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Removal of oil and grease from automobile garage wastewater using electrocoagulation

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Abstract. Wastewater from automobile garages and workshops is an important contributor to the water pollution. Oil and grease is one of the major content of wastewater from vehicle garages. Wastewater from a public transport depot at Thrissur district in Kerala, India was collected for the study. A batch reactor has been devised to assess the efficacy of electrocoagulation in removing oil and grease from the wastewater. Aluminium and iron were tested as the anode material with stainless steel as cathode. Experiments were conducted to investigate the effect of various operating parameters such as current density, pH, time and salt concentration on oil and grease removal. The results shown that aluminium is superior to iron in removing the oil and grease from the wastewater. The reactor with aluminium as anode was able to remove 90.8 % of the oil and grease at a current density of 0.6 A/dm^2 in 15 minutes. The calculated specific energy consumption is also less for aluminium in comparison with iron.

1. Introduction

Environmental pollution is a potential threat to living conditions in the earth. Overpopulation has resulted in the larger utilization of natural resources which paved the way for the increase of pollution in the environment. The conservation of the natural sources such as air, water etc. is the responsibility of each human being for their next generations. Water conservation is one area which requires a significant attention. It is reported that in underdeveloped countries about 80% of the water used for irrigation contains pollutants to a level more than their limits [1]. In day to day life water is polluted in many ways. Industries are one of the major sources of water pollution. These include industries like oil and gas production units, oil refineries, edible oil industries, textile industries to name a few [2]. Industries pollute the water with different contaminants. Water from oil and gas industries, petroleum and petrochemical industries contains large amount of oil [3]. One of the major contributor of pollution from such industries is the oil and grease generated and used in their daily operations. Similarly the events like oil spills have affected the balance of an entire life in maritime fields. Kuwaiti oil fire was one of the instances of an oil spill that caused a discharge of 42 Billion US Gallons of oil to the sea; and affected the sea life adversely by contaminating the flora and fauna. Thus the impact of oil content in water is of high significance and separation of oil from water hence become highly important. Another important area where large quantity of oily wastewater generated is the automobile service stations. The automobile service stations use large amount of water for washing and maintenance activities. Thus the possibility of mixing of water and oil particles is unavoidable in the units. Water discharging from the automobile workshops and garages causes water pollution in

urban areas [4]. Water is consumed in large amounts (1000-25000 liters) in these service stations. Water treatment is unnoticed in most of these vehicle garages and workshop.

There are several methods available for oil removal from effluent, such as physical treatment, chemical treatment, biological treatment, membrane treatment etc. [3]. Physical treatment requires longer time, and has lower removal efficiency. Moreover they cannot remove colloidal and dissolved matters effectively. Chemical treatments include chemical precipitation, chemical oxidation, photo catalytic treatment, ozone treatment etc. These processes have widely used in industrial plants. But these methods need further treatment mechanisms for the removal of large amounts of sludge and require the help of trained operators. Biological treatments and membrane treatments also demand for skilled labor and overall efficiencies of treatment plants are also a cause of concern.

Electrocoagulation technique (EC) is one of the modern technologies in wastewater treatment. It is the combination of chemical and physical treatments [5]. It is an electrochemical method which applies the basic precepts of traditional water treatment methods, coagulation and flocculation [6]. In contrast to conventional coagulation method in which particles known as coagulants are added to aggregate the pollutant, EC uses electrodes to release coagulants. Electrocoagulation has been under research for removal of pollutants from wastewater. Electrocoagulation has the advantages like low sludge production, high process efficiency, and the effluent need no further treatment. The viability of electrocoagulation is being investigated in several studies which includes the treatment of wastewater including dairy, dye and textile, heavy metals containing wastewaters and wastewaters from the pulp and paper mill industry treatment [7-9]. Hence the possibility of electrocoagulation treatment for smaller water treatment units like automobile garages is investigated.

A method to treat the wastewater using electrocoagulation is proposed for the wastewater from vehicle garages. The used water from Kerala State Road Transport Corporation (KSRTC) Thrissur depot is taken for analysis. KSRTC depot Thrissur uses large quantities of water (5000 liters per day) and large quantity of oil contained wastewater is brought forth. Treatment of this wastewater has large scope because recycling and reuse of the same water can save large amounts of water.

