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Effective Process Conditions and Reactor Design Parameters for Oil Separation by Electrocoagulation

S. L. J. Wijeyekoon, R. A. K. P. Abeysinghe, U. Karunaratne and M. W. Jayaweera

Abstract: Thermal power generating plants, service stations and oil refineries generate oily wastewaters which are recognized to be a severe threat to aquatic environments. Electrocoagulation has received considerable attention lately as a clean technology option yet absence of reactor design criteria and scientific understanding of the complex phenomena involved remain as a drawback to its widespread application. Laboratory experiments were conducted to determine the optimum operating parameters such as electrode type, influent pH, initial oil concentration, electrode polarity change, electrode surface area: reactor volume, current density and electrode spacing on COD removal efficiency. The effective pH for oil removal is dependent on the anode material used. A pH of 4 is suitable when Al is used where as the effect of pH is negligible for iron electrodes. High removal efficiencies are obtained for moderate oil concentrations of 400-500mg/l as COD. The optimum current density and electrode surface area to volume ratio were 46.9 A/m2 and 8.5 m^2/m^3 respectively. The electrode polarity switch leads to rapid dissolution of the electrodes and improved COD removal efficiency. The developed design parameters enable the design of low cost compact treatment units that could be powered by DC sources for effective oil separation from wastewaters.

Keywords: Current density, electrocoagulation, electrode spacing, oil separation

1. Introduction

Industries such as edible and crude oil refineries, petrochemical and thermal power generation plants, service stations, restaurants etc. produce oily wastewaters that are recognized to be a formidable challenge to treat and constitute a major threat to the local environments and eco systems. In thermal power plants the oily wastewater is generated in heavy fuel oil separators, machine shop, from steam cleaning in workshops, radiator cleaning, from fuel unloading by road tankers and during cleaning of engine parts. In garages, dismantling of engines and removal of used oil from the engines are the main sources of waste oil generation. In addition, waste oil is generated from repairs to crankcase, gearbox, brakes and such other parts of vehicles. Leaking flanges, pumps, storage tanks, filling and decanting operations in refineries, food preparation and cleaning operations in both small and large restaurants generate oily wastewaters. Varying concentration of hydrocarbons are common constituents in industrial wastewaters and can be found as free floating, emulsified, dissolved or absorbed to suspended solids. Effluents with waste oil cause both surface and ground water pollution leading to destruction of sensitive eco systems and contamination of drinking water sources. The resulting effects on the environment include; impact on fish populations, destruction of phyto-planktons and on aesthetic quality of receiving water bodies. Further effluents discharged to crop fields badly affect soil permeability and hence crop productivity.

The majority of oil and grease removal technologies are physical separation unit operations that make use of the difference in density of water and oil. However oils and fats are partly soluble in water and are present in separable, dissolved and emulsified states. Most of the technologies used remove only the separable fraction of oils and fats and therefore has only a limited effect in reducing the COD

Eng. (Dr.) S.L.J. Wijeyekoon, B.Sc. Eng. (Hons) (Moratuwa), M.Eng. (Tokyo), PhD (Tokyo), C. Eng., MIESL, Senior Lecturer in Environmental Engineering attached to the Department of Chemical and Process Engineering, University of Moratuwa. He is a consultant in the fields of Environmental Management, Cleaner Production and Sustainable Environmental Technologies.

Eng.(Miss) R.A.K.P.Abeysinghe, B.Sc. Eng. (Hons) (Moratuwa), AMIE(SL), Postgraduate student attached to the Division of Environmental Engineering, Department of Civil Engineering, University of Moratuwa.

U. Karunaratne, BSc (Kalaniya), MSc (Moratuwa), currently employed at Caterpillar Power Generation Systems LLC, Embilipitiya Power Plant.

Eng. (Dr.) M.W. Jayaweera B.Sc. Eng. (Hons). (Moratuwa), PhD. Saitama University, Japan, C. Eng., MIESL is a Senior Lecturer in Environmental Engineering at the Department of Civil Engineering, University of Moratuwa. He has considerable experience in environmental management and pollution control.

load from such wastewaters. Further, majority of the oil and grease sources are either small and medium scale industries or small service sector entities that are located in highly urbanized or residential areas releasing small quantities of wastewater that do not require an Environmental Protection Licence (EPL) to operate. They do not have the financial capability to invest in wastewater treatment plants (WWTP) nor have the technical capacity to operate and maintain WWTP and neither have space to locate treatment units. Therefore an efficient, cost effective, compact treatment unit that do not require pre or post treatment with simple maintenance requirements needs to be developed for treatment of wastewaters from such facilities. [21]

There are several methods currently practiced in many industries to remove oil and grease from wastewater. The most widely used methods for free oil separation are; API and CPI separators, three chamber pits with skimming, fat traps, dissolved air flotation, filtration and chemical coagulation. However conventional technology options for oil and grease removal are capital intensive, require larger foot print, are less efficient and need frequent operation and maintenance when considerable presence of emulsified oil is encountered.

