Investigation of the Electrocoagulation Treatment Technique for the Separation of Oil from Wastewater

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ABSTRACT

Oily wastewater represents a dangerous threat when discharged to receiving bodies. This research investigates electrocoagulation as a simple, effective and economic technique for treatment of such wastewater. Bench scale reactors were used to evaluate the factors that may affect the treatment of a wastewater obtained from Kuwait Gulf Oil Company. Aluminum was used as a sacrificial anode. Electrodes were arranged at different configurations (horizontal, vertical and vertical anode with horizontal cathode) to select the optimal one. Other tested operation parameters include time of treatment, current density, the distance between the electrodes, anode tubes diameters and the electrolyte concentration of the emulsion. The treatment efficiency was evaluated by comparing the initial and final turbidity of the treated wastewater. Experimental results indicate that the efficiency of oil separation increased with the increase of the treatment time, current density, anode diameter and concentration of electrolyte. However, it decreased with the increase of distance between electrodes. The horizontal arrangement gave the best results. The data shows that oil separation increases slightly with increasing temperature. The optimum time and current density for oil separation was determined as 30 min and 30 mA cm$^{-2}$, respectively. These parameters reduced the turbidity of the wastewater from 95-5 NTU.

Key words: Aluminum electrode, electrocoagulation, oil emulsion, turbidity, wastewater

INTRODUCTION

Oil in wastewater may exist in many forms including free floating, dispersed and emulsified with the later to be the most difficult to treat (Jang and Lee, 2000). Oily wastewater is discharged to receiving bodies in amounts of millions of tons annually causing dangerous troubles. Since, it is characterized by high chemical and biochemical oxygen demand, high concentration of sulphide and ammonia and high concentration of suspended solids (Diya'uddeen et al., 2011).

Large amounts of such liquid wastes are generated by different activities such as crude oil production, refinery, petrochemical and lubricant production units, automobile industries, aircraft plants, metal finishing, metal working, textile industry and paper mills (Benito et al., 2002; Libralato et al., 2008; Zhou et al., 2008; Tobiszewski et al., 2012; Dermentzis et al., 2014). Food industries is also responsible for wastewater containing oils (Fouad, 2014).

Oily wastewater has a complex composition because it may contain mineral, vegetable or synthetic oils, fatty acids, emulsifiers, corrosion inhibitors and bacteriocides. Emulsion will be formed once oil comes in contact with water in the presence of emulsifying agents which facilitate their stabilization. Oily wastewater is harmful to the aquatic environment because it may form a
layer of oil on the water surface rejecting air to be absorbed by water organisms and become incorporated into sediments. Even very low oil concentrations are toxic and hazardous to micro-organisms responsible for biodegradation and even peril human health through biological enrichment and biomagnifications. Consequently, efficient separation of oil in aqueous as well as in non-aqueous solution has drawn significant concerns.

Several traditional processes employing physical, chemical and biochemical techniques can all be applied for treatment of oily wastewater. Examples of these processes are heating, centrifugation, fenton processes, membrane techniques, adsorption, ozonation, filtration and coagulation (Jang and Lee, 2000; Canizares et al., 2008; Salahi et al., 2010; Giwa et al., 2012). However, conventional wastewater treatment methods remain unsatisfactory (Zhou et al., 2008). Conventional coagulation which is widely used technique has many drawbacks including the requirement of high amount of coagulant, long operation time, high treatment cost, large area of construction, corrosion problems due to the decrease in pH and problems with produced sludge (Martinez-Delgadillo et al., 2010; Karhu et al., 2012). Biological processes are generally less expensive than the chemical equivalents. They are often employed to treat the organic fraction in industrial wastes. Their efficacy decreases as the concentration of pollutant increases. Furthermore, some organic compounds are resistant to biological cleanup (Zhang et al., 2011).