The objective of the present research is to examine the feasibility of electrocoagulation in treating automobile garage wastewater and to determine the optimum operational conditions.

2. Mechanism of electro-coagulation

Electrocoagulation (EC) is a complex process involving many chemical and physical phenomena. It is carried out in an electrolytic cell/ reactor where a DC voltage is applied across the electrodes. The anode used is a sacrificial electrode, it provide ions into the wastewater stream to be treated. The ions which are the major contributor for coagulation are produced 'in situ' by the dissolution of anode. Broadly, the phenomenon of EC involves three successive stages: (i) electrolytic oxidation of the 'sacrificial electrode' and thus the formation of coagulants, (ii) destabilization of the contaminants and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs [10]. The coagulants remove the dissolved organic part by precipitation and suspended fines by adsorption and density separation.

In the present research two different anode materials were studied to investigate its capability in oil removal process. Mild steel and aluminium were the materials selected as the anode and stainless steel is used as the cathode. The electrochemical reactions with iron as the anode material are presented in the following equations [11]:

Anode:

$$Fe \rightarrow Fe^{3+} + 3e^- \qquad E^0 = -0.04\,V \tag{1}$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad E^0 = -0.44\,V \tag{2}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^0 = -0.77\,V \tag{3}$$

Cathode:

$$2H_3O + 2e^- \rightarrow H_2 + 2H_2O \qquad pH > 7 \qquad (4)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad pH > 7 \qquad (5)$$

Bulk:

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \quad pH > 7 \qquad (6)$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \qquad pH > 7 \qquad (7)$$

The generated Fe^{3+} (aq) ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides [12]. The metal hydroxide flocs formed can ensure the removal of the organic matter present in the solution predominantly by precipitation and/or adsorption mechanism and subsequent density separation. The hydrogen gas generated as a result of the cathode reaction can assist the flocculated particles to float to the surface. The monomeric forms of metal hydroxides can get polymerized giving various forms of ferric hydroxo complexes viz., $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_2^{4+}$, $Fe(OH)_4^-$, etc. The polyhydroxide complex ($Fe(OH)_n$) formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [13].

When aluminium is used as the electrode material the reactions are as follows:

Anode:

$$Al \rightarrow Al^{3+} + 3e^- \qquad (8)$$

Cathode:

$$3H_2O + 3e^- \rightarrow \frac{3}{2}H_2 + 3OH^- \qquad (9)$$

Bulk:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (10)$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n} \qquad (11)$$

The aluminium hydroxides formed in the above reactions are insoluble and will precipitate along with the suspended or colloidal matter present in the wastewater. All the other mechanism specified above *viz.* coagulation, adsorption, floatation etc. will contribute to the pollutant removal process.

The amount of metal ions (m_{metal}, g) generated can be calculated from Faraday's law (Eq. (12)). The current density (i, Am^{-2}) (Eq. (13)) can be calculated as the current in the EC cell (I, A) per effective anode area below the water surface (A_{eff}, m^2).

$$m_{metal} = \frac{ItM}{nF} \qquad (12)$$

$$i = \frac{I}{A_{eff}} \qquad (13)$$

Where t is the treatment time of the EC process (s), M the molar mass of the metal concerned (g mol^{-1}), n the number of electrons in the oxidation reaction and F Faraday's constant (96,500 C mol^{-1}). It has been experimentally observed that the generation of metal ions has been higher than the value calculated by Faraday's law. This phenomenon has been referred as superfaradaic efficiencies.

The method by which the Fe ion affects the impurities removal is generally explained in terms of two distinct mechanisms: one is the charge neutralization of negatively charged colloids by cations and the other is incorporation of impurities in the amorphous (mono and/or poly) hydroxide precipitate as sweep flocculation. Other contributing factors influencing the efficiency of the EC process are: electrode materials, current density and treatment time, composition of wastewater and the type of pollutants to be removed, conductivity, electrode gap, passivation of the anode, temperature, solution chemistry, etc.

3. Materials and methods

3.1. Wastewater Characteristics

The samples were collected from the workshop of the KSRTC Thrissur depot. Around 5000 litres of water per day is used for different purposes in the KSRTC workshop. The samples were analyzed for its chemical oxygen demand (COD) and oil & grease by fluorescence spectrometry. F-4660 FL, HITACHI Fluorescent spectrometer is used for the analysis. The fluorescence peak is held between 300-340 nm. The excitation wavelength of oil is 337 nm [14]. The other parameters estimated were given below.

