

Electroflotocoagulation of Emulsified Cooling Oils as a Method of Pollution Control

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ABSTRACT

This research includes the removal of pollution produced from used coolant emulsion oils especially soluble oil (7201)*. In many types of liquid effluents, oil – water emulsions can be among the most vexing to treat, even through such streams may contain only very small quantity of oil. Untraditional oil removal operation (electroflotocoagulation) is used in this research, which consist of glass cell 102 cm in height. A sacrificial Aluminum Anode is placed on a perforated glass disc at a distance 24-cm from the bottom. Above it is placed the upper electrode, Aluminum cathode is fixed on a movable glass tube. Product water was fed into settling vessels from the outlet arm 17 cm above the glass disc. Oily flocs and aluminum hydroxide were removed by a second side arm 45.5 cm above the product water arm. Sets of experiments were carried out to find the efficiency of electroflotocoagulation to remove the concentrate soluble oil (7201) from water. Multivariables were studied such as: applied potential, space between the two electrodes, settling time and initial soluble oil (7201) concentration. These variables have effect on the soluble oil (7201) percentage removal. The experimental results were represented in two mathematical empirical correlations and three dimensional graphs which describe the soluble oil (7201) removal efficiency as a function of current, settling time and in the second, initial soluble oil (7201) concentration respectively.

Keywords: Electroflotocoagulation, Treatment oily wastewater.

INTRODUCTION

In the chemical and petroleum industry there is always a need to remove finely dispersed oil from oil – in – water emulsions. This can be achieved by conventional techniques such as, parallel plate interceptors, air floatation devices, bulk reagent addition of flocculent chemicals may be used, but this tends to result in long settling times coupled with severe sludge handling problems. Wastewater may be present in one of five forms such as:- Free oil (drop oil size 20 μ m or larger), physi-

* Code number of Al-Dora refinery for the coolant soluble oil.

cally emulsified (drop oil size 5-20 μ m), chemically emulsified (less than 5 μ m), dissolved, oil wet solids (oil that adheres to the surface of particulate) (Pushkarev. et al., 1983)[1].

One of the major sources of pollution is cutting oil. Cutting oils are oil - in water emulsions employed in metal working to remove heat from the tool and work piece and to minimize friction and wear by providing good lubrication. Jose, (2001)[2] states that cutting oils can be classified into three groups.

- Mineral oils (25% Additives, 75% oil)
- Semi synthetic (30% Additives, 20% oil, 50% water)
- Synthetic (40% Additives, 60% water)

Al-Dora refinery produces 520.1 ton/ year from pure cutting oils (7202), (7203), (7204) and soluble oil (7201), (Al-Dora Refinery, 2000) [3].

The source of cutting oils pollution may come from an oil refinery, factory, rolling industry, metal – cutting equipment, engineering workshops. (Pushkarev, et al., 1983) [1], stated that the consumption of lubricating oil at a modern strip mill shop reaches 4000 ton/year [in Russian]. For various mills the quantity of wastewater are usually from 3000-20000 m³/h. The oil content in the effluents of a modern continuous multi-stand mill for sheet rolling is from 100-200 mg/l.

The most common treatment methods for treating oily wastewater are three methods (Pushkarev, et al., 1983 [1]. They are as follows: 1-Physico chemical, (coagulation with radiation, ultrasonic, sorption, dispersed-air flotation, dissolved-air flotation and sedimentation), 2-Electrical electrolytes, (electrocoagulation, electrostatic field), 3-Biodigradiation.

The removal of finely dispersed oil from oil – in – water emulsions can be achieved by the use of electrocoagulation. (Balmer and foulds, 1986) [4]. In 1906, Dietrich [5] obtained a patent for his work using a variety of anode and cathode geometries, including, plates, balls, fluidized bed spheres, wire mesh, rods, and tubes. He has proven that electrocoagulation was very effective system in the removal of contaminants from water. In 1972, Men [6] stated that the residual concentration of ether-soluble substances in the wastewater from hot rolling could be decreased to 2-3 mg/l after electroflotation. In 1977, Bochkarev, et al [7]., stated that significantly less ions are required to be added electrolytically than chemically, allowing the process to use less metal. In 1977, Osipenko and Pogorelyi [8], reported on the problems encountered with the electroflocculation technique which has been associated with anode life time. Theoretically there are no chemicals to be added and no filters which need cleaning, entailing this process to achieve the best goals. In 1983, Weitraub, et al. [9], reported on a study which deals with the application of electroflocculation and electrocoagulation in separation of oil from oil-in-water emulsions, and they showed that electroflocculation and electrocoagulation make use of the direct introduction of flocculent ions into the emulsion suspension by means of electrical dissolution of sacrificial electrode (e.g. $Fe \rightarrow Fe^{+3}$). The authors also, pointed out that there is too small an effect on the process of oil separation. When the correct dosage of ions is introduced the process of flocculation occurs with good oil separation. In 1986, Balmer and Foulds [4], studied the performance of electrocoagulation process by using four types of iron as the anode combined with a platinum gauze cathode. All of these types of anodes have produced sufficient quantities of flocs and gave the same zero

residual turbidity and 100% oil removal efficiency. Whilst all of these were effective, it was considered that low cost scrape iron turnings represent the ideal anode material for turbidity application.

