Electrocoagulation treatment of oil-based mud wastewater

N A Al-Rubaey#, M G Albrazanjy and M Abdulkareem
Petroleum Technology Department, University of Technology- Iraq, Baghdad, Iraq

Email: 100108@uotechnology.edu.iq

Abstract. Electrocoagulation has been found to be a promising topic for an efficient remediation of water and wastewater. This is due to its ability to eradicate a wide range of pollutants that are generally harder to remove by other available techniques such as filtration or chemical treatment systems. These contaminants may comprise of heavy metals, suspended solids, emulsified oil, and hydrocarbons. Oily mud wastewater indicates a dangerous threat if released to the environment; as a result, treating it is essential in oil industry. This research has examined a new simple, effective and low cost technique called "electrocoagulation" for the handling of oily mud wastewater using turbidity measurements. "Bench scale" reactor was used to investigate features that may affect the treatment. Al metal was applied as a sacrificial anode. Multi-holes electrodes were structured at horizontal configuration to obtain optimal maximum efficiency. Other tested operation parameters include electrolysis time, initial concentration, applied voltage, the distance separating electrodes, initial pH value and added NaCl concentration. This study demonstrated that this process is a feasible method for treating heavily contaminated oily mud wastewater.

1. Introduction
It has been reported that lots of waterwaste are linked to processes coming from drilling of oil and gas that have the possibility to damage the atmosphere around it. The characteristics of these wastes control its risk distinctiveness and environmental impact capability. The well-known assessment of the prospective ecological effect of the waste is the toxicity behind it. This drilling progression produces two principal sorts of wastes; these are the drilling mud wastewater and the cuttings [1-2].

The mud includes the base fluid and a mixture of additives to permit for superior working performance. Practically most of these spices pledge fatal materials into this fluid. This should be taken in account when the produced wastes are handled. The main contamination of expenditure mud is triggered by: oil, biocides, incentive fluid materials, inhibitors, reservoir fluid, and other chemicals. The handling of this waste is a vital topic bearing in mind the high capacity produced daily. Different procedures have been designated for the handling of such wastes, but the utmost commonly implemented are chemical disruption and electrochemical deterioration. Conversely, biological procedures are barely adopted since these wastes frequently have biocides to avert their deprivation. Additionally, when the runoff is extremely contaminated with soluble mixture and they cannot be detached by other methods, distillation can be another choice, even with its high operation cost [3-5].

Elmenay et al. [10] carried out studies on the treatment of drilling fluids wastewater by EC process. They concluded that EC is a handling technique that is capable of being effective compared to conventional treatment methods such as chemical coagulation. They also showed that EC is a technique capable of reaching high removal effectiveness of pigments, BOD, and COD. Other studies such as Razali [11] revealed that the EC can be done into remediation process for oily wastewater with foreign ingredient such as metal particle. The ideal form could be selected from maximum percentage of oil...
recovery. The process of EC was exceedingly reliant on physiochemical features of the effluent (cell design, pH, concentration, conductivity, operating time, current and electrodes material).

There are several advantages that are seen in EC process such as high removal rate, small size, ease of maintenance and small operation costs. Additionally, there is no need for addition of chemical agents, which may produce secondary pollution.

In the current research, the adoption of electrocoagulation as a new technique was proposed for the remediation of drilling muds wastewater. The effect of various parameters such as the acidity effect, current density, EC operating time, and the quantity of NaCl added were investigated. The efficiency of the procedures is calculated by determining the Turbidity values.

2. Electrocoagulation

EC process involves the making of important coagulants materials from electrodes such as Fe/Al through the process of electric current where this current is conducted to these Fe/Al electrodes. The dissociated metal ions are attracted by the contaminated colloidal particles, thus counterbalancing their charge and permitting their coagulation. Then, the freed H₂ gas from the cathode electrode cooperates with the particles giving the flocculation, to allow for the unnecessary substance to be raised and later detached. Various cheap and available metals have been tried as electrodes, such as Iron, Al and St. St. [5-7].

EC comprises of local production of coagulants by conducting oxidation of a suitable anode using direct current. The dissociated ions produce hydrolyze compounds in the electro-coagulator mainly at 7–9 pH range to give various metal complexes and neutral metal hydroxides. These are required for the elimination of soluble and colloidal contaminants via the benefit of a range of supposed mechanisms. This includes ionic complex- ion exchange on the flocs surface active position. Later on, the dragging of the waste product into the swept flocs occurs. Finally, these flocs are detached either by flotation by the H₂ gas freed from the electrode (cathode), and some are removed by sedimentation [8,9].