Table 1. Wastewater characteristics.

Parameter	Values
COD	1450 mg/L
pH	6.5
Fluorescence analysis for oil	1260 mg/L
Total Solids	363 mg/L
Total Dissolved solids	225 mg/L
Total Suspended Solids	138 mg/L
Density	981g/cm^3

3.2. Electrocoagulation Set Up

Experimental set up for electrocoagulation is shown in figure 1. A reactor with a capacity of 2 litres and having dimensions 20cm×10cm×10cm was selected. The reactor was made of plastic. Two different anodes were used for the study *viz.* mild steel and aluminium. The cathode was made up of
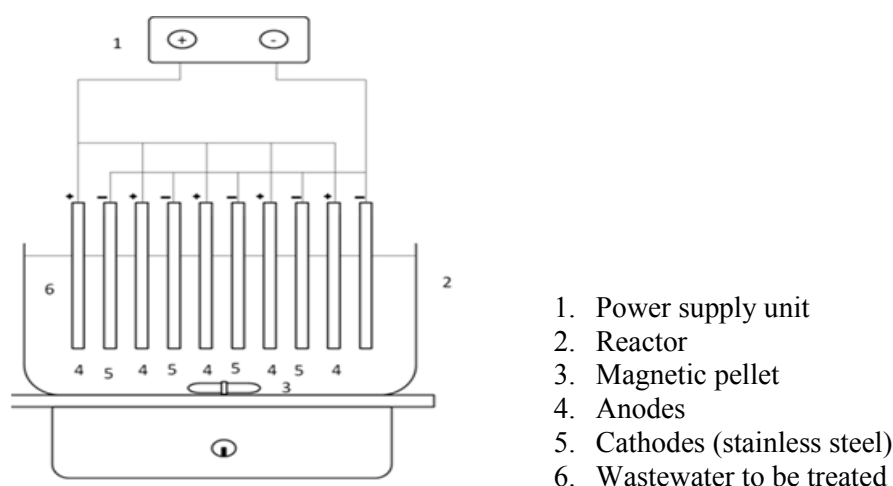

1. Power supply unit
2. Reactor
3. Magnetic pellet
4. Anodes
5. Cathodes (stainless steel)
6. Wastewater to be treated

Figure 1. Schematic of EC reactor

stainless steel and are aligned vertically and parallel to each other with an inter electrode gap of 1 cm. Five pairs of electrodes, of active area (8 cm×4 cm) 40cm^2 each, were used. The electrode plates were cleaned manually by abrasion with sand paper and by the treatment with 10 % hydrochloric acid followed by washing with distilled water prior to every run. All experiments were performed at a room temperature of 30 °C.

Total electrode area for 10 electrodes was 400 cm^2. Number of electrodes were selected and arranged with minimum gap with the objective for efficient EC operation. A DC power supply was used to provide current and potential across the electrodes. APLABS regulated DC power supply was used for the purpose. The input voltage specification was 0-230 V AC, and output voltage was 0-30 V DC .The current output of the power supply specified at 2 A. The power supply had short circuit protection which helped in protecting it from probable contacts with electrodes. A magnetic stirrer was provided in the reactor with varying rotational speeds.

