do not generate secondary pollutants. Some advantages of this process as compared to the conventional methods are easy to operate, less retention time, lower operating costs, or absence of adding chemicals, rapid sedimentation of the electrogenerated flocs and less sludge production and requires a simple equipment. Aim of the present study was to investigate the removal of oil motor manufacturing wastewater by the electrocoagulation (EC) process using iron electrodes in a batch mode operation. The effects of operating parameters such as pH, current density, operating time intensity of current.

2. Mechanisms of electrocoagulation

The electrocoagulation (EC) process involves generation of coagulants in situ by dissolving sacrificial anodes such as aluminum or iron upon application of a direct current. When iron electrode is used as anodes upon oxidation in an electrolytic system, it produces iron hydroxide, Fe(OH)n where n = 2 or 3 [25,26]

\[
\begin{align*}
4Fe_{(s)} & \rightarrow 4Fe_{(aq)}^{2+} + 4e^- & \text{(Anode)} \quad (1) \\
2H_2O + 2e^- & \rightarrow H_2 + 2HO^- & \text{(Cathode)} \quad (2) \\
Fe_{(aq)}^{2+} + 2HO_{(aq)} & \rightarrow Fe(OH)_{2(s)} \text{ (in bulk solution)} \quad (3) \\
Fe_{(aq)}^{3+} + 3HO^- & \rightarrow Fe(OH)_{3(s)} \text{ (in bulk solution)} \quad (4)
\end{align*}
\]

Fe(OH)n remains in the aqueous stream as a gelatinous suspension and may be removed from the wastewater by coagulation, adsorption, co-precipitation and sweep flocculation [27].

3. Materials and methods

3.1. Wastewater source

Oil motor obtained came from maicam (Cameroun), was dissolved with de-ionized water to the desired concentrations, adjusted to pH by HCl or NaOH.

3.2. Experimental and procedure

The experimental set-up containing the specifications of electrode, reactor was reported elsewhere [16]. The EC reactors was made of Plexiglas with dimension of 150 mm x100 mm x100 mm. two cylindric electrodes (one anode and one cathode) with dimension of 15 mm x 4mm (purity P 96.5%) were used in the study. The total effective electrode area was 376,8mm² and the spacing between electrodes was 1cm. The electrodes were connected to an generator(Evolution R300 Jeulin:30V, 5A).Therefore, the electrode were arranged in parallel, and cleaned manually with sandpaper, and they were treated with 10% HCl for cleaning followed by washing with distilled water to their use. The chemicals products (NaCl, H₂SO₄, NaOH) were obtained from Merck. In each experiment, approximately 500 mL of solution was placed in the electrolytic reactor. pH of the solution was adjusted to 2 to 12 and agitated with a magnetic stirrer at 60 rpm (Heidolp 3600 model) in the EC process. A batch study was conducted to optimize parameters such as time, intensity of current, pH and current density. After each electrolyzes time, organic matter, mass of electrode, and energy were measured. Organic matter (mg d’O₂/l), removal anodic, and energy (energy, Kwh/kg) consumptions in the EC process was calculated using respectively the following equations:
\[ OM = \frac{(V_2 - V_1) \times 0.0125 \times 1000}{V} \]

Where:

- \( OM \): organic matter in mg d’O_2/l
- \( V_1 \): Volume of permanganate du blanc en ml
- \( V_2 \): Volume of permanganate necessary to oxide organic matter ml
- \( V \): Volume of the solution

- \( m_{\text{theoretical}} = \frac{10M}{zF} \) (t is operating time(min), I is current(A), M is molecular weight of iron (g/mol), \( F \) is the Faraday’s constant (96,487 C/mol), \( z \) is the number of electrons involved in the oxidation/reduction reaction.

- \( m_{\text{experimental}} \) obtained by differential to weighing of each electrode

Energy = UIt where
- \( U \): tension of current(U)
- \( I \): intensity of current(A)
- \( t \): time of treatment (min)

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**Figure I. Electrochimical reactor at laboratory**

**Results and discussion**

4.1. Effect of time in removing MO

Electrochemical processes are used to improve chemical properties of water [32]. However, the processes are adequate to oxidize contaminations found in wastewater containing complex organic and inorganic compounds. Therefore, to improve performance of electrochemical technique, it has been used along with other oxidation processes including EC process [31, 32]. Figure 3.1 shows MO removal performance by EC process at 40 min, pH 4, and current 0.1 A. The highest MO removal efficiency was less than 40% in 40 min. Results indicated low in removing MO. This is probably due to low production of metallic hydroxide in solution. This may be due to lesser surface area of the electrodes available for the process to take place or because of higher organic matter value of the waste water. It is of great interest to explore the importance of operating parameters for the development of EC, i.e: pH, current density discharge current and operating time.
Fig. 4.1. Effect of operating on MO reduction and removing of oil change wastewater by electocoagulation using iron electrode (I=0.1A, pH=4; m_{NaCl}=1g)

4.2. Effect of different parameters

4.2.1. Effect of initial pH on the removal efficiency.

Initial pH is an important operating factor influencing performance of the EC process. Effect of the initial pH with respect to operating time (30 min) for treatment of oil change was studied at 15.92 A/mm² in the pH range of 2.0–12.0 for the process.

Fig. 4.2.1 shows the influence of initial pH on the MO removal efficiency in the EC process.