In recent years, new and novel processes for efficient and adequate treatment of various industrial wastewaters with relatively low operating costs have been explored due to strict environmental regulations. Electrocoagulation (EC) process has attracted a great deal of attention lately in treating industrial wastewaters because of its versatility and low secondary environmental impact. This technique has certain advantages when compared to conventional methods such as simple equipment with no moving parts, ease of operation, less retention time and therefore small foot print, absence of external chemical addition with ancillary dosing equipment, rapid sedimentation of the electrogenerated flocs, less sludge production and safe operation due to the low voltage applied. EC could be used as an effective and reliable method for reducing or removing a large variety of pollutants in wastewaters. [16] Electro-coagulation has been proved to be an efficient treatment method for multitude of wastewaters. The technology has been successfully used to treat the wastewaters of textile [7, 30], oil wastewater [4, 6, 18, 27, 28], restaurant wastewater [8, 11] and slaughter house effluent [17, 19]. It is particularly more effective in treating wastewaters containing small and light suspended particles (e.g. oily wastewater) because of the accompanying electro-flotation effect. Moreover, and perhaps most importantly, during EC the liquid is not enriched with anions, and its salt content does not increase, as is the case with chemical treatment [21].

It is reported that the EC efficiency is generally high for oily wastewaters [3]. In most applications reported, aluminium or iron are used as electrode materials. EC has a long history as a wastewater treatment unit. However EC has never become accepted as a mainstream wastewater treatment technology. The lack of systematic approach to EC reactor operation and the issue of electrode reliability have limited its implementation. Nevertheless recent technological improvements combined with a growing need for small-scale decentralized wastewater treatment facilities have lead to re-evaluation of electro coagulation as an appropriate technology [12]. Due to the complex interaction of physical and electrochemical processes and to the conflicting and confusing process and design parameters reported, there is a compelling need for re-evaluation of the important parameters for rational elucidation of results and for design of EC cells prior to the industrial application.

A simple electrocoagulating reactor is made up of one anode and one cathode. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals [20].

The scope of this study was limited to laboratory scale, batch reactor operation for separating the effects of various process parameters such as electrode type, influent pH, initial oil concentration and current density on oil removal efficiency, to develop reactor cell design criteria for electrode surface area: reactor volume, electrode spacing and to determine the effect of electrode polarity switch on efficiency and electrode dissolution.

2. Materials and Methods

2.1 Effect of initial pH

The EC was carried out in a beaker of 40 mm diameter and 60 mm deep and having a capacity of 50 ml. Aluminium thin plate of size (0.23 x 10.75 x 77.00) mm was used as anode and cathode. The plates were washed with distilled water and then immersed to a depth of 32 mm in the prepared wastewater. The electrode distance was 26 mm. A variable voltage DC power supply was connected to the circuit consisting of an electrolyte, a precision type milliammeter, and an adjustable resistance in series and a voltmeter connected across the electrodes in the bath. Seven numbers of synthetic wastewater samples were used by adjusting the sample pH with either HCl or NaOH to a value of 2.33, 3.88, 3.90 6.28, 8.04, 10.12, 12.02 with an initial COD of 290 mg/L. The sample size was 40 ml with 30 minute electrolysis duration at the applied current density of 50.7 A /m^2.

2.2 Effect of initial concentration

The EC cell consisted of a glass beaker of diameter 127 mm and 180 mm depth having a capacity of 250 ml (Figure 1). Aluminium thin plates of size (0.60 x 21.20 x 90.00) mm were used as anode and cathode. The plates were washed with distilled water and then immersed to a depth of 50 mm in the synthetic wastewater. 0.185 g of NaCl was added into 200 ml of wastewater to improve the conductivity of the solution. The electrode distance was set at 20 mm. The circuit and electrolysis duration was as same as described in 2.1. Eight no of synthetic wastewater samples with initial COD of 66, 95, 104, 152, 238, 292, 333 and 419 mg/L were used with an applied current density of 100 A /m^2.

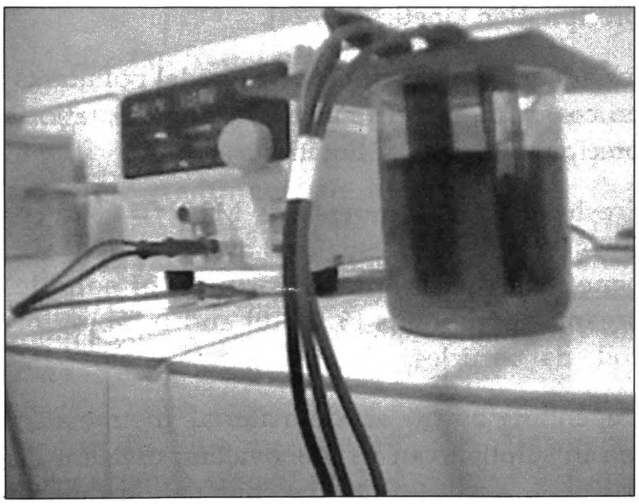

Figure 1. The electrocoagulation cell with variable DC power supply

2.3 Effect of current density

The EC cell configuration and the operation were as same as described in 2.2 above. The applied current through the 200 ml oily water solutions were 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0 amperes and samples were taken for analysis after 30 minutes of electrolysis.

