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Novel Electrocoagulation Electrodes Design for the Removal of Oily Wastewater

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Abstract

Electrocoagulation (EG) is effective in breaking oily water emulsions. New anode design in the EG of oily wastewater lube oil emulsion is investigated. In this study, EG using aluminum sacrificial anode was used for the treatment of oily emulsion. A multi layers 5 discs rotating Al disc with 7 cm in diameter and each layer is 0.5 cm apart is designed to be used as an anode. Variables considered were the disc anode rotational speed (from 250 to 1000 r.p.m), NaCl amount as electrolyte dose (1, 3, 5, 7, 9 g/3litre), pH (ranged from 3 to11), oil emulsion concentration (250 to 1000 ppm). It was found that the percent of oil removal is decreased by the increase of rotating speed (> 750 r.p.m) and NaCl dose (1g/3lit.) while it increase by the increase in pH of the emulsion (>3). The maximum percent removal (79 %) is obtained at pH=9, initial oil concentration = 1000 ppm and r.p.m=750. A comparison of the obtained results were another values of anodes of different shape is held. A treatment of the considered cutting oil is completed at initial concentration of 10 mg Al/g oil, with a slight positive effect of the liquid flow rate. Best results are also obtained with initial pH near 7. Other comparison was carried out with different EG techniques.

Keywords: Electrodes, Anode, Lube Oil, Wastewater Treatment, Electrocoagulation.

1. Introduction

The survival of our human-race depends essentially on the ability to manage our natural resources, protect them from deterioration and utilizing such resources as efficiently as possible. Water; as an example; is one of the highest important natural resources that affect all the aspects of development in human life. Egypt has limited share of water. The main source is the Nile River. In the view of the rapid increase in population in Egypt, it has become imperative to maintain and protect the available water resources from pollution [1].

The Egyptian Government and regulations, in cooperation with legislative bodies, has adopted several laws and limitation for the protection of waterways for the purpose of and to safeguard the water quality. During the last few decades, many countries worldwide are concerned already with water scarcity. Variable water resources in Egypt are limited mainly to the Nile River, rainfall and groundwater reservoirs. The latter is important in the deserts and Sinai. In 1966, renewable water resources in Egypt presented 2189 m^3/capita/yr. Presently, Egypt water resources went down to around 670 m^3/capita/yr. This is mainly due to the continuous annual increase in population at the rate of 2.2%. Therefore [2], the demands for freshwater resources are exerting excessive pressure on the available water supply. As Egypt is faced with these challenges, there is an urgent need to improve the efficiency of water consumption, and to augment the existing water sources with more sustainable alternatives. Numerous approaches are suggested for efficiency improvements. These approaches include mainly wastewater treatment / reuse and groundwater resources management.

the volume of oily wastewater from the industries has increased especially form petroleum industries (lubricating/thermal cracking /greases and etc.) and needs treatment.

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Oily wastewater in industry can exist in several forms: free-floating, dispersed and emulsified [3]. The emulsified oil is the most difficult to treat [4]. They impart high chemical oxygen demand, odor, and turbidity [5-6]. These emulsions typically contain from 100 to 1000 ppm of oil with drop diameter from 0.1 to 10 μm, while the permissible limit for oils and greases in waste water discharged in open water streams is 10 ppm. The removal of oil from oily waste water become essential before it is discharged for final disposal [7-8].

Oil emulsions can be broken and skimmed off by many methods like chemical coagulation, biochemical treatment, adsorption in packed columns with solids but, these methods need long settling time, huge land space, and they involve severe sludge handling problems [9].

