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Novel Electrode Design for Removing CNG Lubricant from Wastewater by Using Electrocoagulation

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Abstract

Lube oil centres are producing a huge quantity of oily wastewaters in Egypt. Compressed natural gas (CNG) lubricant and car park stations are the main source of mineral oily wastewater. A huge quantity of oily wastewater formed during the replacement of engine's lubricant. The treatment of such oily wastewater which contains CNG lubricant has been carried out via Electrocoagulation (EC) with a novel electrode design was investigated. The finely dispersed oil removal from oil/water emulsions by EC using electrolytic cell with novel Al horizontal electrodes is studied. The cell is consisted mainly of a cylindrical plastic container (25 cm in height and 10 cm diameter), a vertical Al sheet as cathode placed at the bottom of the cell and rotating disc as anode. The cathode-anode apart was fixed at a distance of 1.5 cm. Different variables are studied such as the rotational speed of anode (100 - 500 rpm), NaCl dose as an electrolyte, pH, oil emulsion concentration, voltage and time applied. The maximum removal obtained is 87.5% for operating conditions at pH 7.4, initial oil concentration 500 ppm, rpm 480 and 0.5% NaCl; respectively. Although the present data were obtained using batch cell, but it can be utilized in practice to operate a continuous cell providing a flowrate of CNG lubricant wastewater to the cell was extremely low.
Key words: Novel electrode, rotating anode, CNG lubricant, lube oil centers, water treatment and electro-coagulation.

1. INTRODUCTION

Continual rapid industrialization and population growth are making demands on water resources and increasing the prohibited contaminated discharges to aquatic environment. A large oily wastewater amount per year is discharging from lube oil centers and gas stations into the environment. Multiple methods are used to treat this oily wastewater to minimize these pollutants and to break the emulsion. This signifies a worldwide hazard to human health and safety with both instant and long-term consequences for hard work. This is to decrease lack even as sustaining the integrity of most ecologically productive [1-4]. In Egypt, rapid and continues uncontrolled population growth increase will become up to 150 million by 2050. This high population growth rate exaggerates the troubles revealed that fast deteriorating surface and groundwater quality [5]. Environmental protection is considered one of the extreme tasks of the 21st century as reported by Amin et al 2021[6]. Oily wastewater treatment is one of the greatest worrying troubles in many industries, especially in the petrochemical and iron & steel industry. Hence, it is important to improve the quality of treated oily wastewater. Oily wastewater poses significant threats to the soil, water, air and human beings because of the hazardous nature of its oil contents. Oily wastewater means wastewater generated during the refinery process and which contains free oil, emulsified oil, or other hydrocarbons. Oily wastewater originates from a variety of refinery processes including cooling water, condensed stripping steam, tank draw-off, and contact process water. Oily wastewater consists of hundreds of organic and inorganic compounds, some of which severely jeopardize the environment [7]. At 2010, many treatment techniques were applied such as flotation, membrane separation process [8], while in 2016, hydro-cyclone technology, adsorption, EC and biological treatment etc. were implemented by Abd-El-Fatah et al [9].

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EC is defined as a technique based on electrochemically principles that generates coagulant species in situ from the electro-dissolution of sacrificial anodes as stated by Mostefa et al 2004 [10]. In this technique, an electric current destabilizes anode made from iron or aluminum immersed in suspended, dissolved, or emulsified pollutants. The effectiveness of EC process depends on numerous parameters such as pH, electrode type and shape, time and current density. The main challenges related to the EC, process arc electrode passivation and energy consumption were explained by Essaki et al 2008 [11]. When EC was compared with other approaches, it has advantages such as plummeting energy consumption and operating costs. Moreover, there are many advanced processes underline of the term EC showed in Figure (1). An electrochemical process was applied to multiple applications like textile, cellulose, paper mill factories, laundry, and various kinds with different characteristic of oily wastewater [12-16]. EC technique can be operated via separation and degradation. In a separate system, EC involves applying electric current to sacrificial electrodes where coagulants and gas bubbles are generated in situ.