4. Results and discussions

4.1. Calibration of Fluorescence Spectrometry

Fluorescence spectrometer was used for finding the oil content from the fluorescence values of different emission wavelengths. The excitation wavelength of oil is found to be 337 nm. Fluorescence spectrometer generates the spectrum. The emission wavelength is given in the range of 300-500nm. Figure 2 shows the fluorescence emission spectra obtained for a sample.
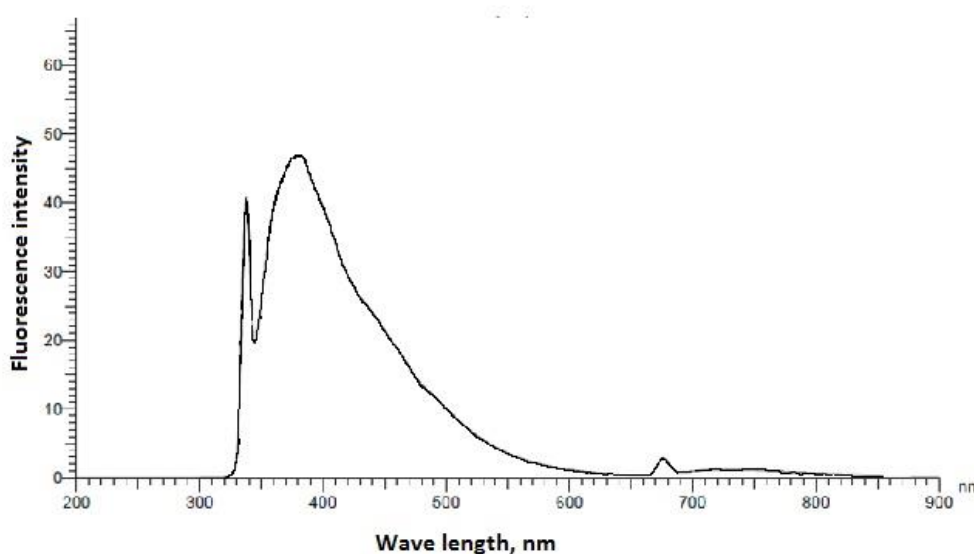

Figure 2. Fluorescence emission spectrum for oil in water emulsion

Fluorescence was calibrated in terms of concentration, ppm. The calibration was done with known concentrations. The calibration curve is shown in figure 3.
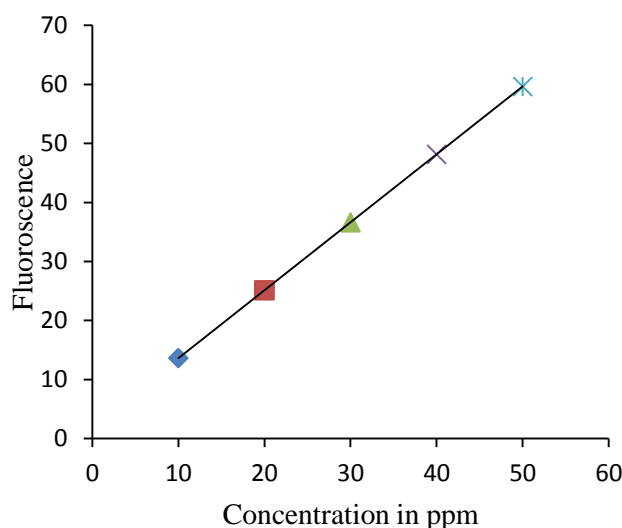
Figure 3. Calibration curve for fluorescence analysis

4.2. Effect of current density on electrocoagulation

Current density is one parameter which can be varied externally .The term current density is the current loaded per unit area. It was observed that there was a direct relationship between current density and the percentage oil removal. The oil removal increases with respect to an increase in the current density. Figure 4 shown below gives the effect of current density on percentage oil removal for the EC using Al electrode and Fe electrode. This is very much in accordance with the Faraday's law of electrolysis. It is evident from equation (12) that the release of anode material in an electrochemical process is directly proportional to the current density.

The consumption of electrode material with the current density were calculated. This is again strongly influenced by operating conditions and wastewater characteristics. Figure 5 shows the influence of current density on the amount of anode material released. As clearly indicated by equation (12) there exists a linear relationship between the current density and the amount of anode material released. Since the equivalent weight of iron is greater than the equivalent weight of aluminium, as per
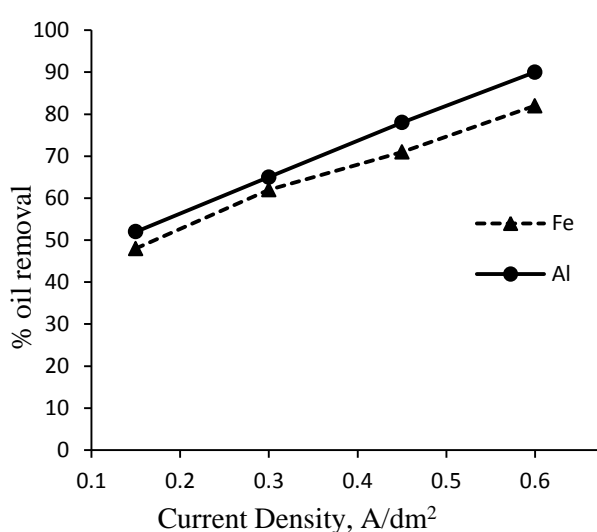