Electro-coagulation has been used to remove a variety of materials, such as dyes, oils, fats, heavy metals, and miscellaneous suspended solids from industrial wastes. Electro-coagulation has made it possible to circulate industrial water liquid with a consequent reduction in the plant operating costs[10].Electro-coagulation is increasingly replacing chemical coagulation techniques because: (1) EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running, (2) Wastewater treated by EC gives palatable, clear, colorless and odorless water, (3) Sludge formed by EC tends to be readily settable and easy to de-water, compared to conventional alum or ferric hydroxide sludges, because the mainly metallic oxides/hydroxides have no residual charge, (4) EC can produce effluent with less TDS content as compared with chemical treatments, particularly if the metal ions can be precipitated as either hydroxides or carbonates (such as magnesium and calcium. EC generally has little if any impact on sodium and potassium ions in solution , (5) Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration[11], (6) The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field neutralizes any residual charge, thereby facilitating the coagulation[12], (7) The EC process generally avoids excessive use of chemicals and so there is reduced requirement to neutralize excess chemicals and less possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used, (8) The gas bubbles produced during electrolysis can conveniently carry the pollutant components to the top of the solution where it can be more easily concentrated, collected and removed. motorized skimmer (9)The electrolytic processes in the EC cell are controlled electrically and with no moving parts, thus requiring less maintenance, (10) Due to the excellent EC removal of suspended solids and the simplicity of the EC operation, tests conducted for the U.S. Office of Naval Research concluded that the most promising application of EC in a membrane system was found to be as pretreatment to a multi-membrane system of UF/RO or microfiltration/reverse osmosis (MF/RO). In this function the EC provides protection of the low-pressure membrane that is more general than that provided by chemical coagulation and more effective [13]. EC is very effective at removing a number of membrane fouling species (such as silica, alkaline earth metal hydroxides and transition group metals) as well as removing many species that chemical coagulation alone cannot remove.

Electro-coagulation is carried out in an electrolytic cell with Al or Fe anode, the anodically dissolved Al^{+++} or Fe^{+++} neutralize the negative charge present on the colloidal particle (oil droplets) with a consequent destabilization of the colloidal solution or the emulsion .As such, it is obvious that the cell design plays a major role in the process of electro-coagulation. Electrodes types may differ according to the design of electrolytic cells, they may be made from one metal (Aluminum /ferric/stainless steel/graphite) [14]. But the common one is the aluminum. The shapes may be also differ, they may be circular, rectangular, tube, cylindrical. The electrodes may be mixture from one metal with another one. Selecting the electrodes type according to the usage.

For water treatment: The common treatment methods can be classified into three main groups: chemical, mechanical and electrical. The chemical techniques are mainly coagulation, flocculation of the emulsified oil droplets. The mechanical techniques are filter coalescence, filtration-adsorption and membrane processes (UF, MF, NF, and RO) and dissolved air flotation (DAF) [15]. Also included within these techniques. The electrical methods are electro-flotation, electro-coagulation and electro-coalescence.

Comparing with different techniques was studied. A SS fixed anode was used in electro-coagulation study, where series of batch experiments were carried out in the lab at different operating conditions: current density, initial concentration, sodium chloride dose and the intensity magnetic field oriented in two different directions, as in an attempt to achieve higher removal efficiency. Results showed that both current density and NaCl concentration have positive effect on removal efficiency in contrast with methomyl initial concentration. Concentration of NaCl (3.5g/l) is recommended from economic point of view. Magnetic field in parallel direction effects positive where 100% removal was achieved through 30 min for 0.029T [16].

For an oil containing wastewater, the following treatment stages are usually considered: Primary treatment, secondary treatment and tertiary treatment. *Primary Treatment*; in which the free oils and the oil-wet solids are separated from the water and emulsified oil, mainly by gravity separation and skimming. Gravity settling is the oldest and the most frequently used technique [17]. The separation process may be accelerated by applying centrifugal force, using hydro-cyclones and centrifuges. *Secondary Treatment:* in which the oil-in-water emulsions are broken up and the dispersed oil is finally removed. This treatment involves treatments such as chemical coagulation, filtration, adsorption activated carbon on etc. *Tertiary Treatment*; used to reduce the COD of the effluent, from the secondary treatment, and its content of inorganic salts and dissolved metals [18]. Adsorption on activated carbon, biological treatment, ionic exchange, and reverse osmosis are, among others, the main technologies applied in this stage. A scheme of general oily waste water treatment scheme is shown in Figure (1).