The theory of EC can be described in three successive stages:
1. Development of a coagulating means over the oxidation of the Al/Fe sacrificial electrode, thus the surface charge will be neutralized. This is followed by destabilizing the particles (colloidal) and breaking down of suspensions.
2. Promotion of the agglutination of particles by the coagulating species, facilitating the establishment and growth of flakes.
3. Release of H₂ bubbles at the electrode (cathode) and O₂ bubbles at the electrode (anode). The rise of these gases to the surface leads to the adsorbing when striking the flakes, carrying-up particles and contaminates in suspension and pushing them to the top of the cell and thus indorsing the clearing up of the wastewater effluent.

Also in the case of Al electrode, we can summarize the reactions as follows [3]:

Anode:
\[
\text{Al (s) } \rightarrow \text{Al}^{3+} \text{(aq) } + 3\text{e}^{-}
\]

Cathode:
\[
3\text{H}_2\text{O (l)} + 3\text{e}^{-} \rightarrow 3/2 \text{H}_2 \text{(g)} + 3\text{OH}^- \text{(aq)}
\]

In bulk:
\[
\text{Al}^{3+} \text{(aq) } + 3\text{OH}^- \text{(aq)} \rightarrow \text{Al(OH)}_3 \text{(s)}
\]

Further spontaneous reactions are produced to make corresponding hydroxides and polyhydroxides:

\[
\text{Al(H}_2\text{O)}_3^{3+}, \text{Al(H}_2\text{O)}_2\text{OH}^+, \text{Al(H}_2\text{O)}(\text{OH})^{2+}
\]

to give further, the following products:

\[
\text{Al(OH)}^{2+}, \text{Al}_2(\text{OH})_2^{4+}, \text{Al(OH)}^6, \text{Al}_6(\text{OH})_{13}^{3+}, \text{Al}_7(\text{OH})_{17}^{4+}, \text{Al}_6(\text{OH})_{20}^{4+}, \text{Al}_{13}\text{O}_{24}(\text{OH})_{24}^{7+}, \text{Al}_{13}\text{O}_{34}^{5+}
\]
Within the electrocoagulation reactor, several distinct electrochemical reactions are produced independently.

3. Experiment set up
The system adopted in this work is graphically presented in Figure 1 [12]. The reaction cell includes chiefly a 1-liter plexiglass beaker. The cathode here is shown as a multi-holes circular Aluminum plate, 9 cm sheet placed horizontally on the lower side of the cell. The anode is also made of a single sheet of Aluminum parallel to the cathode with inter-distance separation of 6mm. The electronic circuit comprise of a power supply (max. 15 V, 2 A) with an ammeter which was coupled in series with the cell to read its current. The system consists of the following devices:
- Reactor (Pyrex glass beaker)
- Electrode Type (Aluminum)
- Home-made DC power supply (0-16V)
- Inolab Conductivity Meter (WTW series model 720)
- Multimeter (Hanna - model HI-9828)- Multi-sensor probes
- BOECO Magnetic Stirrer (model MSH-300N) (50-1250RPM)
- KERN Analytical Balance (model ABS).
- Synthetic pollutants include oily polluted water.

A synthetic-waste solution of 0.8 liter was employed in every experiment. The prepared solution was stirred with the suitable quantity of NaCl that was added to increase conductivity. The synthesized liquid was put into the batch cell. The pH was controlled during each experiment by adding NaOH /HCl solutions to be kept at 7-8. The current from a home-made power supply (DC) was conceded in the synthetic waste liquid through the electrodes throughout the operating time of the EC run. A volume of 10 mL of the treated liquid was tested (5 min interval) for the early 20 min and other runs (10 min interval) for the last time of the experiment. Finally, Al/electrodes were regularly cleaned or changed using standard procedure. For some calculations we had to calculate the removal efficiency using the following formula:

\[
\%RE = \frac{NTUi - NTUf}{NTUi} \times 100
\]

Where \( RE \) is the removal efficiency.
\( NTUi \) is the initial Turbidity.
\( NTUf \) is the final Turbidity.
The turbidity measurements and percentage \( RE \) were applied using different setting by varying the following factors:
- Electrolysis time.
- Applied voltage.
- Electrolyte concentration (NaCl).
- Initial pH of solution.
The synthetic oil mud wastewater solution was prepared for all experiments using oil mud prepared by adding proper amount of: Gasoil, Water, Lignite Emulsifier and Lime [14].