2.4 Effect of electrode material

The EC cell circuit was as same as described in 2.2 above. Aluminium and carbon plates of size (5.15 x 22.56 x 93.00) mm were used as electrodes in combinations as given in Table 1 below. The plates were washed with distilled water and then immersed to a depth of 52 mm in wastewater collected from thermal power plant oily water separator outlet. 0.185 g of NaCl was added into 200 ml of sample to improve electrical conductivity. The electrode distance was 20 mm with 0.001 (A) current applied through the oily wastewater having an initial COD of 305.9 mg/l.

Table 1. Electrode material combinations used

Run #	Cathode	Anode
1	Aluminum	Aluminum
2	Aluminum	Carbon
3	Carbon	Aluminum
4	Carbon	Carbon

2.5 Effect of electrode polarity switching on COD removal efficiency

The EC cell was setup as above with aluminium thin plates as electrodes with 17 cm2 active area and reactor volume of 1000 ml. Initial pH, initial COD and initial conductivity of the synthetic wastewater were 7.25, 514.5 mg/L and 640 µS respectively. The electrode distance was 10mm. The applied current through the oily water solution was 0.2 (A) and the voltage was controlled at 30 V.

Electrocoagulation test runs were carried out by changing the electrode polarity during each 10 minute operation. Samples were taken at the end of each 20 minutes experimentation time

duration for COD analysis. A control experiment was also carried out without polarity change.

2.6 Effect of the variation of reactor volume to electrode surface area

Electrocoagulation test runs were carried out by changing the reactor volume for a fixed electrode surface area. Aluminium thin plates were used as anode and cathode with 25.4 cm^2 active area. Initial pH and initial conductivity of the synthetic wastewater were 6.65 and 640-700 µS respectively. The electrode distance was 10 mm. The applied current through the oily water solution was 0.2 (A) and voltage was controlled at 12 V.

2.7 Effect of electrode spacing on COD removal efficiency

Aluminium thin plates were used as anode and cathode with 25.4 cm2 active area. Initial pH and initial conductivity of the synthetic wastewater were 7.4 and 727 µS respectively. The reactor volume was 300 ml. The applied current through the oily water solution was 0.2 (A) and voltage was controlled at 12 V.

Electro-coagulation test runs were carried out by changing the electrode spacing in the range of 5 to 40 mm. The COD was tested in samples withdrawn at the end of each 20 minutes experimentation time duration.

2.8 Analytical procedures

The COD was analysed according to Standard Methods [1] by the reflux method. Initial samples were taken after homogenization of the added predetermined quantity of oil into the synthetic wastewater solutions. In instances where real wastewater was used, samples were homogenized to disrupt the phase separation by vigorous shaking prior to sampling for analysis. Samples for COD analysis after electrolysis were withdrawn by a pipet, by carefully avoiding the top surface oil film and the settled sludge at the bottom of the beaker. The pH of the solutions were adjusted either by 0.5M HCl or 1M NaOH and measured using a HANNA pH 211 microprocessor pH meter. The conductivity was measured by CON 510 bench conductivity meter made in Singapore.

2.9 Instrumentation used for the experimental setup

A regulated DC power supplier (Protek dual DC power supply 3015B) , that could operate in constant current (0 - 1.5A) or constant voltage (0-30V), was used to power the electro coagulation unit.

3. Results and Discussion

Oil and grease can be separated from wastewater by coagulation, flotation, gravity separation, membrane separation, absorption, adsorption, filtration and by the application of heat and/or chemicals for emulsion destabilization. In electrocoagulation, wastewater purification occurs primarily due to coagulation, flotation and generation of heat.

Main processes which occur during EC are as follows:

(a) Electrolytic reactions at electrode surfaces:

Anode:

$$M \longrightarrow M^{n+}_{(aq)} + ne \quad \text{.....} \quad (1)$$

Cathode:

$$nH_2O + ne \longrightarrow (n/2)\,H_2 + nOH^- \quad \text{.....} \quad (2)$$

where M is metal ion.

(b) The formation of coagulants in aqueous phase:

$M^{3+}_{(aq)}$ and OH- ions generated by electrode reactions (1) and (2) react to form various hydroxo monomeric and polymeric species, depending on pH range, which transform finally into $M(OH)_n$ according to complex precipitation kinetics [23, 24].

(c) Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation, precipitation and/or flotation:

Freshly formed amorphous $M(OH)_n$ "sweep flocs" have large surface areas which are beneficial for a rapid adsorption of soluble organic compounds [6, 8, 10] and trapping of colloidal particles.