Figure 4. Effect of current density on oil removal (pH 7.5 and EC time 15 min).
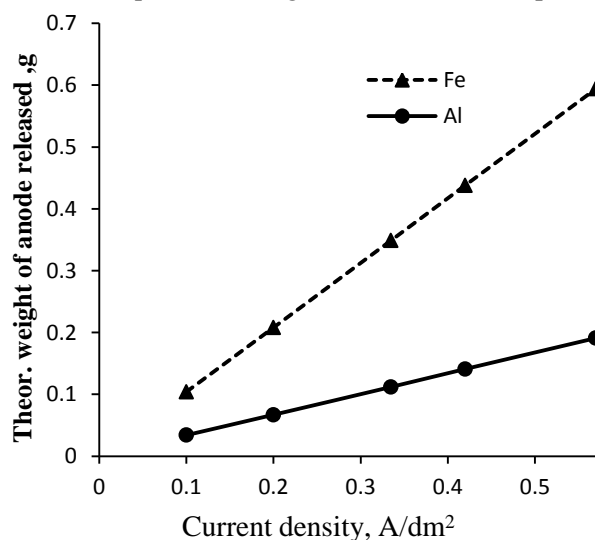
Figure 5. Theoretical weight of anode material released with current density (pH 7.5 and EC time 15 min).

Faradays law the weight of the anode material released is more for iron than aluminium for the same amount of charge passed. In few cases the actual electrode material consumption went beyond the theoretical value, a phenomenon reported as superfaradic efficiency.

4.3. Effect of pH on electrocoagulation

Initial pH has significant role in the performance of electrochemical process [15]. Its effect has been examined by adjusting the pH of the wastewater to the desired value for each experiment by using sodium hydroxide or sulphuric acid. Figure 6 depicts the influence of wastewater pH in percentage oil removal. Oil removal was observed to be varying between pH from 4 to 10. In both cases the maximum removal was observed at near neutral pH.
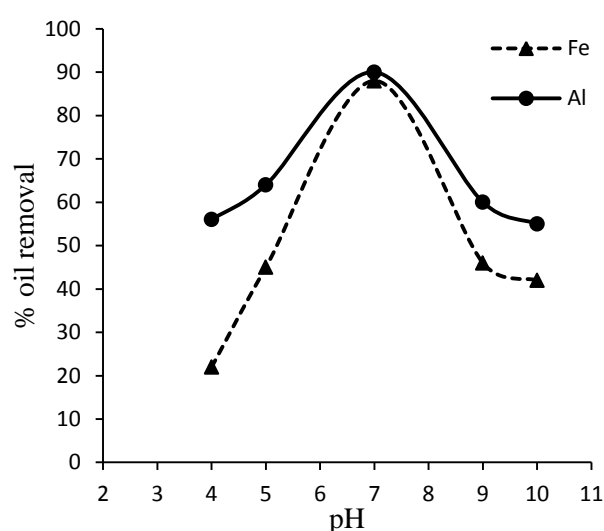

Figure 6. Effect of influent pH on oil removal (current density 0.57 A/dm^2 and EC time 15 min).
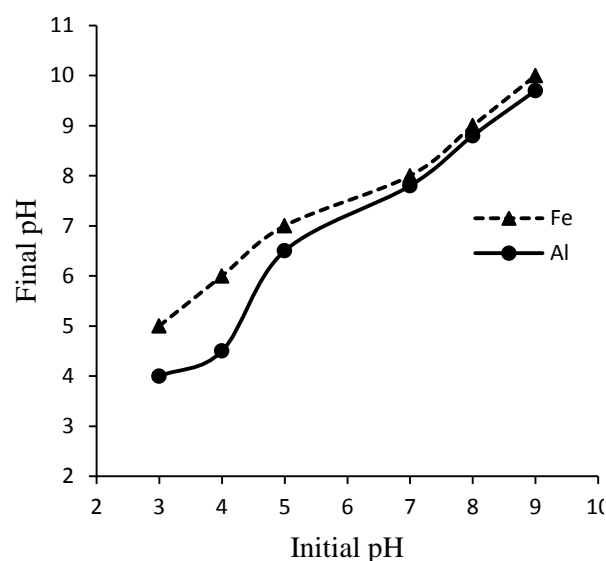
Figure 7. pH change after electrocoagulation (current density 0.57 A/dm^2 and EC time 15 min).