EC is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and considerable technical improvements. There has been relatively little effort to better understand the fundamental mechanisms of the processes. They can provide design parameters to optimize the performance of simple and inexpensive technique.

The process destabilizes and aggregates contaminant particles, ions such as heavy metals, and colloids, using an electrical power [17], charge to hold them in solution. The process traditionally utilizes an anode and a cathode, stimulated by a DC power source to destabilize the charges. This operation separates flocculated materials from water, allowing those materials to be removed, leaving clear water.

Traditionally, the sacrificial anode in EC process is electrolytically oxidized releasing metal ions, forming coagulants, destabilizing contaminants, breaking emulsions and forming flocculants that float to be skimmed at the surface. An electrochemical process offers outstanding benefits when compared to other technologies:

- Can treat both process and wastewater
- Treats a wide range of contaminants
- Operation uses safe, simple equipment
- Typically, does not need to chemical treatment
- Can typically reuse EC treated waters, minimizing waste

EC is effectively removing suspended solids to sub-micro meter levels, breaks emulsions such as oil and grease or latex. It also oxidizes and eradicates heavy metals from water basin without filters or any chemicals addition as stated in [18]. The coagulation process is effective in treating this type of wastewater. In previous studies carried out at 2010, **Matilainen et al** improved efficiency in oil separation, when electric field was applied. In addition, relevant studies approved that the electrodes may produce divalent or trivalent metal ions for coagulation from the electric field during treatment [19].

