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Oil field effluent water treatment for safe disposal by electroflotation

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Abstract

The separation of finely dispersed oil from oil–water emulsion was carried out in an electroflotation cell which has a set of perforated aluminium electrodes. The effect of operating parameters on the performance of batch cell were examined. The parameters investigated are pH, voltage, oil concentration, flotation time, and salinity. The batch experiments have been conducted to optimize electrical input in the effluent. It was observed that at 5.0 V and 0.4 A current is optimum and for this condition the energy consumption was 0.67 kWh/m^3. The optimal treatment time was observed at 20 min. Also oil removal efficiency is 90% at 4.72 pH in 30 min treatment time for 50 mg/l concentration of oil and 94.44% of oil removed within 30 min at 4 mg/l of salinity. It has also been observed that decrease in salinity and increase in oil content of the effluent enhances the efficiency of the electroflotation process.

Keywords: Oil separation; Effluent water treatment; Electroflotation

1. Introduction

Large quantity of effluent is produced during the exploitation of an oil field which is separated at process platform. When oil is produced from water drive reservoirs, oil saturation decreases slowly and water saturation increases. As a result more water is produced along with the oil. Water coning and water channeling also contributes to the increased water production. This oil field water usually contains high concentration of oil, salinity, suspended solids and total dissolved solids.

Major pollutant in oilfield waste water is oil which may range between 100 and 1000 mg/l or still higher depending on the efficiency of demulsification and nature of crude oil. Crude oils are a complex mixture of a large number of hydrocarbons which vary in their toxicity to aquatic and terrestrial life. A few of them are even carcinogenic. Oilfield water also contains suspended solids which include: clay, sand, scale corrosion product likes iron sulphide, iron oxide, bacteria and oil. This waste water can not be disposed off as such by inland or subsurface disposal methods as it will contaminate fresh water resources resulting in ecological imbalance and water pollution hazards. Therefore, it is desirable to treat the effluent suitably prior to inland or subsurface disposal. Produced oil field waters are usually disposed of by re-injection into a disposal well or injection well for water flooding.

Oil in water forms the emulsion. Emulsions are suspensions of droplets, greater than 0.1 μm, consisting of two completely immiscible liquids, one of which is dispersed throughout the other. Emulsions are frequently quite persistent in the environment and resist their decomposition in to their original constituents of oil and water. According to existence of oil in water emulsions are divided in to four categories which are as follows in Table 1. Also, according to stability of emulsion, it can be classified as: unstable, stable, meso stable. The stability of an emulsion is also influenced by its physical and electrical properties [1].

Oils discharged into the water bodies/on soils cause adverse impact. It also affects on industries and water treatment process. Table 2 gives effects of oil discharged effluents [2]. Due to these hazards, oil field effluent treatment must treat before dispose. Treatment of these effluents may result in improved oil/water separation, improved water quality, oil recovery, water reuse, protection of downstream facilities and environmental permit compliance. There are three types of basis treatments for oil–water emulsion (Table 3) [3]. The separation in two phases (water and oil) follows three stages: droplets migrate to the interface between the oil and water bulk phases; at

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Table 1
Emulsion types according to existence of oil in water

Free oil	Mechanically emulsified oil	Chemically emulsified oil	Dissolved oil
Non-miscible with water, rapidly rises to water surfaces. Forming a film or large droplets.	Present in water due to high shear (passing through pump) stabilized by electrical charges.	Miscible with water, stabilized by surfactants, having hydrophobic and oleofilic end.	Water-soluble oil, water is translucent and transparent. Removal by filtration, gravity settling is impossible.
!50 μm	20–150 μm	<20 μm	<5 μm
Macro emulsion	Micro emulsion	Micro emulsion	Mini emulsion

Table 2
Effect of oil-discharged effluents

Effect on environment	Effect on human health	Effect on Industries and water treatment process
(1) Free oil hinders the penetration of sunlight in river water distracting aquatic life and restricts natural cleansing of water in rivers or lakes.	(1) Consumption of untreated chemically emulsified oil disposed in river causes several health problems including cancer.	(1) In steam generation and cooling process, oil contaminated water causes foaming, priming, over heating of tubes, which leads to poor heat transfer from metal to water.
(2) Undesirable odour from oily waste is a nuisance.	(2) Bathing in contaminated oily water causes skin cancer.	(2) Free and emulsified oil can clog and coat the filters and ion exchange beds, decreases effectiveness of filtration and interface with backwashing.
(3) Oily waste may coat the gills of fish and stop the oxygen transfer makes fatal for them.	(3) Fish affected by toxic oils, if consumes can cause nausea and vomiting.	(3) In biological treatment of wastewater a layer of oil adheres to the microorganism creating additional resistances to oxygen and nutrient transfer to biomass and reduces the treatment efficiency.
(4) Untreated oily waste forms a layer on the banks of river causes spoiling of vegetation present on bank.		

the interface droplets coalesce and are taken up into the bulk oil phases; the separated oil is removed from the water surface.