Such a radical change in the percentage removal for different pH may be due to the different chemical reactions happening inside the EC reactor for different pH's. Compounds like $Fe(OH)_2$, $Fe(OH)_3$, etc in the case of mild steel electrode and $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_2^{4+}$, $Al(OH)_3$ etc. in the case of aluminium electrodes were reported to be formed at different pH ranges [16]. The removal efficiencies remained much unchanged at pH less than 4 and more than 10.

This is because compounds like $Al(OH)^{4-}$ is forming at higher H. It shows amphoteric behavior so that less adsorption of pollutant occurs. At lower pH generation of Al^{3+} is more which also reduces the efficiency. Intial pH is an important parameter for EC using mild steel electrodes also. The reactions of mild steel electrodes were different at different pH values. More hydroxide formation can be explained as a reason for higher removal efficiencies around pH 7.The solubility of pollutants were less at neutral pH which aided in the adsorption at coagulant surfaces.

The final pH of the wastewater sample was found to increase during the EC process. When the initial influent pH was low this increase was found marginal. Towards the higher influent pH there was not much increase in the effluent pH. The results are shown in Fig. 7. The increase in pH may be due to the release of OH$^-$ ion during the production of hydrogen gas at cathode.In addition, if some anions such as, Cl^-, SO_4^{2-}, $HSiO_4^-$, NO_3^- are present in the influent wastewater then they can exchange the OH$^-$ ions in $Al(OH)_3$ to release OH$^-$ and this will result in pH increase.

The reduction in pH change at high influent pH is attributed to the reaction of Al(OH)$_3$ with OH$^-$ ions at very high pH to form Al(OH)$_4^-$, leading to a reduction in pH. Moreover oxygen evolution reaction also leads to pH increase.

4.4. Effect of salt concentration on EC
Electrochemical processes depends on the conductivity of the electrolyte. Hence NaCl was added to the influent wastewater to improve its conductivity. By increasing NaCl concentration the conductivity was increased and this in turn increased the current passing through the electrochemical cell and thereby increasing the current density. The effect on percentage removal for different NaCl concentrations is shown in figure 8.
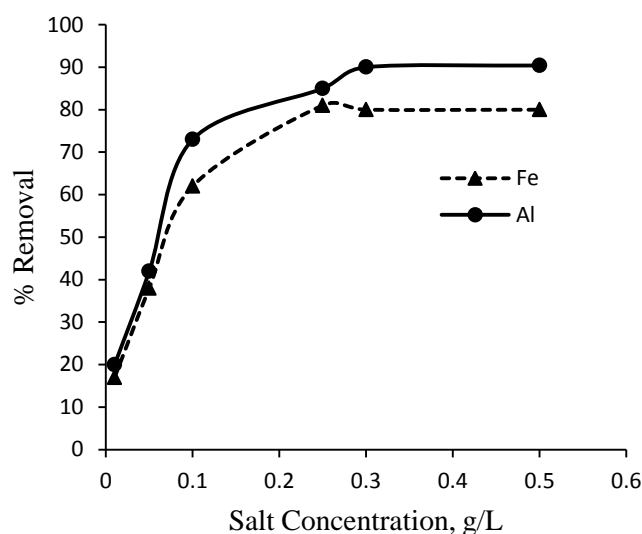

Figure 8. Effect of salt concentration on oil removal (current density 0.57 A/dm^2 and EC time 15 min).

The oil removal was increased as the salt concentration increased and reached the maximum removal of 81% for mild steel electrode at around a salt concentration of 0.25 g/L and 90.4% for the aluminium electrode at around a salt concentration of 0.3 g/L. Addition of NaCl has additional advantages along with increase in conductivity that the chloride ions can aid disinfection of the wastewater.

4.5. Effect of time on oil removal by EC
The time given for EC is an important parameter which influences the oil removal. The influence of time is examined by conducting the experiments for different times starting from 3 minutes to 20 minutes, keeping the other parameters fixed at the following values *viz.* current density 0.5 A/dm^2, salt composition 0.5 g/L, and initial pH 7. The results obtained are shown in figure 9. After 15 minutes it was observed that the percentage removal was attaining a maximum around 90% for the aluminium electrode and 85% for the mild steel electrode.