The effect of pH on the removal process depended on formation of the complexes having a tendency to polymerize and insoluble metal hydroxides formed related to increase the solution pH was precipitated as Fe(OH)_2, Fe(OH)_3. The removal efficiencies of oil change at pH 2.0–7.0 were increased gradually from 26.41% to 96.22% for MO in the EC process. At pH 7.0–12.0 the removal efficiencies of oil change were decreased until 15%. The maximum removal efficiency of MO was 96.22% at pH 7.0. The removal efficiencies were higher at acidic conditions and reduced at high pH levels. The generated iron hydroxides during the EC process might adsorb rapidly the oil change compounds by adsorption. Thus, the EC process was able to remove the color and organic contents efficiently from effluent. At basic pHs, the oxide surface had a net negative charge and might incline to repulse the colloid in solutions. MO removal efficiencies decreased at pH > 7 because hydroxide ions were oxidized at the anode. In addition, Fe(OH)_6^{2-} and Fe(OH)_4^{-} ions may be present at high pH, which lacked a removing capacity [22]. The protons in the solution at lower pHs were reduced to H_2 at the cathode and existence of hydroxide ions was very low [22]. In this study, the major interaction mechanism of the EC process was coagulation. But, other mechanism exist how co-precipitation and adsorption [27]
4.2.2 Effect of current density on the treatment of oil change.

Current density is an important parameter for following the reaction rate in most electrochemical process such as the EC process. Current density determines the rate of coagulant and their generation, its flocs size and distribution, and affects the growth of flocs (Fe(OH)$_2$(s) or Fe(OH)$_3$(s) coagulate particles) in the EC process. In the EC process, the OH$^-$ formation rate is controlled by the applied current density during the electrolysis. Effects of the current density for the treatment of oil change in the EC process was studied in the range of 5–20 A/mm$^2$ at operating time of 0–30 min.

Fig.4.2.2. Effect of current density on MO and removal efficiency in the EC process.

Fig.4.2.2. indicated that the removal efficiency of effluent was increased gradually until 80% for MO at operating time of 30 min when the current density was 15.92 A/mm$^2$. This can be attributed to high current densities; the extent of anodic dissolution (Faraday’s law, increased positively charged polymeric metal species resulting in increased MO removal efficiency. The optimum current density for this study was selected as 15.92 A/mm$^2$ because high current density contributes to the consumption of electrode and energy growing price of process.

4.2.3. Effect of the current quantity on the removal efficiency

Effect of current discharging time, which directly relates to the treatment, on the performance of electro-coagulation process was also investigated in this study to determine the optimum operation for electrical discharge. Effect of the initial discharge for treatment of oil change was studied at 15.92 A/mm$^2$, pH 7.0 in the discharge range of 2.0–12.0 for the EC process.

Fig4.2.3. Effect of discharge current on the MO removal efficiency in the EC process at (pH=7; current density=15.92 A/mm$^2$, m$_{NaCl}$=1g).
The results are summarized in Fig.5 which indicates that the removal of MO was improved instantly and significantly when the current was discharged increase. This observation was due to the acceleration of the Fe$^{2+}$ and Fe$^{3+}$ generation via electrochemical oxidation of anode which are responsible to metallic hydroxide (Fe(OH)$_2$(s) or Fe(OH)$_3$(s) coagulate particles) in the EC process produced. Fig.4.2.3 indicated that the removal efficiencies of oil change were increased gradually with the current discharge from 51.43%, 73.80% and 85.4% when the current discharge was 8A.min and for the current 0.2A; 0.3A; 0.4A respectively. It is interesting to observe that, for a same quantity of discharge, efficiency of treatment depend of current. In conclusion, amount of Fe$^{2+}$ and Fe$^{3+}$ released from anode material which affect formation of metallic hydroxide depended on the electrolysis time and current discharge in the EC process are responsible theremoval efficiencies of MO and color, and controlling the reaction rate in the EC.

4.2.4. Effect of current on the electrode mass and energy consumption.

Table 1 illustrates consumption of electrode and energy with different current over the course of electrocoagulation process.

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Removal efficiency MO (%)</th>
<th>Consumed energy (kwh/kg)</th>
<th>Theoretical mass (mg)</th>
<th>Experimental mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>51.43</td>
<td>0.309</td>
<td>0.095</td>
<td>0.104</td>
</tr>
<tr>
<td>0.3</td>
<td>73.8</td>
<td>0.369</td>
<td>0.122</td>
<td>0.145</td>
</tr>
<tr>
<td>0.4</td>
<td>85.4</td>
<td>0.901</td>
<td>0.134</td>
<td>0.167</td>
</tr>
</tbody>
</table>

pH = 7
J = 15.92 A/mm$^2$

Table 1: Experimental results on the energy and mass consumption at different current in the EC process.

In general, current of the solution is effective on performance of the process, electrode mass and energy consumption rate [26]. The results of the study showed that, during the electrochemical process, the electrode and energy consumption increased. Values high of electrode and energy consumptions were obtained in the EC process at 0.4A. The increase of electrode consumption during the EC process might be related to the electrochemical and chemical dissolution of iron electrode. Many studies report an increase in electrode consumption during the electrocoagulation process that results correspond with the results of the present study [27, 28, 30].

Conclusion

Experiments on the removal of MO from maicam industry by electrocoagulation were carried out. In this study, effect of the operational parameters on the EC process was evaluated based on removal efficiency. The optimum operating conditions for oil change were determined as 15.92 A/m$^2$ and pH 7 for this process. EC process resulted in higher removal efficiency (96.22% of MO, in 30 min). Amount of electrode and energy consumed depend of current, it increases with current to impose. The obtained results indicated clearly that the EC process was very effective for the removal of oil change. The EC process is a promising technology for applications in wastewater treatment.

References

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