In 1993, Naomi, et al. [10], estimated the overall treatment operating costs in the field of oily waste (electricity, aluminum electrodes, operation, and maintenance). It was found that these costs will vary upwards from \$ 0.50 / 1000 gal to \$ 3.0/ 1000 gal, depending on emulsion strength, and unwanted component concentrations.

Also for experiments Donini, et al., 1994 [11], suggested that electrically added aluminum ions were much more active than chemically added aluminum ions meaning that less aluminum was required and that this process could be used to treat a number of different pollutants which could not be handled by chemical flocculent such as alum (aluminum sulphate). In 1995, Fredrick and Jan [12], investigated advances in electroflocculation have proven effective in breaking oil-water emulsions, and show promise in removing some organic compounds and heavy metals from wastewater. USDA, 1995 [13], showed that when the system of electrocoagulation is used in place, the operating costs including the electric power, replacement of electrodes, pump maintenance, and labor can be less than \$ 1.0 per thousands gallons for some application.

Vivian, (2000) [14], has applied the new technology of electroflocculation in the field of industrial application. He was found fats oils and grease (FOGs) removal rates in excess of 99.95% and reduced the power requirements for the system treating. Also the notes of reduced the power requirements was indicated by Powell water system Inc.

In 2002, Avner [15], stated that the turbidity decreases from 30NTU to less than 1NTU by used electroflocculation treatment of wastewater and 60% cost reduction from than conventional flocculation process.

In 2003, Mehmet et al. [16], were investigated treatment of textile wastewaters by electrocoagulation using iron and aluminum electrode material. The results show that iron is superior to aluminum as sacrificial electrode material, from COD removal efficiency and energy consumption points.

In 2004, Mollan et al. [17], it was concluded that, electrocoagulation consists of a number of benefits; compatibility, amenability to automation, cost effectiveness, energy efficiency, safety, and versatility.

In 2007, Vepsalainen et al. [18] studied the removal of natural organic matter from paper mill mechanically and surface water treated water by integrating electrocoagulation with chemical coagulation. The experimental work was performed to remove oil pollutants from wastewater. This experiments includes treatment methods of wastewater by coagulation, flocculation with and without chemical coagulants, Mohammed, 2007 [19].

In 2008, Chithra et al.[20], were carried out experiments to treat synthetic Bismarck Brown dye effluent using electro coagulation covering a wide range in operating conditions. In 2009, Sulaymon et al. [21] studied on electrolytic method for the removal of zinc from wastewater using a flow-through cell with a malgated copper screen cathode.

In 2012, Vepsalainen [22], carried out experiments using electrocoagulation in the treatment of industrial waters and wastewaters with main parameters such as initial pH and current density.

A renewed interest in electrocoagulation has spurred by the search for reliable, cost effective method for treatment of polluted water, Satish, (2013) [23].

The aim of the present work is to study the possibility of using electrocoagulation (electroflotocoagulation) as suitable treatment method for removal of soluble oil (7201) from an industrial wastewater. The parameters were studied in this research they are:- Concentrations of soluble oil (7201), the value of current, voltage used, and space between the two electrodes (Anode & Cathode).

Experimental Work

The experiment test studied the effect of different parameters on removal efficiency of oil from water. The parameters are: applied potential, space between two electrodes, settling time and initial soluble oil (7201) concentration. By selection of a suitable synthetic emulsion of concentrate soluble oil (7201), it is possible to carry out the separation. A schematic flow diagram for the equipment is given in Figs. (1) and (2). The apparatus consists essentially of (1) two electrodes. (2) Glass tube (3) movable glass tube (4) emulsion storage drum (5) power supply. The original glass cell was 102 cm high, as shown in Fig. (1) consists of an inlet at the bottom, above which the sacrificial Aluminum Anode, is placed on a perforated glass disc at a distance 24 cm from the bottom, above which is sited the upper electrode, Aluminum Cathode is fixed on a movable glass tube. Product water is fed into settling vessels from the outlet arm 17 cm above the glass disc. Oily flocs may be readily removed by a second side arm 45.5 cm above the product water arm. The small amount of flocculated material is carried over with the product water, whilst still permitting the bulk of the flocculated material to be taken off from the upper outlet. The two electrodes are connected to a variable 30v, 2A DC power supply and voltage supplied was monitored via a voltmeter.

The electrolytic cell consists of:

- Aluminum Anode (44 mm) in diameter with active surface area approximately (1475.8 mm²).
- Aluminum Cathode (35 mm) in diameter with active surface area approximately (760.66 mm²).

The following steps give a description of the procedure used in this study. and more details as shown in reference **AL-Rikaby, (2004) [24]**.

- Manufacturing a number of aluminum anode and aluminum cathode in the form of circle plate.
- Measuring the weight of aluminum anode.
- Instating the aluminum anode and aluminum cathode in the electrolytic cell.
- Preparation of emulsion.

Tap water (940 – 950 μ mohs/cm is used to produce synthetic emulsion samples. 1000 mg, 1500 mg and 2000 mg of soluble oil (7201) which are used in addition to 1 liter of water followed by vigorous mixing via magnetic stirrer for 10 minutes enough to the formation of stable emulsion in concentration of 1000 ppm, 1500 ppm and 2000 ppm respectively. The results of this study are divided into four sections.

1- Studying the soluble oil removal efficiency and approximate power consumption of different currents, different initial soluble oil concentrations and different spaces between electrodes, before injection of fresh water, Fig. (1).