Many techniques are available, including a variety of filters [4], chemical dosing, and reverse osmosis, gravity separation, ultra-filtration [5], micro-filtration [6], biological process [6], air flotation [7,8], membrane bioreactor [9], carbon adsorption, chemical coagulation, electrocoagulation, electroflotation [10], etc., for separation of oil–water emulsions. The advantages and disadvantages of these processes are summarized in Table 4.

Electroflotation is a simple process that floats pollutants to the surface of a water body by tiny bubbles electrolysis. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. The electroflotation technique depends upon generation of hydrogen and oxygen gases during electrolysis of water. Gas bubbles formed on electrode surface contact with oil drops; then the attached oil–gas combinations rise up to the surface where oil may be removed by any skimming method.

Electroflotation technique has three principal advantages. First, dispersed gas bubbles formed from electrolysis are extremely fine and uniform (with average bubble diameter around 20 μm). Second, varying current density gives the possibility of varying any gas bubble concentrations in the flotation medium, thereby increasing the probabilities of bubble-oil drop collision. Third, selection of appropriate electrode surface and solution conditions permits one to obtain optimum results for a specified separation process [11].

Ho and Chan [10] studied the electroflotation of palm oil mill effluent (POME) using lead dioxide-coated titanium anode on a laboratory scale. The feasibility of the process was determined by monitoring the effluent quality as a function of electrolysis time. About 40% of the COD of the dissolved substances of POME could be anodically destroyed together with 86% of sus-

Table 3
Treatment types of oil–water emulsions (Cheremissionoff and Tabakin [3])

Primary treatment	Secondary treatment	Tertiary treatment
Separation of floatable free oil from dispersed emulsified and soluble fractions, oil wet solids. Utilize sedimentation, flotation and centrifuge related technique.	Breaking of oil water emulsion to remove dispersed oil. Utilizes chemical treatment and filter coalescence or other techniques.	Removal of finely dispersed soluble oil fractions. Utilizes ultrafiltration, biological treatment and carbon adsorption or other techniques.

Table 4
Summary of oil removal processes

Process	Advantages	Disadvantages
Gravity separator		
• API	Economical and simple operation	Limited efficiency
• Corrugated plate separator		Susceptible to warmer conditions
Air flotation		
• Dissolved air flotation	Handles high solids shock loads	Sludge disposal problem when coagulant is used
• Induced air flotation		Requires chemicals
Filtration	Handles high solids	Requires back washing
Chemical coagulation, flotation and sedimentation	Handles high solids concentration in suspensions, also oil droplets	Excessive chemical sludge produced, costly
Membrane process (ultrafiltration)	Soluble oil removal	Low flux rates, membranes fouling and membrane life reduced
Biological treatment	Remove soluble oils, high tolerance for oil and grease	Pre treatment requires
Carbon adsorption	Removes soluble and free oils, high efficiency	Regeneration requirement, expensive treatment
Electrocoagulation	Removes soluble oils, BOD and COD, high efficiency, low cost	Replacement of aluminum or iron electrode
Electrocoflotation	Removes soluble oils, high efficiency, low cost, no secondary sludge disposal problem	Replacement of aluminum or iron electrode

pended particles, made up of mainly plant cell debris, floated off.

Honsy [11] carried out experiments for the separation of oil from oil–water emulsion by electroflotation technique. A lead anode and stainless steel screen cathode were used for the separation of finely dispersed oil from oil–water emulsion in an electroflotation cell and examined the effect of operating parameters on the performance of batch cell. The parameters investigated were electrical current, oil concentration, flotation time and flocculant agent concentrations. A well-fitted empirical correlation represents the change in percentage oil removal with wide range of operating conditions was presented. The oil separation reached 65% at optimum conditions; 75% in the presence of NaCl (3.5 wt.% solution); and 92% with the presence of NaCl and at optimum concentration of flocculant agent. Electrical energy consumption varied from 0.5 to 10.6 kWh/m^3 according to experimental conditions.

The effect of change in diameters of hydrogen and oxygen gas bubbles on the recovery of quartz fines in electroflotation were studied [12]. A change in electrode surface geometry and current density changes the bubbles diameters as well as bubble flux thereby affecting flotation recoveries was observed.

Mansour and Chalbi [13] separated dispersed oil from oil–water emulsions in an electroflotation cell equipped with insoluble electrodes: titanium coated with ruthenium oxide as anode and stainless steel screen as cathode. The effect of operating parameters such as current density, oil concentration, flotation time and coagulant concentration, on the performance of the electroflotation cell was examined. Oil removal reached 70% at optimum conditions; 75% in the presence of NaCl (3.5 wt.%); and 99.5% in the presence of both NaCl and an optimum concentration of coagulant. Electrical energy consumption varied from 0.4 to 1.6 kWh/m^3 according to experimental conditions. The performance of the oil removal process was also represented by a first order kinetic rate model.