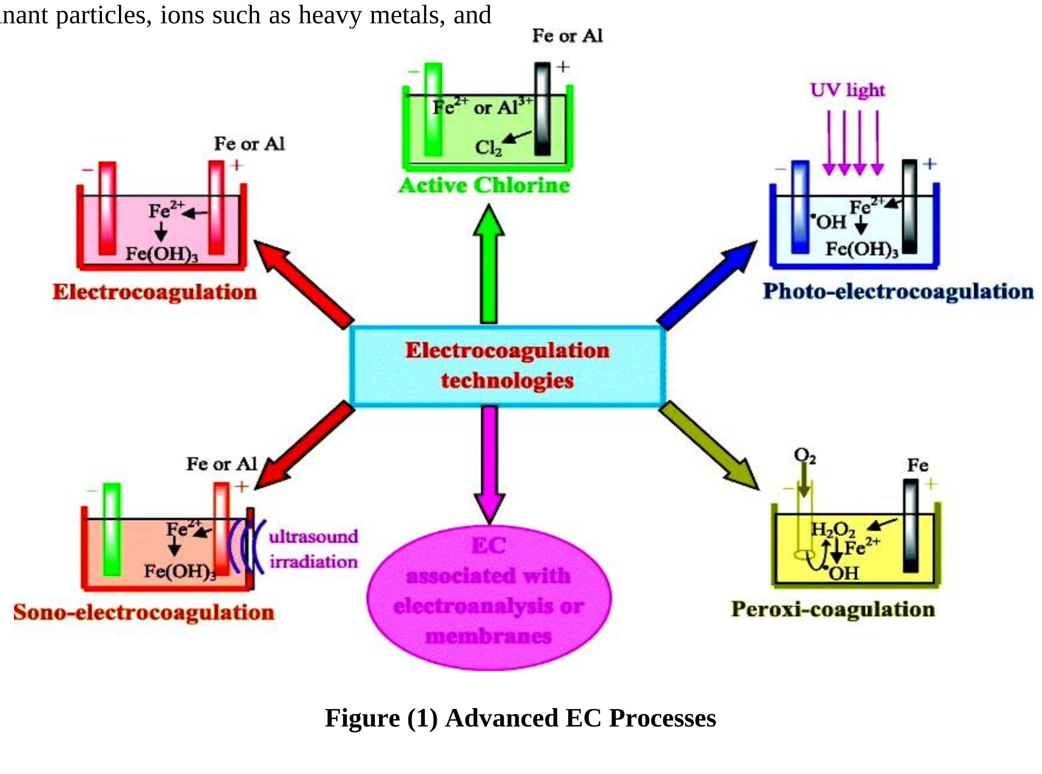


Figure (1) Advanced EC Processes

The use of aluminium and iron electrodes in the EC process was found to be effective as concluded by **Hakizimana, 2017** [20]. His experimental work was based on anodic dissolution of metallic aluminium or iron. Consequently, the formation of aluminium or iron ions in the vicinity of the anode, were converted immediately to the corresponding hydroxides. These hydroxides, in the process of coagulation and flocculation, were highly adsorptive and adherent to emulsified and colloidally dispersed oils. The mechanism can be expressed with the aid of chemical equations as follows:
A current is passed through a metal electrode, oxidizing the metal (M) to its cation (Mn^+)

$$M \rightarrow Mn^{+} + e^{-} \quad (1)$$

Simultaneously, water is reduced to hydrogen gas and hydroxyl ion (OH^-)

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \quad (2)$$

EC thus introduces metal cations in situ, electrochemically, using aluminium or iron sacrificial anodes. The cation hydrolyses in water forming the corresponding hydroxide; equations 4-6 illustrate this in the case of aluminium anode:

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^{+} \quad (3)$$
$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^{+} + H^{+} \quad (4)$$
$$Al(OH)_2^{+} + H_2O \rightarrow Al(OH)_3 + H^{+} \quad (5)$$
$$2H^{+} + 2e^{-} \rightarrow H_2(g) \quad (6)$$

Hydrogen (H_2) is evolved at the cathode by the electrolysis of the water. The evolution of the hydrogen gas aids in mixing and hence flocculation leading to the flotation of the hydroxide floc together with the oil sorbed on the porous surface of the floc.

EC is carried out in an electrolytic cell with Al or Fe anodes, the dissolved Al^{+3} or Fe^{+3} neutralized the negative charges present on the colloidal particles as oil droplets, with a consequent destabilization of the colloidal solution or the emulsion as reported [21]. Consequently, it is obvious that the cell design plays a major role in the process of EC. Electrodes types may differ according to the design of electrolytic cells, they may be manufactured from one metal (Aluminium /Iron/Stainless steel/Graphite); **Cañizares, 2007** [22]. Generally, aluminium is the common electrode. Its shape is different; it may be circular, rectangular, tube, cylindrical. The electrode may be mixture from multiple metals according to the usage. [23]

The oily wastewater should be purified. For an oil containing wastewater, EC may be used for the treatment. The distribution diagram of oily wastewater as shown in Figure (2)

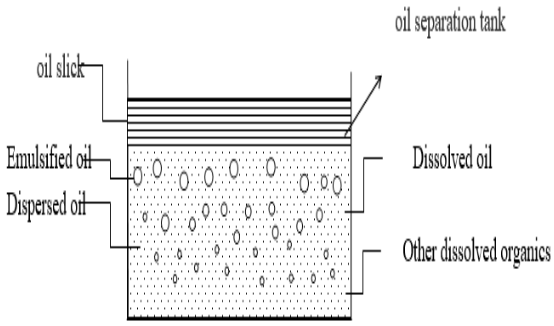


Figure (2) Distribution diagram of oily wastewater

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this study: fresh water, emulsifier, compressed natural gas engine oil (SAE 20W50/API SG), sodium chloride (99.9% salt), sodium hydroxide 99% from Merk Company and hydrochloric acid 30%.

2.2 Experimental Setup

All experiments concerning the applications of the EC have been carried out in a batch reactor Figure (3) represents the experimental reactor setup as follows:

(i) Plastic cylinder filled with 2.00 liter of oily wastewater.
(ii) Horizontal circular Al/Al electrodes.
(iii) Rotating vertical Al disc 7 cm diameter anode.
(iv) The Al disc was connected with insulated Al shaft.
(v) Cylinder diameter was measured before and after each run to make sure that no significant dimensional change had taken place during the experiment.
(vi) The cathode-anode separation was fixed at a distance of 1.5 cm.
(vii) The electrodes were connected to a digital D.C 220 V power supply, with a variable output of 0–20 V, with variable current 0–2 A.