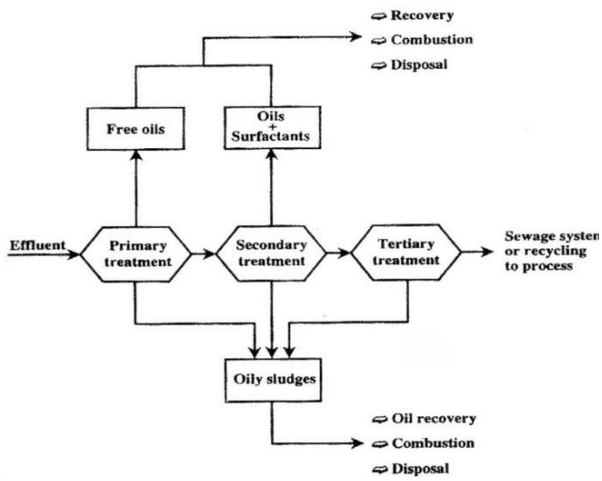

Figure (1): General Oily Wastewater Treatment

Alaa et.al studied the configuration of new electrode in the removal of total organic carbon from municipal wastewater using EG technique. They used electrode configuration induces a dielectrophoretic force by using an asymmetrical aluminum electrode with an alternating current power supply. They found that the maximum removal efficiency obtained is 87.7% at 30 min, 600 mA applied current, and 0.5 cm interelectrode distance. Under these operating conditions, the TOC removal [19].

2. MATERIALS AND METHODS
2.1 MATERIALS

For electro -coagulation, the materials used are: fresh water, emulsifier, engine oil (SAE 20W50/ API SL) from bp company, sodium chloride (99.9%) from Merk company and hydrochloric acid 30%.

2.2 Experimental Setup

All experiments concerning the application of the electro-coagulation were performed in a batch reactor. The reactor was cylindrical plastic filled with 3l volume of oily wastewater and was made from Pyrex .The reactor consisted of horizontal circular Al/Al electrodes with five rings. The anode was a rotating Al disc, while the cathode was Al sheet placed at the cell bottom.

The electrodes were connected to a digital D.C power supply having an input of 220 V and variable output of 0–20 V, with variable current 0–2 A. (five rings discs with diameter of 7cm).

The following figure for experimental setup (Figure 2)

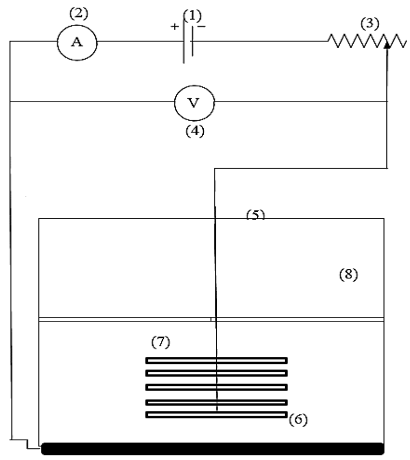

Figure (2): Schematic Diagram of the Experimental Setup

1.	**D.C power supply.**	5	**Cylindrical plastic container**
2.	**Ammeter.**	6	**Vertical Al sheet (cathode).**
3.	**Variable resistance.**	7	**Rotating Al plate (anode).**
4.	**Voltmeter.**	8	**Emulsion level.**

2.3 Variable studied

Variables studied were: the disc anode rotational speed (250, 500, 750 and 1000 rpm), electrolyte (NaCl) dose (1, 3, 5, 7, 9 g/3litre), pH of the oil emulsion (3, 5, 7, 9 and 11), Concentration of oil emulsion (250, 500, 750and 1000 ppm).