Several electrochemical methods have been investigated for the treatment of wastewater containing oils (Yang, 2007; Canizares et al., 2008). Electroflotation, electrodeposition and electrocoagulation are important techniques (Yang, 2007; Rangel et al., 2013). In recent years, there has been increased interest in the application of electrocoagulation in the treatment and purification of industrial wastewater (Khouri et al., 2007; Chaturvedi, 2013). Electrocoagulation is a wastewater treatment process involving the generation of coagulants in situ by the dissolution of metal ions electrochemically from the anode with the simultaneous formation of hydroxyl ions and hydrogen gas at the cathode. The metal ions form floculates which traps the contaminants while the hydrogen gas floats these particles (Gomes et al., 2009). The apparatus used contains pairs of metal sheets (anode and cathode) immersed in the wastewater. The anode is made of the metal that is intended as coagulant such as iron or aluminum. When passing current between the two electrodes, the metal electrode is oxidized to form metal ions (Fe$^{2+}$, Fe$^{3+}$, Al$^{3+}$) which react with the hydroxyl groups to form the coagulant. The formed coagulants react with the oil particle to form agglomerates that settle under the effect of gravity to the bottom of the tank or float to the surface of water by attaching themselves to the hydrogen molecules formed due to the electrochemical process. The possible mechanisms for Al are represented by the following equations (Nasution et al., 2013; Fouad, 2014):

**Anode:**

\[
\text{Al (s)} \rightarrow \text{Al}^{3+} (aq) + 3e^- \quad (1)
\]

\[
\text{Al}^{3+} (aq) + 3\text{OH}^- \rightarrow \text{Al (OH)}_3 \quad (2)
\]

**Cathode:**

\[
3\text{H}_2\text{O} (l) + 3e^- \rightarrow \frac{3}{2} \text{H}_2 + 3\text{OH}^- (aq) \quad (3)
\]

\[
\text{Al (s)} + 3\text{H}_2\text{O} \rightarrow \text{Al (OH)}_3 + \frac{3}{2} \text{H}_2 \quad (4)
\]
Electrochemical treatment of wastewater has many advantages such as safe and easy application and environmentally-friendly nature (Martinez-Huitle and Brillas, 2009; Yavuz et al., 2010). Saving of energy is an important advantage of electrochemical techniques. Other advantages include better performance (because the cell geometry can be designed to maximize product yield) ease of control, ability to accept fluctuation in influent wastewater quality and reduced amount of residue (Canizares et al., 2002; Fouad, 2014).

Electrocoagulation is efficient in removing suspended solids as well as oil and greases (Ni’am et al., 2007). It removes metals, colloidal solids and particles, petrochemical hydrocarbons and soluble inorganic pollutants from aqueous media (Yilmaz et al., 2007; Moussavi et al., 2011). The technique has been tested for treatment of wastewater containing variety of the pollutants including foodstuff, dyes, polymeric wastes, fluorine, chemical and mechanical polishing wastes, nitrate, phenolic wastes and refractory organic pollutants (Giwa et al., 2012; Chaturvedi, 2013).

Factors that may affect the efficiency of electrocoagulation may be classified into: (a) Factors related to the properties of the treated wastewater like nature of pollutants, pH of wastewater, temperature and amount of wastewater and (b) Design of the treatment apparatus and treatment parameters like voltage, current, type of sacrificial anode and alignment of electrodes.

Most of the researches conducted to study the electrocoagulation used the traditional vertical cells (Canizares et al., 2002; Gurses et al., 2002; Adhoum and Monser, 2004; Golder et al., 2007). The goal of this study is to compare the effectiveness of three designs of electrocoagulation reactor towards the separation of oil from wastewater and to determine the different factors that may enhance the treatment process. To obtain this objective wastewater obtained from Kuwait Gulf Oil Company was examined using aluminum as a material for the anode at different operation conditions. The results were interpreted in terms of final turbidity of the treated wastewater as an indicator for the efficiency of the treatment process.

MATERIALS AND METHODS

Materials: Oily wastewater samples used in this study were obtained from Kuwait Gulf Oil Company (KGOC). The conductivity of sample was adjusted to the desired level by adding an appropriate amount of sodium chloride. Aluminum electrodes were used as anode and cathode.