2-Computation of the practical and theoretical Aluminum Anode consumption at different currents, different initial soluble oil concentrations, before injection of fresh water.

3-Study the removal efficiency of oil at different currents values and different settling times

4-Studying the soluble oil removal efficiency at different current after injection of fresh water, see Fig (2)

Results and Discussion

Effect of Applying Potential on Soluble Oil (7201) Removal Efficiency

Figures (3&4) show the soluble oil removal efficiency for initial oil concentrations ($C_0 = 1000, 1500, 2000$ ppm) and spacing between electrodes are ($S = 5, 3$ mm) respectively. These figures show that the removal efficiency of soluble oil increases as voltage increase until reaching complete removal of soluble oil. This agreement with aluminum dosing calculation equation as: (Vik, et al., 1984) [25], (Paul, 1996) [26],

$$m = \frac{1000}{96500} \times \frac{a}{v} \times \frac{it_t}{v_o} \quad \dots(1)$$

where: m-iron or aluminum dissolving (mg/L), a-atomic mass of iron or aluminum, v-valiancy, v_o -volume of electrolytic cells (liters), i-current in amperes and t_t -times in seconds.

Effect of Sacrificial Aluminum Anode Consumption on Soluble Oil (7201) Removal Efficiency

The removal efficiency of soluble oil increases as SAAC increased for different initial oil concentrations ($C_0 = 1000, 2000$ ppm) respectively (Figs. 5 & 6), and this is due to the increased of Aluminum hydroxide flocs as current increases.

Effect of Electric Current on Sacrificial Aluminum Anode Consumption

It has been found that the values of SAAC tend to increase as current value increases. Figures (7&8) show that the values of electric current are used to determine the values of dosage parameter of aluminum, theoretical consumption can be found by using Faraday's law Eqn.(1). Figure (9) shows the difference between PSAAC and TSAAC before injection of fresh water at different current. The values of difference (E) tend to increase as current value increases and this is due to increasing of aluminum hydroxide flocs which may tend to form a boundary of soluble oil and flocs near the aluminum anode surface in which the oil concentration exceeds that in the water above aluminum anode surface. This enrichment of oil concentration is called concentration polarization and on the other hand the conductivity of soluble oil is very poor, thus, the actual sacrificial aluminum anode consumption is always less than theoretically estimated.

Effect of Settling Time on Soluble Oil (7201) Removal Efficiency

The results of effects of settling time on removal efficiency are shown in Fig (10). These results are presented after treatment. The removal efficiency of soluble oil tends to increase as the values of settling time increase, the increase of soluble oil removal efficiency as a function of the settling time indicates that electroflotocoagulation can be used successfully. The analysis of results in Fig (10) indicates that the settling time required to achieve complete removal of soluble oil reduces as current increases, visual observation indicates that the size of flocs produced from electrocoagulated process increases with the increase of current. The analysis of results Fig (10) indicates that the increasing of settling time without treatment by electroflotocoagulation gives very little removal of soluble oil (7201), whereas after 800 min the removal efficiency of soluble oil (7201) did not exceed (1.869 %).

Effect of Applied Potential on Electrical Energy Consumption

Figures (11,12) show the increasing of APC (kWh/L) with the increasing of applied potential, at initial soluble oil concentration of $C_0 = 1000, 2000$ ppm and spacing between electrodes $S = 5, 3, 1.5$ mm.

For example: Fig. (11) indicates that the values of 2164.32×10^{-6} , kWh/L as APC are required to achieve complete removal of soluble oil (7201) with initial oil concentration of ($C_0 = 1000$ ppm) and spacing between electrodes is 5 mm with value of applied potential equal to 200mA and 15 v respectively. But the current and applied potential increases to 270mA and 20v as respectively to achieve complete removal of soluble oil with initial oil concentration of $C_0=2000$ ppm at spacing between electrode 5mm as shown in Fig. (12) .

The electrical energy consumption in kWh/L per liter of water treated is given by equation (2), (Balmer, and foulds 1986) [4] which illustrates that the electrical energy consumption is a function of current, applied potential and flow rate. The flow rate is constant in this experimental work and equal to ($4.99 \text{ cm}^3/\text{s}$), thus, the electrical energy consumption is a function of current and applied potential.

$$EEC(kwh / L) = 3.6 \times 10^{-3} \frac{iV}{Q} \quad \dots(2)$$

Where: Q-the water flowrate $\text{cm}^3/\text{sec.}$, EEC-Electrical energy consumption in kWh/L., V-applied potential (volt)

Operating Cost (Energy + Material Cost) of Electroflocculation

It could be noted that the using of high electrolyte conductivity and small electrode spacing give low energy consumption for electrocoagulation process, as shown by the following equation (3), (Balmer and Frouds, 1986) [4]:-

$$i = VR \quad \dots(3)$$

Where: R- is the electrolyte conductance. Assume an energy price of (0.001 \$/ kWh), and consumable aluminum electrode material cost is $\approx (10 \text{ \$}/ \text{kg})$, (Vivian, 2000) [14]

Operating cost = energy cost + consumable Aluminum Anode cost

From the results the Aluminum dosage required to achieve complete removal of soluble oil is (3.7296 mg/l) at approximate power consumption was ($2164.32 * 10^{-6}$ kWh/ L).