Depending on the anode material, the metallic ion in solution can be monovalent, divalent or trivalent. According to the coagulation theory, the efficacy of coagulation increases and the

amount of coagulant (metallic cations) required decreases with the increasing valency of the metal ion in solution. The metal ion hydrolyses and forms complex metallic flocs that are responsible for adsorption of oil and sweeping of emulsified oil droplets from the wastewater. The simplified overall reactions can be represented as follows:

$$M^{+n}{}_{(aq)} + nH_2O \longrightarrow M(OH)_{n(aq)} + nH^{+}{}_{(aq)} \quad \text{(3)}$$

$$xM(OH)_{n(aq)} \longrightarrow M(OH)_n{}_{x\,(aq)} \quad \text{(4)}$$

The electrons released at the anode can electrolyse water and precipitate cations in solution. Electrolysis of water molecule at the cathode results in the evolving of hydrogen gas as shown in (2), that aid in the flotation of oil to the surface. The NaCl added to improve the conductivity of electrolyte can precipitate at the cathode as shown in equation (5).

$$Na^{+} + e^{-} \longrightarrow Na_{(s)} \quad \text{(5)}$$

The following half reactions at the anode that evolve oxygen and chlorine gas also aid in the electroflotation of oil.

$$2H_2O - 4e^{-} \longrightarrow O_{2(g)} + 4H^{+} \quad \text{(6)}$$

$$2Cl^{-} + 2e^{-} \longrightarrow Cl_{2\,(g)} \quad \text{(7)}$$

Further, the splitting of water at high applied voltage results in the heating up of the solution that also aid in the breaking of oil emulsions. However heating and water splitting is considered energy inefficient, and the low voltages applied in this study does not make this mechanism of oil removal a significant one. Once the emulsion is broken, the oil droplets can either coagulate or float to the surface and thereby be separated from the bulk solution.

3.1 Effect of initial pH

Coagulation and precipitation reactions are highly pH dependent and therefore need pre and post treatment pH adjustment as the reaction products also affect the final pH. The pH of the wastewater solution will not only affect the type of complexes formed but also the water splitting reaction as given in equation (6). The sacrificial electrodes may also be chemically attacked by H+ ions in acidic medium or by OH- ions in alkaline medium [11, 22]. However, when there is significant buffering of pH, the effect of pH on the electrochemical reactions is less pronounced.

The pH of the initial wastewater solution was varied in the range 2-12 by adding 1M NaOH or 0.5M HCl to investigate its effect on the COD removal efficiency. Figure 2 shows the removal efficiencies of COD as a function of the initial pH. At the extreme pH of 2 and 12, the COD removal efficiency is drastically decreased. Between pH of 4 and 10, decreasing removal efficiency is shown with increasing pH. Similar variation is reported in [19] for aluminium electrodes. The effect of pH on COD and oil and grease removal is negligible when iron electrodes are used [28]. If pH variation of the wastewater is significant or in the alkaline range, aluminium as an electrode material may not be a suitable option. However most industrial oily wastewaters lie in the pH range of 5.6-8.8 and therefore pre pH adjustments may not be required for most industrial wastewaters treated by EC.

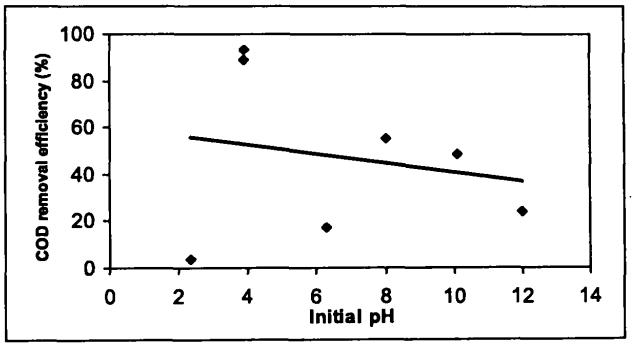

Figure 2: The effect of influent pH on COD removal efficiency

The EC reactions with aluminium electrode are similar to the chemical coagulation reactions using alum as the coagulant. Electrolytic dissolution of aluminium anode produce the Al^{+3} and Al(OH)3+ ions and complexes at low pH and finally $Aln(OH)_{3n}$ as shown in equation (1), (3) and (4).

The formed aluminium polymer will settle with pollutant oil particles by adsorption and charge neutralization. Both processes rely mainly on various aluminium intermediate products formed during hydrolysis of Al^{+3}. It has been reported that this is achieved at pH 5.0 -6.0 according to the following reactions [8]. At alkaline solution pH, the cathode and anode reactions respectively are:

$$Al_{(s)} + 4\,OH^{-} = [Al(OH)_4]^{-} + 3e^{-} \quad \text{(8)}$$

$$4OH^{-} - 4e^{-} = 2H_2O + O_{2(g)} \quad \text{(9)}$$

At acidic solution pH, the cathode and anode reactions respectively are:

$$2HO_3^+ + 2e = H_{2\,(g)} + 2H_2O \quad \text{..... (10)}$$

and anode reaction;

$$Al_{(s)} - 3e = Al^{3+}_{(aq)} \quad \text{..... (11)}$$

The decrease of COD removal at pH< 2 and > 12 was probably due to less Al $(OH)_3$ floc formation. The $Al(OH)_3$ gelatinous floc is thought to be responsible for the removal of soluble COD by adsorption. The optimum pH for alum coagulation lies between 5.5 and 6.5. At low pH, due to the hydrogen gas bubbling, enhanced removal is possible due to both coagulation and flotation mechanisms. A high COD removal efficiency of 93.1 % was obtained at pH 4 due to this dual effect. As the alkalinity and buffering capacity of each wastewater is different, when aluminium electrodes are used, a simple pH effect study would help determine the optimum pH range for the particular wastewater.