Experimental procedures: Three experimental electrode design sets were used in the separation of oil from oily wastewater to enhance the separation rate. In all sets, rectangular container (prespex cell) with 10×10 cm square base and 15 cm height is used. The height of the reactor enabled us to change the distance between the anode and the cathode. The Al electrode is used as a cathode and the back of the Al plate was insulated with epoxy. The electrical circuit consisted of a 20 V D.C. power supply with a voltage regulator, variable resistance, multi-range ammeter connected in series with the cell and D.C. voltmeter was connected in parallel with the cell to measure its voltage. The parameters to be studied were time of treatment, Current Density (CD), the distance between the horizontal electrodes and the sodium chloride content of the emulsion. A refinery wastewater samples obtained from a local petroleum refinery was used in this study. The samples were collected from Kuwait oil refinery’s wastewater treatment system. The samples to be analyzed were collected during each run using a 10 mL pipette. The samples were taken from the same location at the cell. The turbidity of the samples were determined using a turbidity meter as an indication of the oil concentration. The three sets are as follows:

Horizontal electrodes set: As shown in Fig. 1a, the anode was made of an array of separated horizontal solid cylinders. The cylinder length was 8 cm; four different cylinder diameters (D) were
Fig. 1(a-c): (a) Horizontal cell experimental setup (separation between electrodes is 1.5 cm), (b) Vertical cell experimental setup (separation between vertical electrodes is 1.5 cm) and (c) Horizontal cathode and vertical anode cell experimental setup (separation between vertical electrodes is 1.5 cm)

used namely 3, 5, 6 and 8 mm. The horizontal cylinders were fixed at their ends to two Al strips, the cylinder array was held in position by a vertical Al strip welded to one of the horizontal strip. The vertical Al strip worked also as anode current feeder. The vertical strip and the two horizontal strips holding the horizontal cylinders were insulated with epoxy. Cylinder diameter was measured before and after each run to make sure that no significant dimensional change had taken place during the experiment. The cathode-anode separation was fixed at the required distance (H).

Vertical electrodes: Figure 1b shows the usual cell that consisted of a rectangular container (same dimensions as above cell) equipped with two parallel vertical Al plate electrodes. The back of the two electrodes was insulated with epoxy resin to protect the electrodes from corrosion. Electrode separation was 1.5 cm. Cathode and anode were Al with current flowing via insulated Al wires welded to the electrodes. The temperature was controlled through the use of a water path.

Horizontal and vertical electrodes: The cell consisted of rectangular container (with the same dimensions as the above cell) with horizontal cathode and vertical anode as shown in Fig. 1c. Two Al plate electrodes were used. The back of the two electrodes was insulated with epoxy resin. The
two electrodes were separated by 1.5 cm apart. Cathode and anode were Al with current flowing via insulated Al wires welded to the electrodes. The temperature was controlled through the use of a water path.

RESULTS AND DISCUSSION
Horizontal electrodes
Effect of time on oil separation efficiency: In this research, turbidity was used as a measure of the oil concentration in the wastewater and treated water. The change in turbidity with time during the electrocoagulation process is depicted by Fig. 2a. As seen in the figure, the oil separation efficiency has a direct relationship with the time. Increasing the treating time caused considerable decrease in water turbidity. The figure indicates that the electrocoagulation process, involves two stages which are destabilization and aggregation (Ni’am et al., 2007). The first stage is fast, whereas the second stage is relatively slow. The turbidity decreased from an initial value of 95-5 NTU corresponding to separation efficiency of 94.7%. This value was obtained after 40 min of operation. However, 89% separation efficiency was achieved after 30 min. According to Faraday’s law the time of current passage increases the quantity of electricity applied to the cell which leads to more aluminum ions to liberate at the anode. These ions with their positive charges will neutralize the oil droplets that are negatively charged. This effect enhances the separation of the neutralized oil droplets and makes them float on the surface. On the other hand, more hydrogen gas bubbles will be created at the cathode by the increase of the treatment time. These hydrogen bubbles will push the oil drops upwards by bouncy force thus increasing the efficiency of oil separation and decreasing turbidity of the emulsion.

Effect of anode diameter on oil separation efficiency: The relation between the anode diameter and the turbidity of oily wastewater after 30 min of treatment was shown in Fig. 2b. It can be depicted from the figure that as the diameter of the anode increases the efficiency of separation increases. This may be related to the increase of the effective surface area of the anode by increasing the anode diameter (Jang and Lee, 2000). This in turn facilitates aluminum oxidation to positive aluminum ions which are responsible for the neutralization and coagulation of the negative charges carried by the dispersed droplets of oil. El-Shazly et al. (2011) explained the direct relationship between the anode diameter and oil separation efficiency by the decrease in the annular space between the anode and the cathode. This decrease in space will enhance the agitation conditions of the emulsion which prevents the accumulation of anodic and/or cathodic products on electrodes which in turn decreases polarization.