2.3 Variable Studied

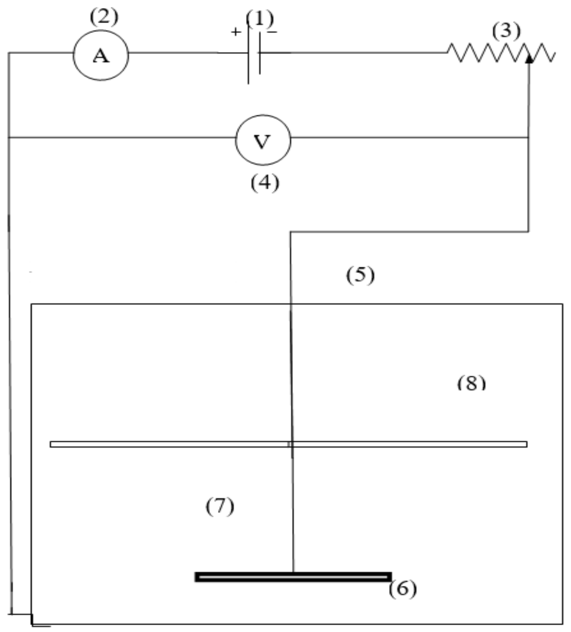
Variables studied were: the disc anode rotational speed (ranged from 100 to 500 rpm), electrolyte (NaCl) dose (0.5%, 1%, 2%, 3%, 4%, and 5%/ per litter), oil emulsion with pH (2.3, 5.4, 7.4 and 11, respectively) and concentration of oil emulsion (from 100 to 500 ppm).

2.4. Procedure

2.4.1. Emulsion Preparation

A stable synthetic emulsion to simulate the oil emulsions present in practice, therefore, to prepare oil-in-water emulsion with 500mg/l oil concentration. The following steps were carried out: A weight of 0.5 g of lubricant oil used and 0.025 g of DO emulsifier (provided by The Starch and Yeast Co. (Alexandria–

Egypt)) were added to 100 ml tap water in 1l glass beaker, The DO emulsifier is a brown liquid. Nonionic surfactant resulting from the condensation of polyethylene glycol ($HO(C_2H_4O)_{13}H$) with oleic acid ($C_{17}H_{33}COOH$), i.e. the polyethylene oleateester ($C_{17}H_{33}COO(C_2H_4O)_{13}H$). It forms a stable emulsion with water and resists the presence of dilute acids, alkalis, and Ca and Mg salts.



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

Figure (3) Schematic Diagram of the Experimental Setup

It is used as emulsifier for some mineral oils. The solution was stirred vigorously with a mechanical stirrer. The emulsified solution was completed to 1 litter with tap water. The pH value was adjusted at the desired value by using hydrochloric acid (HCl) or caustic soda (NaOH), just before starting the run. To simulate brackish water and sea water, 15g and 35g of sodium chloride (NaCl) were added, respectively, to the tap water before stirring.

2.4.2. Sampling procedure

Samples were collected after 15 min during each run, using a 10 ml pipette; the samples were taken from the same location of the cell. Samples were settled for 45 min. The samples were analyzed using a turbid meter. 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.

2.4.3. Experimental utilities:

Balance, Turbid meter, Mechanical stirrer with Range: 0-2000 rpm, pH meter

3. RESULTS AND DISCUSSION

3.1. Calibration Curve

The calibration curve in Figure (4) shows the relation between different concentrations of oil and their turbidity. Then it is used to determine the concentration of any sample that has got certain experiment by measuring its turbidity.