3.2. Effect of current density

Current density is one of the important parameters in EC as it is the driving force for pollutant separation. The current density affects the rate of electrode dissolution and power consumption which are directly related to the efficiency and economics of the process. As the efficiency and treatment costs are inversely related, optimum current density is dictated by the level of treatment required and the affordable cost of treatment desired.

Figure 3 represents the effect of current density on COD removal efficiency with a 30 minute operating time. The data exhibit significant scatter with greater than 90%. COD removal efficiencies at both low and high current densities applied. The best efficiencies were obtained (100% COD removal efficiency) for current densities of 46.9, 140.7, 187.5 and 468.9 A/m2 at the initial concentration of 122 - 292 mg/L used. This suggests that the smaller current densities applied are sufficient for the separation of the oil and the higher current densities used constitute a power wastage.

At high current densities, the temperature of the electrolytic solution increases as the resistance builds up due to ion migration and depletion. Further, the high rate of gas evolution at high

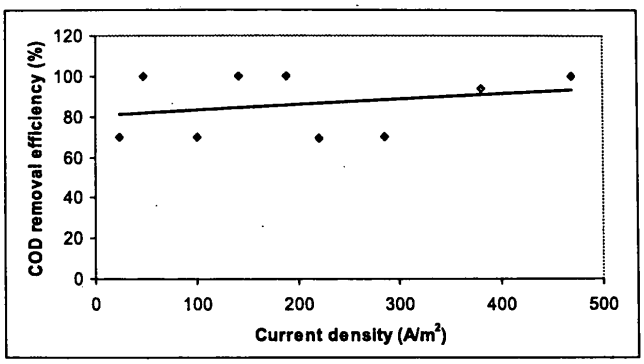

Figure 3: The effect of current density on COD removal efficiency

current densities disturbs the sedimentation and impedes settling of the flocs. With the cell configuration used, the optimal current density was 46.9 A/m² considering higher COD removal efficiency and low power consumption.

The current densities were changed from 23.4 A/m² to 468.9 A/m² which result in power consumption of 0.75 kWh/m3 to 15 kWh/m³. The electrical energy consumption increases nonlinearly with increasing current density due to strong impact of current density on cell voltage by means of various over potentials [19]. Kobaya et al (2005) also reported increasing removal efficiencies at higher current densities and concluded that 1 kWh/m³ is an economic power consumption with a current density of below 125 A/m². Xu and Zhu (2004) concluded that for the reactor configuration used, the optimum current density was in the range of 10 - 14 A/m² with a power consumption of 0.60 - 0.84 kWh/m³. It is clear that the current density and the power consumption are largely dependent on the cell configuration used and therefore improved cell configurations would further improve the efficiency and cost of treatment.

3.3. Effect of initial oil concentration

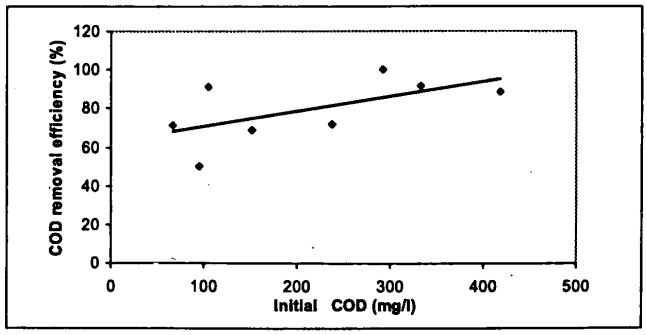

Figure 4: The effect of initial COD on COD removal efficiency

Oil concentration in industrial wastewater can vary from a few mg/L up to 5000 mg/L as COD. The concentration of oily wastewater from thermal power plants fluctuate between 66 mg/L to 1080 mg/L as COD and in most instances was found to be below 500 mg/L. No single technology would have the same efficiency of removal for such a wide range of oil concentration. Efficiency of removal is technology and initial concentration dependent. Very low initial concentrations are difficult to remove and hence efficiencies of removal are lower. On the other hand, high initial concentrations enhance separation depending on the driving force applied and will "underperform" when moderate concentrations are encountered.

Figure 4 shows the COD removal efficiencies at different initial COD concentrations when the current density was 46.9 A/m^2. Removal efficiencies above 50% were obtained with higher efficiencies at high concentrations. At higher concentrations the oil emulsion droplets are closely dispersed and therefore there is a high tendency and probability for the droplets to adsorb onto the $Al(OH)_3$ floc. At lower oil concentrations longer electrolysis time may improve the removal efficiency. The results show that an efficiency greater than 90% could be achieved when COD concentration above 300 mg/L.

3.4. Effect of electrode material

Different electrode materials and material combinations can be used for electrocoagulation of wastewater. Al - Al [7, 9, 15, 18], Al - Fe [5, 12, 17, 19, 29], Fe - Fe [13, 25, 28, 30] electrodes have been used for different type of wastewaters. Depending on the electrode material used, the cation responsible for coagulation, the effective pH of coagulation, the gas bubble size, the final quality of the water produced and the cost of electrode replacement and the chemical and electrochemical reactions involved are different and will affect the performance and economics of the process. Al and Fe electrodes are commonly used as aluminium and iron salts are used as common coagulants. However carbon electrodes have not been investigated as the coagulation properties of carbon are not known.