Fig. 2(a-b): (a) Relation between turbidity and time for horizontal electrodes and (b) Relation between turbidity and different anode diameters (for horizontal electrodes)
Effect of distance between electrodes on oil separation efficiency: When considering the optimization of the operating cost of the electrocoagulation process, it is important to consider the distance between the electrodes. If the wastewater conductivity is high, it is recommended to have a bigger space between electrodes. In case of moderate conductivities, a smaller distance is required. Both of these options will reduce the energy consumption without changing the treatment efficiency (Crespilho and Rezende, 2004). Figure 3 shows the effect of the distance between the anode and the cathode on the separation of oil from oily wastewater. As the distance decreases, the efficiency of oil separation from oily wastewater increases. This can be attributed to the decrease in ohmic resistance due to the shortening of the path of the electric current between the anode and the cathode.

Effect of current density on oil separation efficiency: The current applied in the electrocoagulation reactor determines the amount of coagulant ions released from the anode. Thus, increasing the current density (C.D.) will increase the number of coagulant ions and consequently increase the oil separation efficiency. Another effect of the high current density is the increase of rate of generation of the hydrogen bubbles and the decrease of their size. Both of these two factors will, to a certain extent, increase the efficiency of oil separation from oily water (Un et al., 2009). However, exceeding the optimum current would lead to wasting energy due to heating up of the water and decrease in current efficiency. Other factors may affect the current density selection such as pH of the water, temperature as well as flow rate (Chen, 2004).

In order to investigate the effect of current density on turbidity removal electrocoagulation process, three values were tested (0.005, 0.02 and 0.03 A cm$^{-2}$). Figure 4 illustrates the effect of current density on the efficiency of oil separation. It was found that the efficiency of treatment increases as the applied current density increases in the range of 0.005-0.03 A cm$^{-2}$.

Effect of electrolyte concentration on oil separation efficiency: Through a series of experiment, the effect of sodium chloride concentration on the separation of oil from oily wastewater was studied as shown in Fig. 5. It is evident from the figure that the efficiency of separation increases as the sodium chloride concentration increases. This result can be explained as follows: sodium chloride is a strong electrolyte. In solution it is present as positive sodium ions and negative chloride ions, these ions share the already present ions in the emulsion in carrying out the electric current across the cell. In other words, introducing the sodium chloride to the water, increase the conductivity of the emulsion and decreases the fraction of the applied potential

![Fig. 3: Relation between turbidity and distance (h) between electrodes (for horizontal electrodes) at different electrocoagulation time](image-url)
that is consumed to conquer the resistance of the emulsion and accordingly increase the fraction of the applied potential directed to the electrochemical coagulation. Yildiz et al. (2007) stated that adding electrolyte to the water will increase the delivery of coagulant ions to the medium. However, it must be taken into consideration that increasing the electrolyte concentration implies high concentration in chloride ions in the emulsion. These negatively charged chloride ions will compete with the oil droplets in the emulsion towards migration to the anode which decreases the separation efficiency of oil (Fouad, 2014). This is depicted by Fig. 5 which indicates that the highest separation efficiency (equivalent to lowest turbidity) is achieved at the lowest electrolyte concentration (2% NaCl).

**Vertical electrodes**

**Effect of distance between electrodes on oil separation efficiency:** The relation between oil separation efficiency and distance between electrodes followed the same pattern of the horizontal configuration. The smallest the distance between anode and cathode, the better is the separation efficiency. However, comparing the results of horizontal position of the electrodes (Fig. 3) with that of the vertical position (Fig. 6) indicates that the former is more effective in oil separation from oily wastewater. This can be explained as follows: in case of horizontal electrodes arrangement the
aluminum ions liberated from the anode was moving under two effects ionic migration under the effect of the applied potential and the gravity force and these two effect enhance the ion movement greater than that in the case of vertical electrode where the effective driving force for the ions was only ionic migration under effect of the applied potential.