2.4. Procedure

A synthetic emulsion mixture of oil/water was prepared by dissolving 15 g oil in 15 l water to obtain 1000 ppm concentration. This mixture was then subjected to mechanical stirring for 15 minutes to form a stable oil/water emulsion. The desired amount of oil mixed with fresh tap water was used under agitation for 30 min, for obtaining very stable or soluble synthetic oil wastewater. This quantity will be stored to carry out several experiments. All experiments performed at 25°C.

Methods of analysis samples were periodically taken out from the reactor and then turbidity measurements of the reaction solutions were immediately performed. Samples were taken from the cell using a pipette tube. Each experiment lasted 60 min, where the samples are taken at (0, 5, 10, 20, 30, 45, 60 min). Turbidity removal efficiency was calculated from the ratio of the concentration change to the initial concentration expressed in percentage as given in Equation:

$$T\ (\%) = \frac{C_o - C_t}{C_o}$$

Where, T, Co and Ct are percent of turbidity removal, initial and at a specific time turbidity concentration respectively.

2.5. Analysis Sets

Balance, turbidity meter to measure of the residual oil in the sample, Mechanical stirrer to achieve mixing of the solution during treatment, Range: 0-2000 rpm, pH meter were used in the experimental.

3. Results and Discussion

3.1. Calibration curve

Figure (3) shows the calibration curve driving the relation between oil concentrations and their turbidity.

In Figure (4), 750 r.p.m gave the highest possible % removal (53.11%) after 60 mintues.it is clear from the Figure (4) that the beganinig the highest % removal was at 750 r.p.m. Other hand, 1000 r.p.m gave a negative % removal.This can be attributed to that such a high r.p.m can give a contradicting effect to electro-coagulation, namely reformation of the emulsion again. The purpose of stirring is to form a stable and homogeneous emulsion by breaking large liquid drops into smaller drops. The resuts show that the dependence of emulsion stability on stirring speed, the relative emulsion volume after 15-min stirring followed by 24-h resting is plotted against time, which clearly indicates that a more stable emulsion was achieved with higher stirring speed [20].

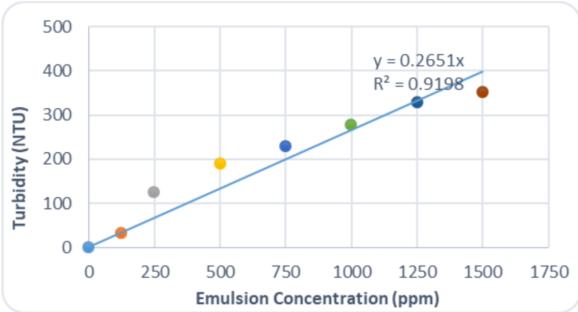

Figure (3): Emulsion Concentration Calibration Curve Using NTU of the Turbidity Meter

3.2. The effect of rotating speed

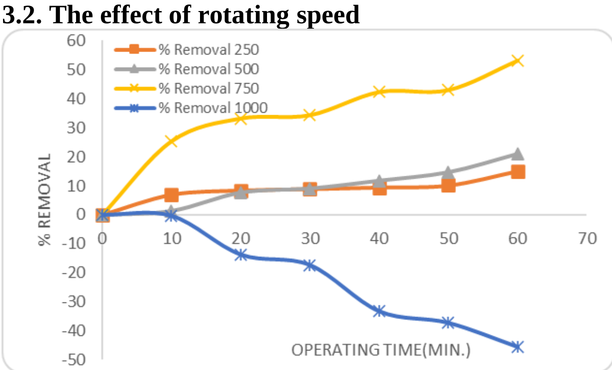

Figure (4): The Effect of Rotating Speed (rpm) on % Removal (C_o=1000 ppm)