Table 2. Comparison of performance with different anode and cathode material combinations

Anode	Cathode	Initial COD (mg/L)	Final COD (mg/L)	COD Removal %
Al	Al	305.9	147.1	51.9
C	C	305.9	156.9	48.7
Al	C	305.9	147.1	51.9
C	Al	305.9	176.5	42.3

Table 2 presents the different combinations of anode and cathode material used and the COD removal efficiencies obtained at the initial COD concentration of 305 mg/L. Higher COD removal efficiencies were obtained when the anode material was Al, irrespective of the cathode material. Marginally lower efficiencies were obtained when carbon was used as the anode material. In all combinations, the pH change of the final solution was negligible from the initial pH of 7.7 to 7.4 - 7.6 range.

When Al is used as the anode material, the coagulant is generated from the sacrificial Al anode while H_2 is simultaneously evolved at the inert cathode. The Al^{3+} hydrolyses, with dynamic changes in the aqueous speciation of aluminium dictating both the coagulant availability and physical form. Initially the Al^{+3} contribute to charge neutralization of the pollutant particles as isoelectric point is attained. Here a sorption coagulation mechanism occurs resulting in the formation of loose aggregates. As time progresses, further Al^{+3} addition result in precipitation of amorphous $Al(OH)_3$ that contribute to pollutant aggregation via an enmeshment mechanism. The final stage is pollutant removal where the coagulant aggregates interact with bubbles and are floated to the surface or settle to the bottom of the reactor [12].

It is known that smaller the bubble size, higher the specific surface area and better is the separation efficiency of a flotation process. In addition, larger bubbles can disturb floc settling although it can help to a certain extent the collision frequency required for coagulation. The production of large bubbles in EC is associated with the structure of the electrode. The rougher electrode surfaces of carbon electrodes can provide larger adhering forces to bubbles and therefore produce bigger size bubbles than when using a smooth-surfaced Al electrode. However, formation of rough electrode surface is inevitable

due to dissolution of electrodes with continued use. The low COD removal efficiency of carbon electrodes can be attributed to the poor coagulation and flotation effect.

Although the efficiency of removal is marginally low for carbon electrodes, the amount of sludge generated is visibly less due to the absence of metal hydroxide flocs and formation of oxide films that retard removal efficiency is also absent. The separation is primarily due to the flotation and most of the oil remains as a layer on the water surface that could be easily separated. This uncontaminated oil could be used for a secondary purpose in other applications.

3.5 Effects of electrodes polarity switching

Passivation of electrodes due to prolong operation and oxide film formation on electrode surface reduce separation efficiency with use. Film formation retard electrode dissolution and therefore reduces coagulation. Such condition reduces the current efficiency of the electrocoagulation process. However conditions that favour or inhibit film formation on electrodes are yet unknown and more research is needed to resolve the above. Switching of polarity may help in prolongation of passivation of electrodes. The effect of electrodes polarity switching on COD removal efficiency is shown in Fig. 5.

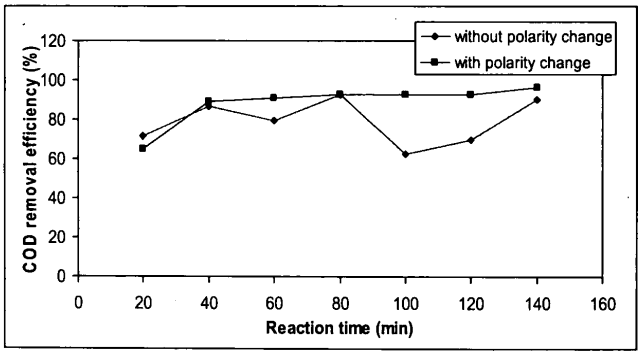

Figure 5: The effect of electrodes polarity switching on COD removal efficiency

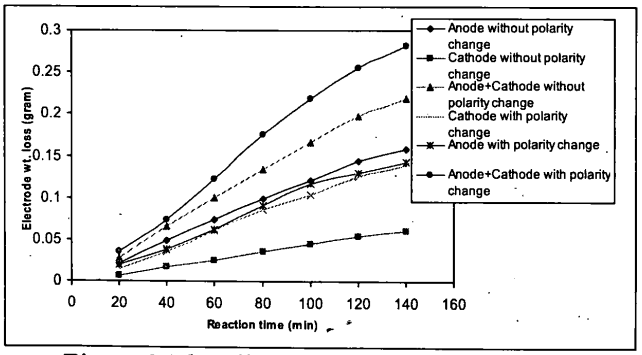

Figure 6: The effect of polarity switching on electrode dissolution

After 20 minutes of reaction time, 64.8% COD removal efficiency was achieved with polarity change and 71.7% COD removal efficiency was achieved without polarity change. However with extended operation, electrode polarity change had a consistently high removal efficiency achieving over 90%. The final difference in efficiency for the two modes of operation is marginal. Electrode weight loss data (Fig. 6) show the rapid anode dissolution compared to the cathode with conventional operation and almost equal rate of dissolution of electrodes when the polarity is switched periodically. The total electrode weight loss is higher in the polarity switching mode that partly explains the higher efficiency of the process. Passivation could be the other reason for slower electrode dissolution rate when operated in the conventional mode.