Operating cost in 1 \$ / (1 m^3) = $[2164.32 * 10^{-6} * 0.001 + 10 * 3.7296 * 10^{-6}] * 1000$

Therefore, the cost per one cubic meter of water is equal to (0.0395 \$) only.

The Analysis of Empirical Correlation

The experimental results of this study are used to develop empirical correlation. The dependent and independent variables were introduced into a computer program. The interaction between the three variables of current, time, or(7201) concentration with soluble oil (7201) removal efficiency are presented in three dimensional curve as shown Figs. (13&14) , respectively. The non-linear regression is used to analyze the collected data. The obtained relationship describes the soluble oil (7201) removal efficiency as a function of other parameters:

$$R\% = 47.48546 + 0.339565 * I + 0.227970 * T - 0.0003018 * I^2 - 0.000611 * I^2 - 0.000663 * T^2 \quad \dots(4)$$

Correlation coefficient = 0.989 AVE % = 1.07 %

$$R\% = 63.58184 + 0.326852 * I - 0.011633 * C_0 - 0.000434 * I^2 - 45.644 \exp[-5 * I * C_0] + 0.1 \exp[-6 * C_0^2] \quad \dots(5)$$

Correlation coefficient = 0.978 AVE % = 6.5

The results of the statistical analysis, especially of the high values of the correlation coefficients indicate that the experimental and modal data are in excellent agreement. A correlation between the experimental and calculated results for soluble oil removal efficiency is given in Figs. (15) and (16).

CONCLUSIONS

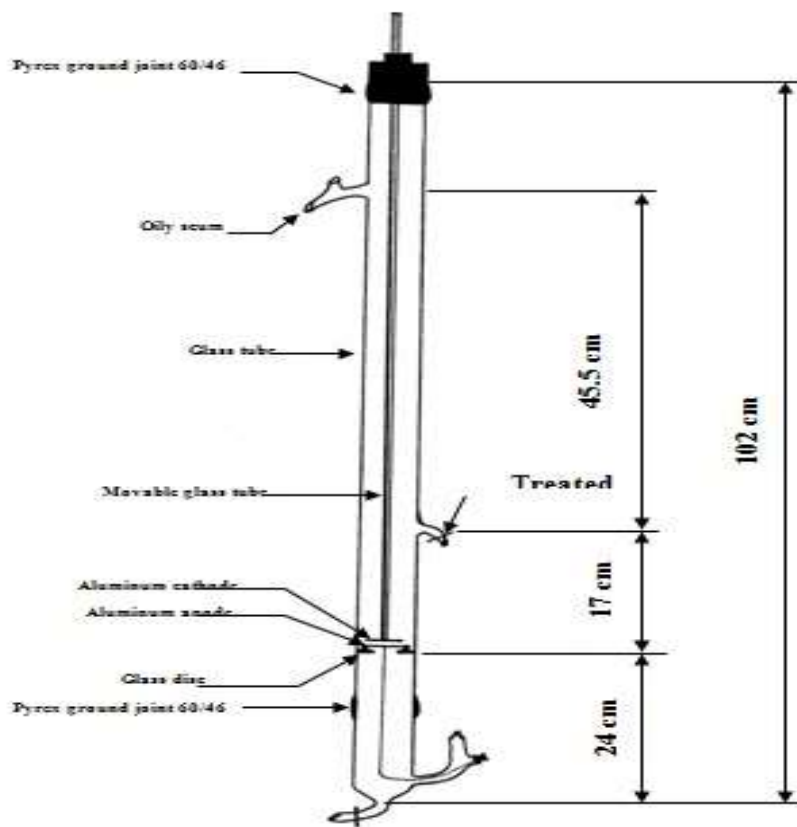
In general the following conclusions are extracted from the present study: -

1. The rate of production of aluminum ions in the process of electrocoagulation is controlled by the rate of electric current. This can be conveniently adjusted to match the required ion dosage in relation to the oil removal efficiency.
2. It was found from the results that the alum dosages and operating currents required to achieve complete removal of soluble oil are approximately (3.7296 and 5.0349 ppm), (I=200, 270) at initial soluble oil (7201) concentration of ($C_0 = 1000, 2000$ ppm) respectively.
3. The operating cost (energy + material) of electrocoagulation is found to be cheaper than that of chemical coagulation.

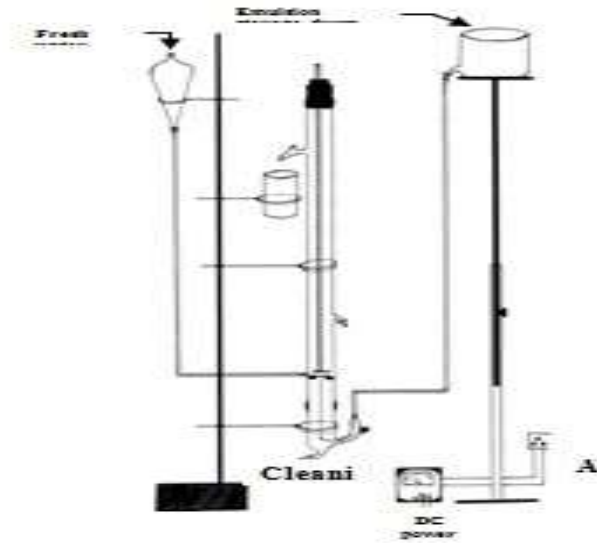
Nomenclature & Abbreviations

Symbol	Definition	unit
E	Difference between PSAAC and TSAAC	ppm
I	Electrical current	mA
Q	Emulsion flow rate	Cm ³ /s
R	Electrolyte conductance	-
R%	Soluble oil (7201) removal efficiency	-
V	Potential difference	Volt
Abbreviations	Definition	unit
APC	Approximate power consumption	kWh/L
AVE	Absolute Average Error	-
C	Soluble oil (7201) concentration	ppm
C ₀	Initial Soluble oil (7201) concentration	ppm
D _a	Alum dose	ppm
EC	Electrical coagulation	-
FOGs	Fats, oils and greases	-
kWh	Kilo watt hours	-