4. Results and Discussion
The first attempt was to find the proper initial concentration which was a significant parameter in defining RE. Increasing initial turbidity would decrease final turbidity with a resultant increasing in RE. Thus increasing initial concentration from 50 NTU to 500 NTU resulted in an increase in RE from 80% to 90%. Figures 2 and 3 show the increase in RE with increase in initial concentration. Reported information regarding the effect of initial concentration can be put in two groups; rise in initial concentrations may lead to a decrease in RE, whereas others assumed that the increase in initial concentrations should lead to an increase in RE as in the current study.
In order to study the effect of electrolysis time on turbidity, a number of runs were executed using initial Turbidity concentration of 500 NTU, applied voltage of 10v and two multi-hole horizontal plate parallel of Al anodes. The evidence presented in Figure 4 shows that Turbidity of the treated wastewater decreased with time of the reaction, reaching to about 95% since Al/ions in the synthesized liquid increased by rising the operating time. An agreement was found with the previously reported data.

To study the outcome of changing applied voltage, other runs were performed at three different voltages: 5, 11, and 15V. Turbidity removal was found to increase with increasing EC time and applied voltage. Increasing the applied voltage from 11 to 15 V increases the removal efficiency from 40 to 90%. These experiments were done at Ci of 500 NTU, pH of around 7 and electrode distance of 0.6 cm. It is clear that as the voltage increased, the electrode weight consumed or dissolved also increased.

The effect of using different applied voltages on the Turbidity removal efficiency is one of the important features, which may influence the EC process, not simply for the dosing rate of coagulants but likewise for the gas bubbles formation, in addition to the dimension and the growth of flocs. This
may control the handling proficiency of the EC process along with prompting both the liquid stirring and the mass transfer near the Al/electrodes. This may be credited to the point that at higher applied voltage, the dissociation of Aluminum ions rises consistent with Faraday’s law. Aluminum ions experience hydrolysis founding which generate additional slurry. Besides, more H₂ gas bubbles are created at the cathode with increase of applied voltage. These gas bubbles would improve the mixing amount of aluminum hydroxides with pollutants, thus boosting the flotation capability, resulting in increase of elimination of pollutants. Consistently, it was revealed that the quantity of H₂ bubbles intensified and their diminutions with applied voltage, consequently ensuring quicker removal of pollutants and mud flotation. In addition to pollutants adsorption on Aluminum hydroxide and its other attached hydroid composites, Al/ions out of the electrode (anode) may interact straight with the pollutants, which then causes the solution to be deposited in the form of salt (insoluble) [15].

**Figure 5.** Effect of using different applied voltage on Turbidity

Effect of NaCl concentration on the turbidity removal process is presented in Figure 6. It demonstrates the impact of the added salt on the turbidity removal percentage under the 500 NTU of initial Turbidity, pH of 7, applied voltage of 11v, electrodes distance of 0.6cm. It was found that, as NaCl concentration added (1g/l), the Turbidity removal percentage increased at the beginning of the process (first 10 min), however the effect was diminished later on.

**Figure 6.** Effect of adding salt on removal efficiency over the operating time
Figure 7 displays the performance of the current during the EC process for 11v and fixed inter-electrode distance of 6mm and initial concentration of 500NTU. It is clear that there has been a continuous decrease in the current over the 20min period of time. Approximately 40% decreased in the current value in this case, which is serious compared with our previous results with oily contaminated wastewater [13], where under 10% reduction in the current was observed and approximately similar to the obtained results with Zinc contaminated water which gave current reduction of about 50% [12].

![Figure 7. The drop of current during the operating time](image)

5. Conclusion
Electrochemical process known as electrocoagulation is the technical field of applying electricity as the electromotive force to motivate chemical reactions in an emulsion. The contamination caused by releases of oily drilling mud wastewater is nowadays a cause of environmental deprivation and promotes at present a certain interest. In this work applying electrocoagulation for the treatment of these wastewater has been proposed. The effect of applied voltage, initial concentration, the operating time, and the amount NaCl added were considered, and the efficiency of the processes is investigated by determining the Turbidity. The processes were carried out in batch mode cell using horizontal Aluminum electrodes setting. The initial results obviously establish the EC permits the turbidity removal of about 95%. Thus, Electrocoagulation is a clean technology that can be applied in a diverse procedures, is a “green technology” and may also produce useful by-products.

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