3.3. The effect of NaCl dose:

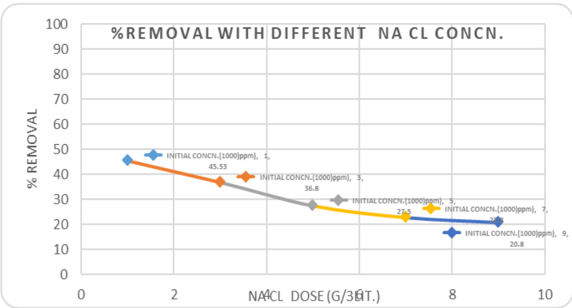

Figure (5): The Effect of NaCl Dose on % Removal (C_o=1000 ppm , rpm =750)

Figure (5) shows the negative effect of increasing NaCl dose on the % Removal , Where % removal decreased sharply from 45.53% to 20.8 on increasing NaCl dose from 1 g to 9 g. the separation efficiency increases with decreasing Na Cl concentration, this may be attributed to the fact that de-emulsification by electrophoresis (electrical migration of the negatively charged oil droplets to the anode) decreases with increasing Na Cl concentration where the competing Cl- migrates to the positively charged anode in preference to the charged oil droplets. Simply, when NaCl concentration increases, the Na+ increases and then the attraction to Cl- will increases and less Cl- available for Al+++ passivity. Farther increase of Na Cl dose (Up to 5 grams) gave a slight decrease of % removal. This negative effect of Na Cl may be illustrated due to the fact that the increasing of Na Cl dose will lead to less diffusion of Al+++ ions and hence less coagulation.

3.4. The effect of the pH value:

Figure (6) shows the effect of pH on the % removal the range of pH studied (3 -11), pH has a different effect in both acidic medium and alkaline medium.

The formation of negatively charged aluminum hydroxide colloid at pH> 7 did not diminish the separation efficiency as expected probably because of the dominance of other promoting effects such as the low pH at the anode surface arising from the hydrolysis of the dissolved $AlCl_3$.

The insignificant effect of the pH within the range (3-11) observed in the present work is consistent with the finding of other investigators who tested the effect of pH on the electro-coagulation efficiency. Alkaline values (pH = 9) gave the highest % removal (79 %), while increasing pH will lead to sharp drop of the % removal (down to 30 %).

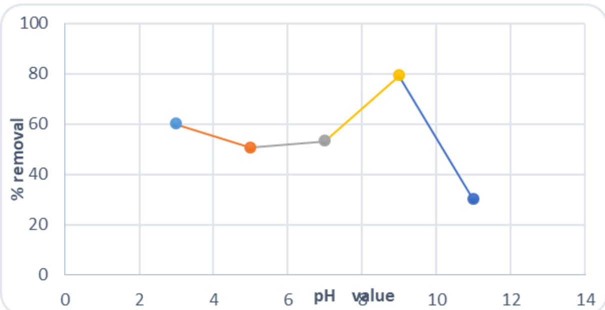

Figure (6): The Effect of pH on % Removal (C_o=1000 ppm, r.p.m =750)

4. CONCLUSIONS

1- The present work has shown that the performance of a cell with circular horizontal electrode is superior.
2- The present results have shown that the electro-coagulation is an efficient way for treating oil-water emulsions. However, the final oil concentration was above the maximum permissible value. Another electro-coagulation process can be used in conjunction such as ultra -filtration to demulsify completely oily waste water emulsions.
3- A new anode design is tested in the electro - coagulation of lube oil emulsion
4- Best operating conditions that gave79%Removal value are: pH=9, 750r.p.m and C_o=1000 ppm)
5- Very high r.p.m (1000 r.p.m) gave a negative effect of % removal. Due to emulsion oily water was formed at higher r.p.m.
6- High NaCl dose decreases the % Removal.
7- Although the present data were obtained using a batch cell, these data can be utilized in practice to operate a continuous cell provided that the flow rate (feed rate) of the emulsion to the cell is extremely low.
8- Further electro-coagulation studies on oil separation from oil/water emulsion should be extended to the use of iron scrap instead of Al in building the cell electrodes with the hope of further improving the economy of the process in view of the low cost and availability of iron scrap.

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