NTU	Naphlometric turbidity unit	-
ppm	Part per million	mg/L
PSAAC	Practical Sacrificial Aluminum Anode Consumption	ppm
S	Space between two electrodes	mm
SAAC	Sacrificial Aluminum Anode Consumption	ppm
TSAAC	Theoretical Sacrificial Aluminum Anode Consumption	ppm
TSS	Total suspended solid	mg/L



Figure(1) .Electroflotocoagulation cell



Figure(2) The schematic diagram of laboratory scale system of Electroflotocoagulation

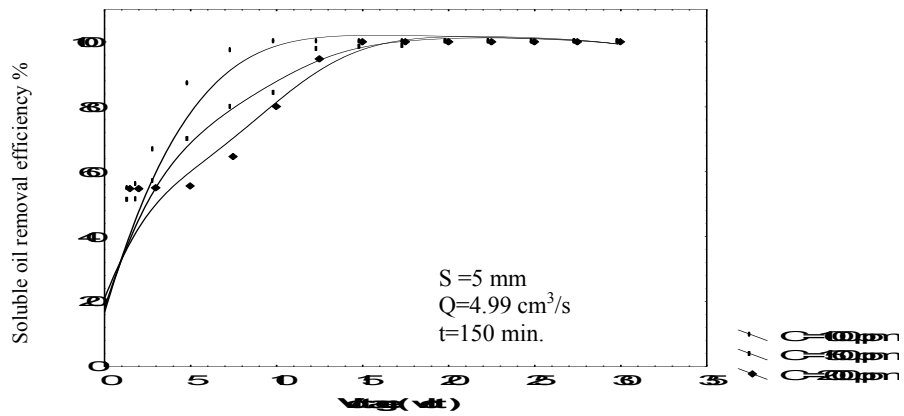


Figure (3) Effect of voltage on the removal efficiency of soluble oil (7201)

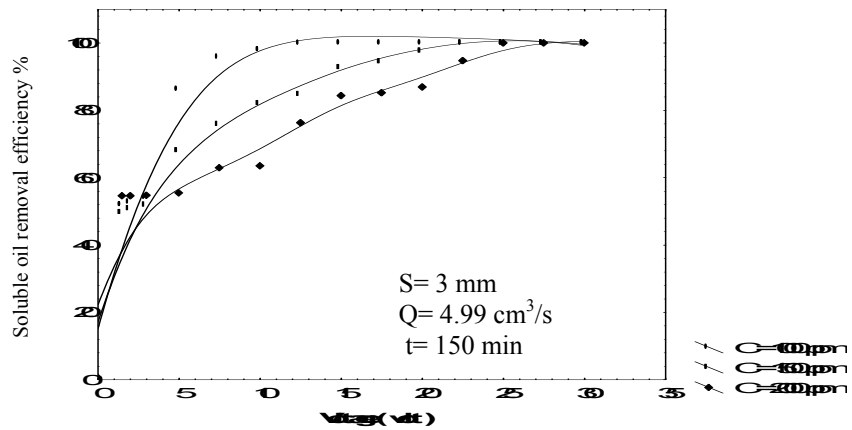


Figure (4) Effect of voltage on the removal efficiency of soluble oil (7201)

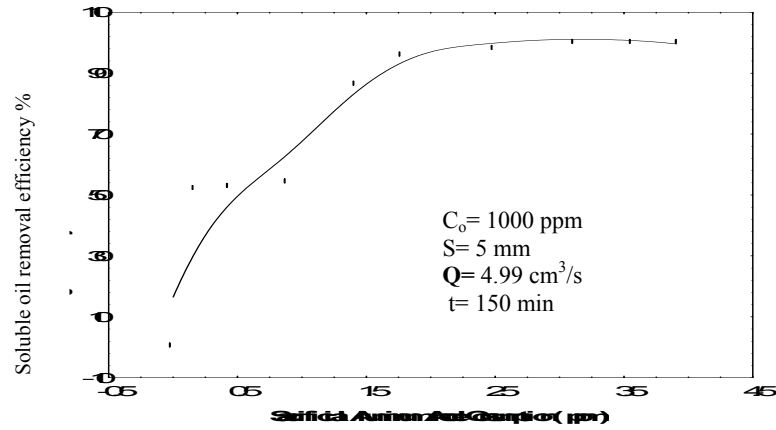


Figure (5) Effect of sacrificial Aluminum Anode Consumption on soluble oil (7201) removal efficiency