3.6 Effect of the variation of reactor volume to electrode surface area

A critical design parameter for EC is the ratio of reactor volume to the electrode surface area. The effect of the variation of reactor volume on COD removal efficiency is shown in Figure 7. The reactor volume was changed keeping the surface area of electrodes constant. When reactor volume was 300ml, the COD removal efficiency was highest and it was 100% for 25.4 cm2 effective electrode surface area. The highest COD removal efficiency was achieved for 8.5 m^2/m^3 of Surface area / reactor volume ratio which falls within the range reported in literature [12]. However, this parameter needs to be optimized for the reactor configuration and operating conditions used for a particular application.

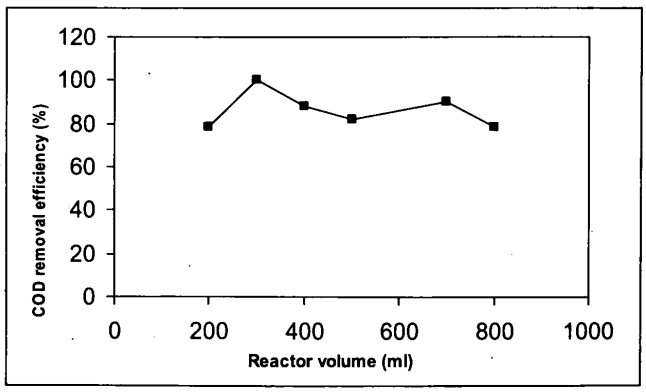

Figure 7: The effect of reactor volume on COD removal efficiency

3.7 Effect of electrode spacing

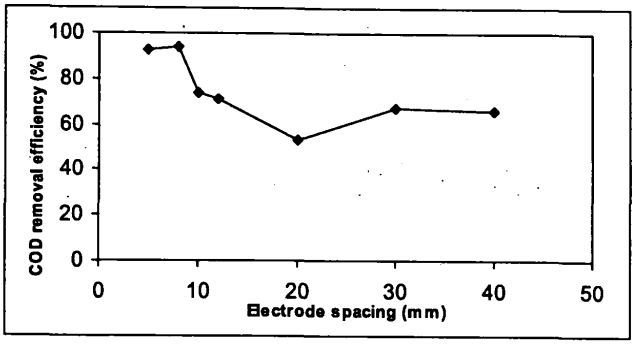

Figure 8: The effect of electrode spacing on COD removal efficiency

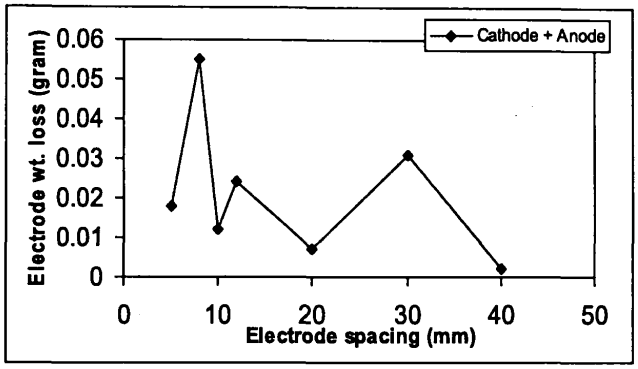

Figure 9: The effect of electrode spacing on weight loss in electrodes

Figure 8 represents the effect of the electrode spacing on COD removal efficiency. To explore the effect of the electrode spacing, the electrode surface area to volume ratio was kept constant at $8.5 m^2/m^3$.

Over 90% COD removal efficiency was attained when electrode spacing was less than 10 mm. Above 10 mm the efficiency dropped below 80 %. According to the results obtained here, the optimum electrode distance was 8 mm. This result is consistent with the observation made in [17] and [28]. The electrode weight loss data (Figure 9.) clearly show the higher rate of dissolution when spacing is 8mm and hence the resistance is low. The obtained results help in the design of electrocoagulation reactor cells for effective operation.

4. Conclusions

EC was found to be an effective method for the treatment of oily wastewaters. The effects of operational variables such as electrode type, influent pH, current density, initial oil concentration, and design variables such as electrode polarity change, electrode surface area: reactor volume and electrode spacing on performance were examined. A pH close to 4 is suitable when Al anodes are used and extremely acidic or basic pH is unsuitable for EC. Current density of 47 A/m2 is preferable for having a high COD removal efficiency in 30 minutes. High oil removal efficiencies are obtained for moderate oil concentrations of 300 - 500 mg/L as COD. The COD removal efficiency depends on anode material and the removal efficiency was high, when the aluminium electrode was used as anode. Higher COD removal efficiency was achieved with polarity change and COD removal efficiency was highest when surface area / reactor volume was 8.5 m2/m3 and at 8 mm electrode spacing. The developed design parameters enable the design of low cost compact treatment units that could be powered by DC sources for effective oil separation from wastewaters.