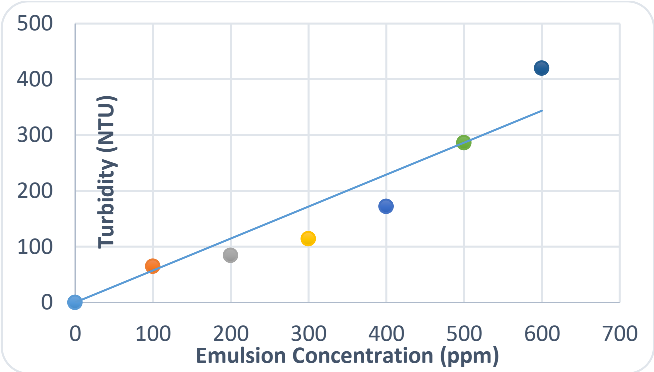


Figure (4) Calibration Curve of the Emulsion Concentration Using NTU of the Turbid meter

3.2. Effect of Rotating Speed

3.2.1. Low speed rotation

Figure (5) shows the effect of low rpm with different emulsion concentrations on the % removal. The slow rpm (100) is better than high rpm (480) in low concentration at low concentration. This may be attributed, as mentioned earlier; H_2 bubbles play an important role in the process of EC, namely, mixing the anodically dissolved Al^{+3} with the emulsion and flotation of the coalesced oil.

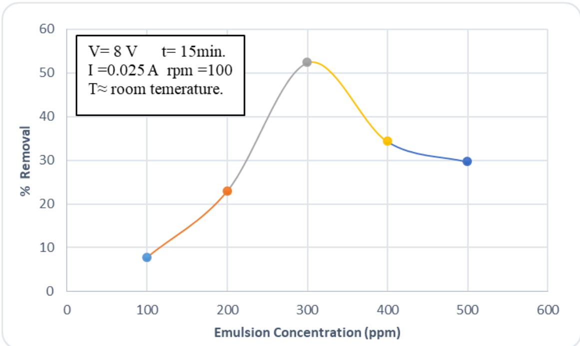


Figure (5) Effect of Low rpm with Different Emulsion Concentration on % Oil Removal.

3.2.2 High Speed Rotation

Figure (6) shows the effect of high rpm (480) on the % removal by using different concentration. The data show that the performance of high rpm 480 is superior to low rpm (100) at high concentration at the same operating conditions.

As a result of Figures (5 and 6), the maximum separation efficiency of 72.4% % was obtained from vertical electrode cell at high rpm.

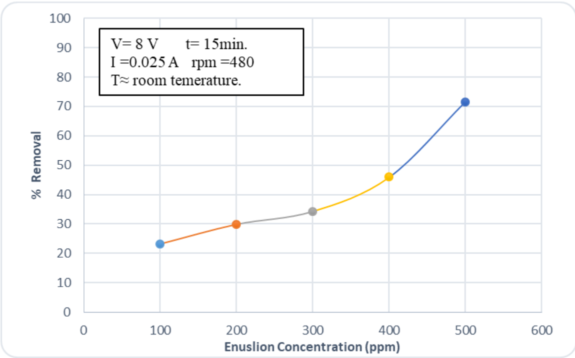


Figure (6) Effect of High rpm with Different Emulsion Concentration on % Oil Removal

3.3. Effect of NaCl Dose

Six NaCl concentrations were used. Figure (7) shows that for a given set of conditions the separation efficiency increases with decreasing NaCl concentration, this may be attributed to the fact that demulsification by electrophoresis (electrical migration of the negatively charged oil droplets to the anode) decreases with increasing NaCl concentration where the competing Cl^- migrates to the positively charged anode in preference to the charged oil droplets.

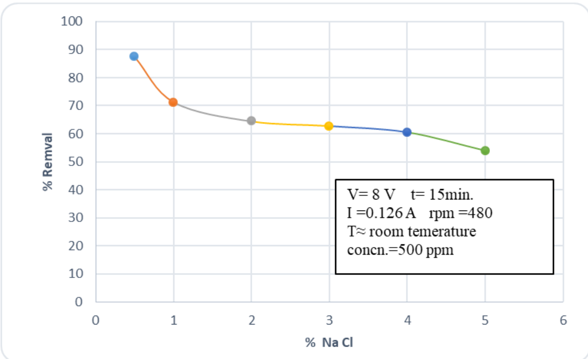


Figure (7) Effect of NaCl Concentration on % Oil Removal

Simply, when NaCl concentration increases, the Na^+ increases and then the attraction to Cl^- will increases and less Cl^- available for Al^{+3} passivity. Figure (7) shows that the maximum separation efficiency in (0.5% NaCl) is 87.5% with a residual oil concentration of 54.6 ppm of the initial concentration 500 ppm an extra measure such as ultrafiltration should supplement EC to clean sea water from oil contamination.