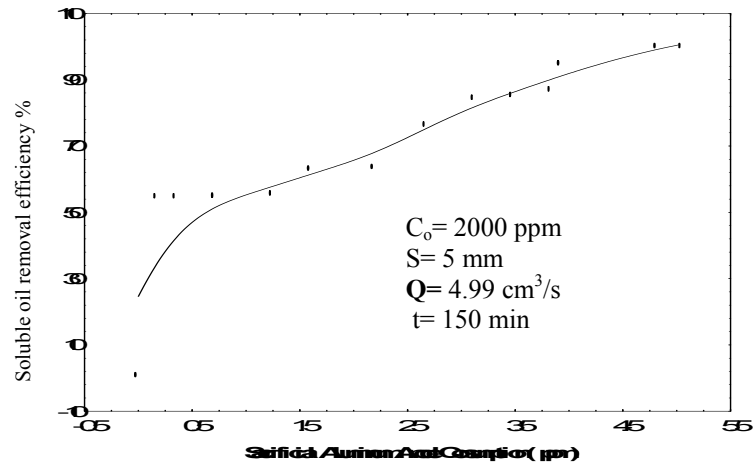


Figure (6) Effect of sacrificial Aluminum Anode Consumption on soluble oil (7201) removal efficiency

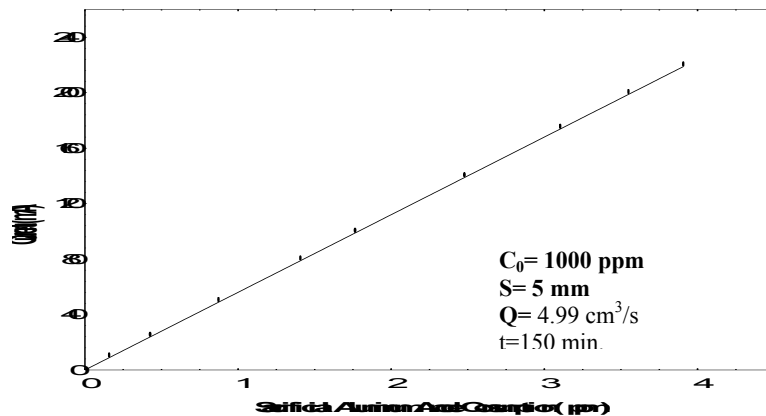


Figure (7) Effect of current on sacrificial Aluminum Anode Consumption

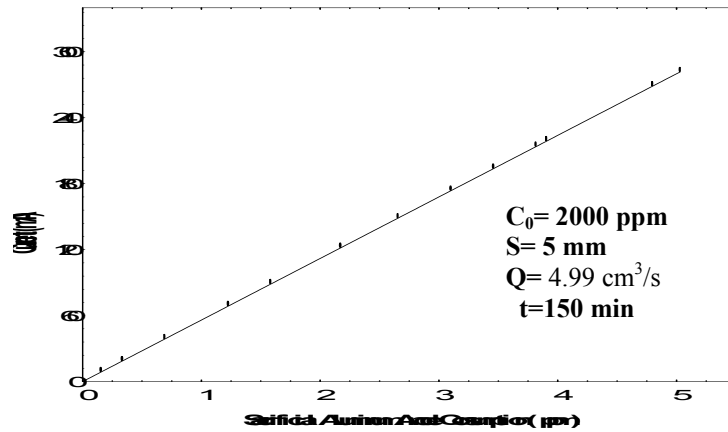


Figure (8) Effect of current on sacrificial Aluminum Anode Consumption

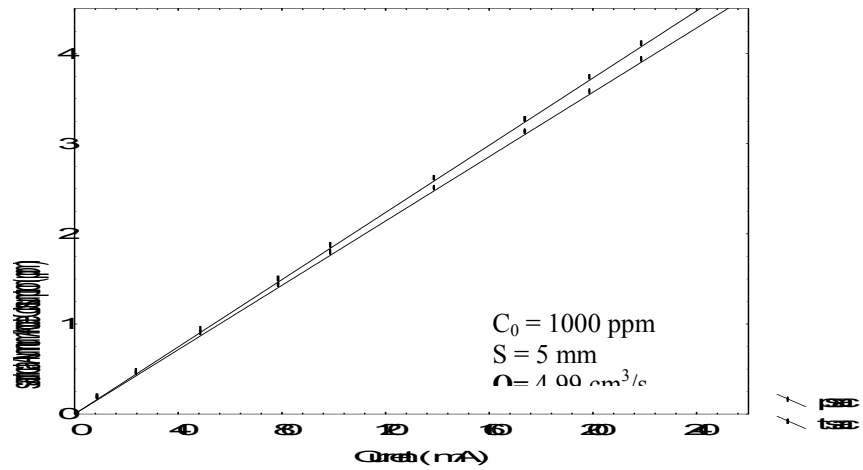


Figure (9) Effect of current on practical and theoretical sacrificial Aluminum Anode consumption before injection of fresh water