In the EC process the anode materials produces metal ions during electrolysis. As discussed earlier this metal ions are the primary motive for the destabilization and the resulting removal of the colloidal matter present in the wastewater. If the time provided for the EC was low then the metal ion dosage was not enough to destabilize the colloidal matter and hence resulted in low percentage oil removal. Furthermore the higher value of percentage removal was attributed to the overall progression of electrolytic process comprising electro coagulation, electrolytic oxidation and the floatation.
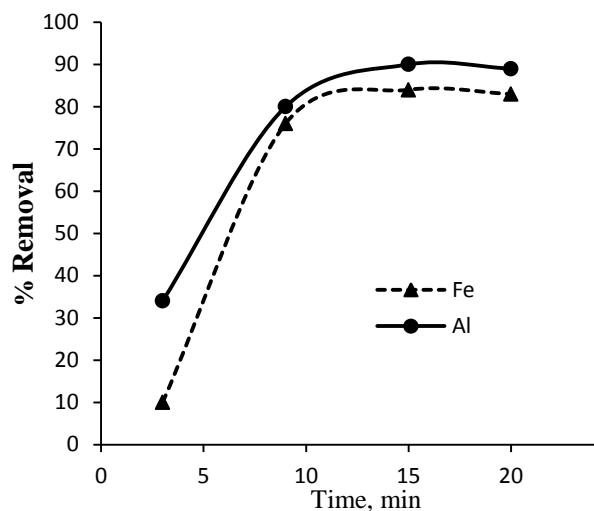
Figure 9. Effect of time on oil removal (current density 0.57 A/dm^2 and pH 7.5).
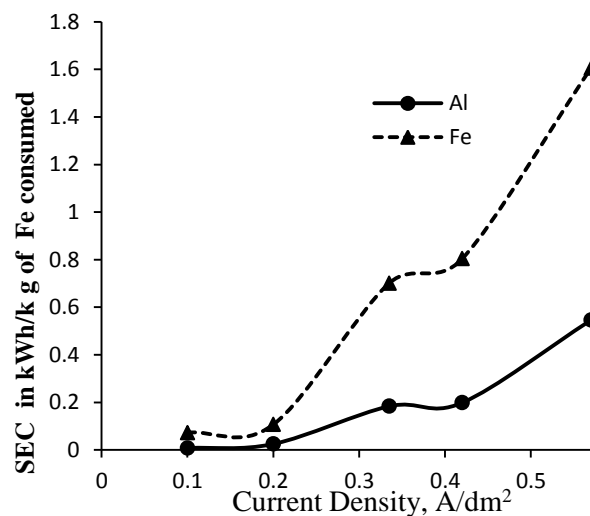
Figure 10. Effect of current density in SEC.

4.6. Specific Energy Consumption (SEC)

The study can be made more meaningful by estimating the energy consumptions for the process. This was examined in detail by estimating the specific energy consumption (SEC) based on the amount of anode dissolved (SEC in kWh/(kg of Fe), using the following equation:

$$\text{Specific Energy Consumption} = \frac{\text{Energy Consumed}}{\text{kg of Fe consumed}} \tag{14}$$

The figure 10 shows the SEC calculated against different current densities. It is evident from the figure that the SEC for the EC process is fairly less for aluminium anode in comparison with iron anode for the same current density. This information can be very much useful in making decisions on the selection of anode material for EC.

5. Conclusions

The viability of EC process for the removal of oil and grease from an automobile garage was investigated. The experiments were done with two different anode materials *viz.* mild steel and aluminium. In both cases stainless steel was used as the cathode. The influence of various operating parameters such as current density, pH, salt concentration and time were examined. Effective removal of the oil and grease from the wastewater were observed during the study. Compared to mild steel anode aluminium anode has given better removal. The optimum operating conditions for the given EC system with aluminium anode were estimated as current density 0.6 A/dm^2, pH 7, EC time 15 min and a salt composition of 0.3 g/L. The same for the EC system with mild steel anode were current density 0.57 A/dm^2, pH 7, EC time 17 min and a salt composition of 0.25 g/L. The calculated SEC is also in favour of EC with aluminium anode as its SEC is far below than that of iron anode. Based on the results obtained from the present experiments it may be concluded that EC with aluminium anode and stainless steel cathode may be considered as a good treatment option for treating automobile garage wastewater. Also among these two anode materials used aluminium stands superior to iron in performance.

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