3.4. The effect of the pH value

Figure (8) show the effect of pH on the rate of demulsification and separation efficiency within the range of pH studied (2.3-11), pH has a different effect in both acidic medium and alkaline medium

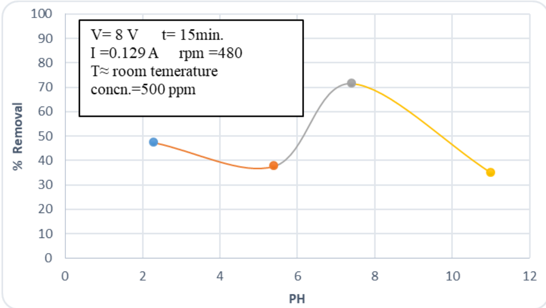


Figure (8) Effect of pH on % Oil Removal

The formation of negatively charged aluminium 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 2.3-11 observed in the present work is consistent with the finding of other investigators who tested the effect of pH on the EC efficiency.

3.5. Electrical Current

Figures (9 and 10) show that, within the present range of conditions, electrical current has no effect on the final separation efficiency.

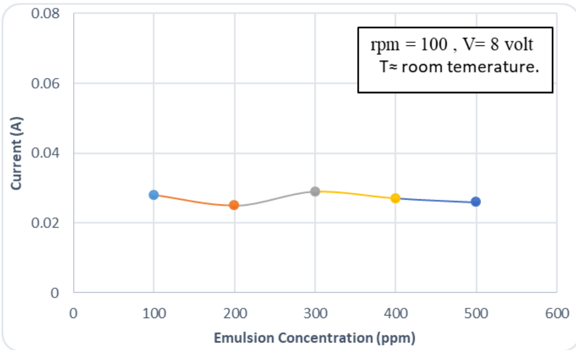


Figure (9) Effect of Different Concentration with Low rpm on Electrical Current

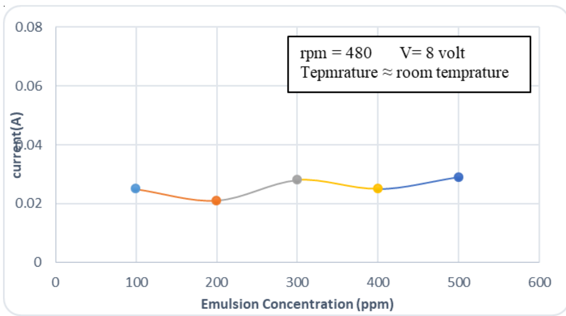


Figure (10) Effect of Different Concentration with High rpm on Electrical Current

4. CONCLUSIONS

- The present work has shown that the performance of a cell with circular horizontal electrode is superior.
- The present results have shown that the EC is an efficient way for treating oil-water emulsions where the oil content can be decreased below the permissible value. However, the final oil concentration was above the maximum permissible value. Another EC process can be used in conjunction such as ultra-filtration to demulsify completely oil-sea water emulsions.
- Study of the effect of the variables such as pH, speed rotation, electrical current, and NaCl concentration on the rate of demulsification has revealed that the rate of demulsification increase with using small % of NaCl. Electrical current was found to have little effect on the rate of demulsification.
- 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.
- Further EC 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.
- A new anode design is tested in the electro - coagulation of lube oil emulsion
- Best operating conditions that gave 87.5% Removal value are: pH=7.4, 480 rpm. 0.5 % NaCl and Co=500 ppm)
- High NaCl dose decreases the % Removal.

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