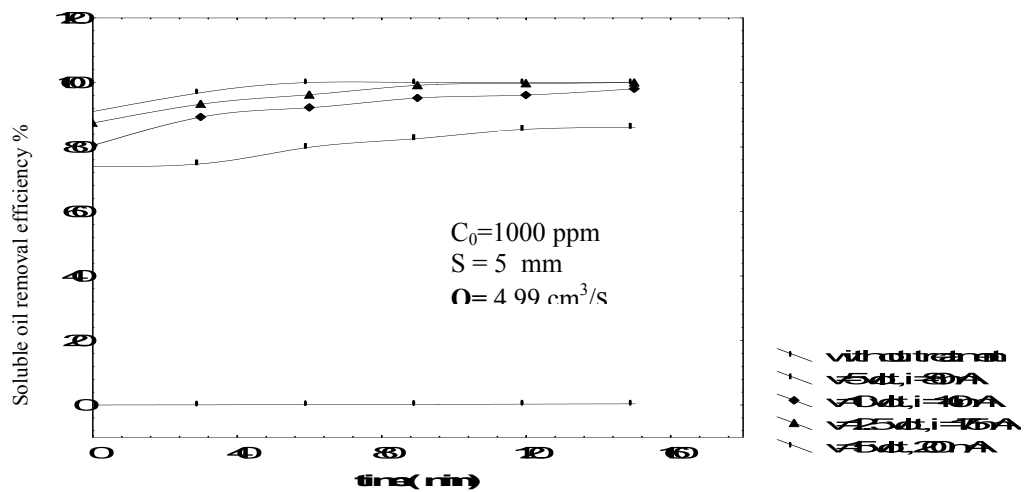


Figure (10) Effect of setting time on soluble oil (7201) removal efficiency

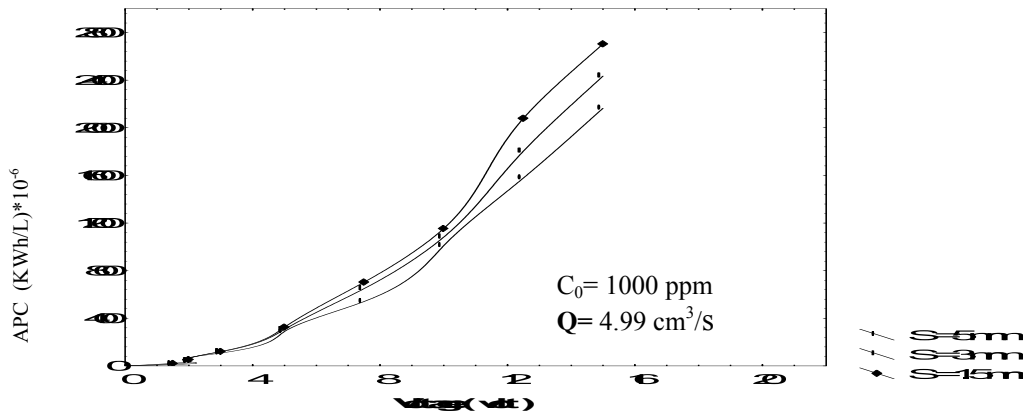


Figure (11) Effect of voltage on approximate power consumption

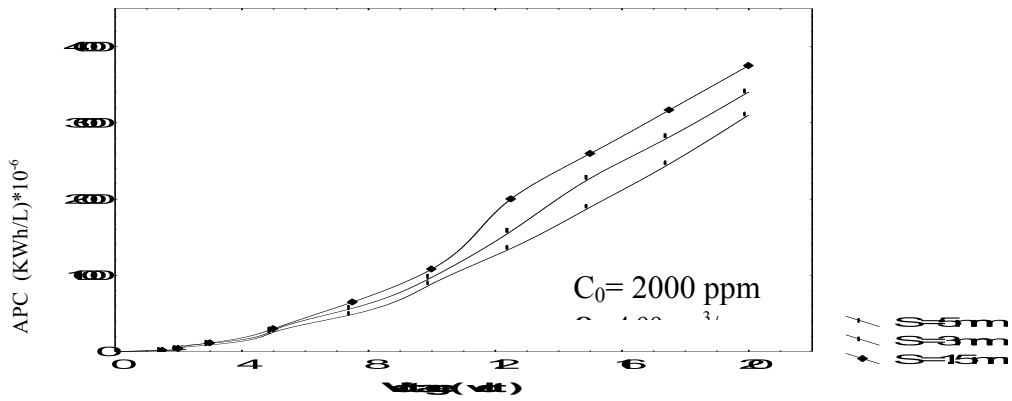


Figure (12) Effect of voltage on approximate power consumption

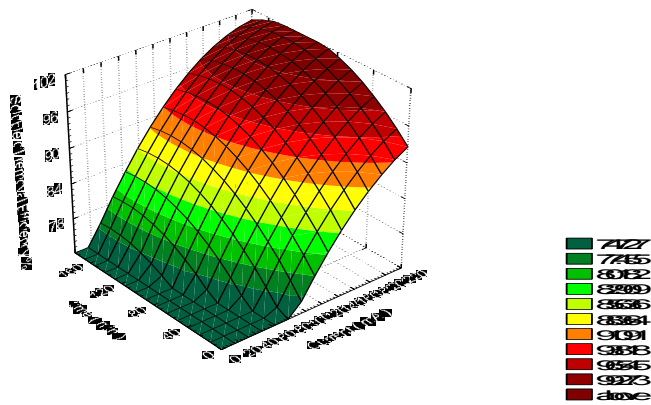


Figure (13) Effect of current and settling time on the soluble oil (7201) removal efficiency