Effect of current density on oil separation efficiency: The relation of current density and oil separation efficiency, as illustrated by Fig. 7, was a little bit different from the previous design. The highest separation efficiency was obtained at a current density 0.02 A cm\(^{-2}\) not at 0.03 A cm\(^{-2}\). There is a critical value of current density. Exceeding this value will cause deterioration in effluent quality (Chen et al., 2000). Phalakornkule et al. (2010) mentioned that the increase of current density would cause increase in the number of bubbles formed during electrocoagulation. These particles help the suspended solids to float to the surface of the reactor. However, these too many bubbles may interfere with the oil separation process due to the decrease of the probability of collision among oil droplets which in turn may cause the decrease of the floc size.

Effect of electrolyte concentration on oil separation efficiency: Figure 8 indicates that the electrolyte concentration has a significant effect on the separation efficiency of the oil. A
concentration of electrolyte of 1% resulted in 80% separation efficiency of oil compared to 94.5% separation efficiency when using 4% electrolyte. However, these results are different from that obtained in case of horizontal configuration of electrodes. In their investigation of use of electrocoagulation for treatment of petrochemical wastewater using vertical electrode, Giwa et al. (2012) found that increasing the electrolyte concentration achieved better turbidity removal efficiency. This agrees well with the result of this research. The configuration of the electrodes together with factors like electrolyte concentration plays an important role in the separation efficiency of oil from wastewater.

**Horizontal-vertical electrodes:** In a third series of experiments a new arrangement was used. In this arrangement the anode was horizontally fixed while the cathode was erected vertically. All the previously mentioned variables were studied (i.e., current density, distance between anode and cathode and the sodium chloride concentration) (Fig. 9a-c). All these variables show similar results to that of vertical configuration.

However, this arrangement was the least efficient in regard of oil separation. This can be due to the extended path between the anode and the cathode which will increase the effective ohmic resistance between the anode and the cathode and will accordingly decrease the electrochemical processes at the anode and at the cathode. Also, when the anode is erected vertical the liberated aluminum can move directly downward the anode without being subjected to the stirring action of the hydrogen bubbles liberated at the cathode. Thereby, no intimate collision will occur among aluminum ions, oil dispersed droplets and hydrogen bubbles, consequently the oil separation form oily wastewater will decrease.

**Temperature effect on two horizontal electrodes:** A further study for the effect of temperature on the separation efficiency was performed. The horizontal configuration of the electrodes was selected since it showed the best separation efficiency. The effect of temperature on the electrocoagulation process received little attention from researchers (Chen, 2004). The effect of temperature is not straightforward and may follow many mechanisms. Temperature may affect rate of reactions, solubility of metal hydroxides, liquid conductivity, kinetics of gas bubbles or small colloidal particles, movement of the ions produced and collision between particles present in the
Fig. 9(a-c): (a) Relation between turbidity and distance between electrodes, (b) Relation between turbidity and current densities and (c) Relation between turbidity and NaCl concentration (for vertical electrodes) at different electrocoagulation times.

Fig. 10: Relation between turbidity and temperature on two horizontal Al electrodes arrangement at different electrocoagulation times.

suspension and produced during electrolytic process (Ibrahim et al., 2001; Yang and McGarrah, 2005; Martins et al., 2006; Daneshvar et al., 2007; Un et al., 2008).

Figure 10 shows the effect of temperature on the variation of oil concentration with time. The data in Fig. 10 indicates that oil separation increases slightly with increasing temperature up to 60°C and decreased again at 80°C. This result is in agreement with that reported by Cerqueira and Marques (2012). They stated that the efficiency achieved with aluminum electrodes increases with temperature up to the 60°C, above which the efficiency decreases.
CONCLUSIONS
The separation of oil from oily wastewater by electrocoagulation method using Al anode was studied. It was found that the efficiency of oil separation increased with increase in time of treatment, current density, anode tubes diameters sodium chloride concentration but it decreased with increase in distance between the two electrodes. Also it was found that the horizontal arrangement is the best one. The data shows that oil separation increases slightly with increasing temperature at best studied conditions. Thus the optimum conditions to be used as design parameters are 0.03 A cm\(^{-2}\) as current density, 30 min as electrocoagulation time, 2% for NaCl concentration and the temperature to be between 40 and 50°C. The optimum electrode arrangement was found to be horizontal Al cathode and array of horizontal parallel Al cylinders (anode) with distance of 1 cm.

REFERENCES