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References

1. American Public Health Association (APHA), Standard Methods for Examination of Water and Wastewater, 17th ed., Washington DC, 1992
2. Ebbing, Darel, Houghton, electro chemistry, 705-707
3. Ford, D., Technologies for removal of hydrocarbons from surface and groundwater sources, Oil *in Freshwater: Chemistry, Biology, Countermeasure Technology,* (edited by Vandermeulen, J.G. and S.E. Hruey), Pergamon Press. New York . pp. 413-430. 1978.
4. Ashraf Y. Hosny, Separating oil from oil-water emulsions by electroflotation technique, Separations Technology 6 (1996) 9-17
5. Baklan V. Y and Kolesnikova I. P. Influence of electrode material on the electrocoagulation. Journal of Aerosol Science, 27 (1996), 209-210
6. Calvo L.S., Leclerc J.P., Tanguy G., Cames M.C., Paternotte G., Valentin G., Rostan A., Lapicque F., An electrocoagulation unit for the purification of soluble oil wastes of high COD, Environ. Prog. 22 (2003) 57-65.

7. Can O.T. , Kobya M. , Demirbas E. , ayramoglu M. , Treatment of the textile wastewater by combined electrocoagulation, Chemosphere 62 (2006) 181-187

8. Chen X., Chen G., Yue P.L., Electrocoagulation and electroflotation of restaurant wastewater, J. Environ. Eng. 126 (2000) 858-863.

9. Chen X., Chen G. and Yue P. L. Investigation on the lectrolysis voltage of electrocoagulation. Chemical Engineering Science 57 (2002), 2449 - 2455.

10. Chen X., Chen G., Yue P.L., Novel electrode system for electroflotation of wastewater, Environ. Sci. Technol. 36 (2002) 778-783.

11. Chen X., Chen G., Yue P.L., Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65-76.

12. Holt P.K., Barton G.W., Mitchell C.A., The future for Electrocoagulation as localized water treatment technology, Chemosphere 59 (2005) 355-367

13. Irdemez S., Demircioglu N. and Yildiz Y. S. The effects of pH phosphate removal from wastewater by electrocoagulation with iron plate electrodes. Journal of Hazardous Materials B137 (2006), 1231 - 1235.

14. Jia-Qian Jiang, Nigel Graham, CecileAndre, Geoff Kelsall H., Nigel Brandon, Laboratory study of Electro-Coagulation-flotation for water treatment Water research 36 (2002) 4064-4078.

15. Khemis M., Leclerc J., Tanguly G., Valentin G. and Lapicque F. Treatment of industrial liquid wastes by electrocoagulation : Experimental investigations and an overall imnterpretation model. Chemical Engineering Science 61 (2006), 3602 - 3609.

16. Kobya M., Hiza H., Senturka E., Aydinera C., Demirbasb E., Treatment of potato chips manufacturing wastewater by electrocoagulation, Desalination 190 (2006) 201-211

17. Mahmut Bayramoglu, Mehmet Kobya, Murat Eyvaz , Elif Senturk, Technical and economic analysis of electrocoagulation for the treatment of poultry slaughterhouse wastewater, Separation and Purification Technology 51 (2006) 404-408

18. Manuel Carmona,, Mohamed Khemis, Jean-Pierre Leclerc, François Lapicque, A simple model to predict the removal of oil suspensions fromwater using the electrocoagulation technique, Chemical Engineering Science 61 (2006) 1237 - 1246

19. Mehmet Kobya, Elif Senturk, Mahmut Bayramoglu, Treatment of poultry slaughter-house wastewaters by electrocoagulation, Journal of Hazardous Materials B133 (2006) 172-176

20. Mollah M.Y.A, Morkovsky P., Gomes J.A.G, M. Kesmez, Parga J., Cocke D.L., Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B114 (2004) 199-210.

21. Mollah M.Y.A, Schennach R., Parga J.P., Cocke D.L, Electrocoagulation(EC)-science and applications, J. Hazard. Mater. B84 (2001) 29-41.

22. Picard T., Feuillade G.C., Mazet M. and Vandensteendam C., Cathodic dissolution in the Electrocoagulation process using Aluminium electrodes,The Royal Society of chemistry 2000 Vol2, 77 -80.

23. Pykhteev O.Y., Ofimov A.A., Moskvin L.N., Hydrolysis of iron(III) aqua complexes, Russ. J. Appl. Chem. 72 (1999) 9-20.

24. Rebhun M., Lurie M., Control of organic matter by coagulation and floc separation, Water Sci. Technol. 27 (1993) 1-20.

25. Sengil I. A. and Ozcar M. Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. Journal of Hazardous Materials (2006)

26. Shen F., Chen X., Gao P., Chen G., Electrochemical removal fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987- 993

27. Tezcan U., Una, U¢gur S., Koparal A.S. Electrocoagulation of olive mill wastewaters, Separation and Purification Technology (2006)

28. Xinhua Xu, Xiangfeng Zhu, Treatment of refectory oily waste water by Electrocoagulation process. Chemosphere 56 (2004) 889-894

29. Yousuf M., Mollah A., Schennach R., Parga J. R. and Cocke L. Electrocoagulation - science and applications. Journal of Hazardous Materials, B84 (2001), 29-41

30. Zaroual Z., Azzi M., Saib N., Chainet E., Contribution to the study of electrocoagulation mechanism in basic textile effluent, Journal of Hazardous Materials B131 (2006) 73-78

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