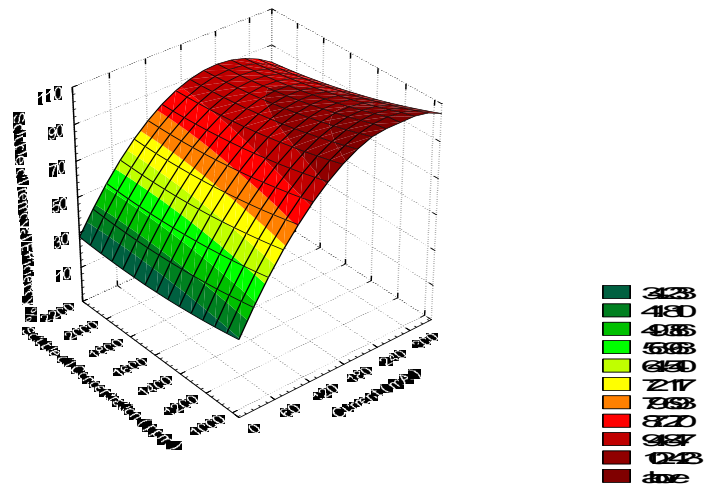


Figure (14) Effect of current and initial soluble oil (7201) concentration on the removal efficiency of soluble oil (7201)

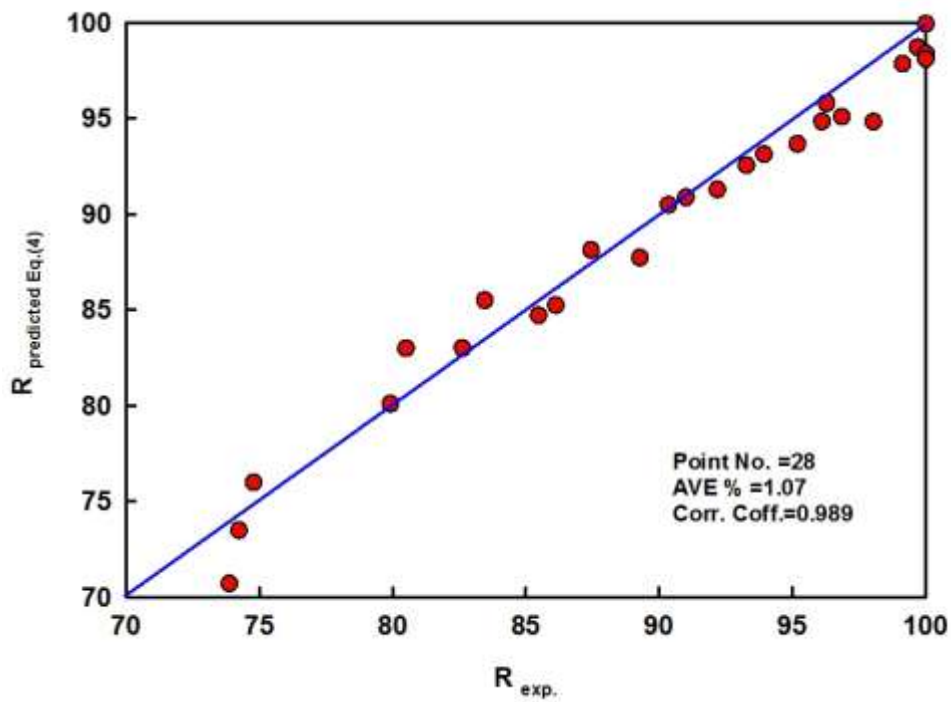


Figure (15) Predicted values of Eq. (4) versus Experimental values

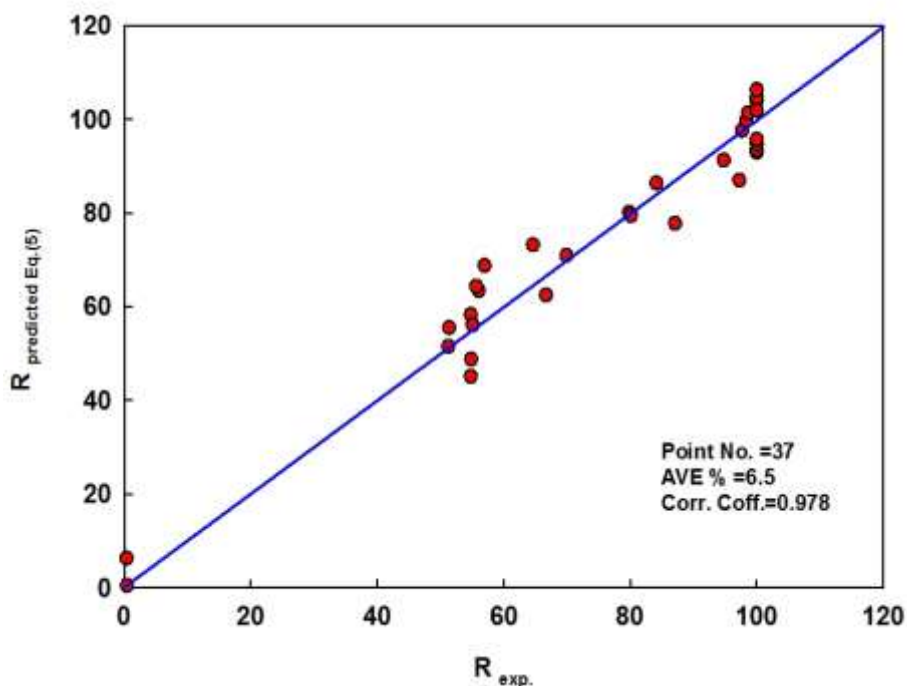


Figure (16) Predicted values of Eq. (5) versus Experimental value

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