Mostefa and Tir [14] studied flocculation coupled with electroflotation for waste oil/water emulsion treatment. The effects of operating conditions on the performance of the coupling of flocculation with electroflotation were studied by measuring chemical oxygen demand, turbidity and conductivity. The efficiency of oil separation reached 99% for a concentrated emulsion of 4 wt.% at optimum conditions.

Ibrahim et al. [15] studied the removal of finely dispersed oil from oil–water emulsions of different Egyptian oil crudes by either batchwise or continuous processes. The effect of various operating and design parameters was studied. The recommended conditions for operating batch runs were as follows: current density from 5 to 20 mA/cm^2, pH 6, and temperature from 30 to 40 °C. According to the data obtained from continuous runs, at almost complete separation of oil, the minimum power consumption was 0.08 kWh/m^3 of a 200 mg/l emulsion flowed at 300 ml/min.

Marcos et al. [16] investigated the application of electrochemical technology, employing a dimensionally stable anode (DSA), for the remediation of wastewater from the oil extraction industry. Samples from the oil–water separation box of an effluent treatment plant were used to voltammetry, chronoamperometry and electrolysis studies using a DSA anode.

From the available literature, it was found that the effect of several operating and system parameters on the electroflotation efficiency and thereby the removal of oil from the oil–water effluent has not been studied in detail. In view of this, it was though desirable to study the electroflotation for the removal of oil from the oil–water effluent. In the present paper, the experiments have been carried out for the removal of oil from oil–water effluent using electroflotation technique in batch and flow systems. Also

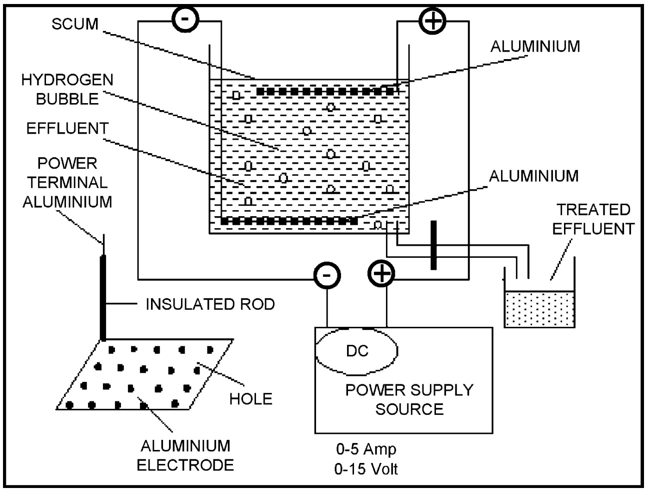

Fig. 1. Schematic diagram of the laboratory scale batch electroflotation system.

the effect of operating and system parameters such as: pH, oil concentration, voltage, flotation time and salinity on oil removal from oil–water effluent using electroflotation have been studied.

2. Experimental details

Direct current electrofloatation technique was used for crude oil removal from oil field effluent water. Electrolysis was conducted in a batch system to investigate the effect of such factors as concentration, pH, voltage, salinity, flotation time, etc.

2.1. Experimental set-up

A rectangular cross section vessel (200 mm × 85 mm × 120 mm) of volume, 2.04×10^{-3} m^3 was used for electrofloatation. The vessel was fabricated from transparent perplexes material sheets of 5 mm thickness. Aluminum plates (150 mm × 72 mm × 2 mm thick) perforated uniformly with 2 mm drill bit to facilitate passage for upward movement of the oil droplets to the surface were used as the electrodes. The electrodes were fully submerged with 15 mm spacing. A regulated DC power supply 15 V/5 A was used to apply potential between the anodes and cathodes. A experimental set-up is shown in Fig. 1. In the present arrangement of the electrodes (anode at bottom and cathode at top), effective flotation was obtained because of quick dispersion of the small bubbles generated into the wastewater flow. Quick bubble dispersion is essential as important as the generation of tiny bubbles. When the anode and the cathode are leveled, such an open configuration allows both the anode and the cathode to contact the wastewater flow directly. Therefore, the bubbles generated at both electrodes can be dispersed into wastewater rapidly and attach onto the flocs effectively, ensuring high flotation efficiency.

2.2. Wastewater sample

Crude oil was supplied by Oil and Natural Gas Corporation (ONGC), INDIA. It was used without any treatment to prepare oil–water emulsion (wastewater) of different oil concentration by mixing with the distilled water. Few specifications of the crude oil used are available such as: total sulfur = 0.33 wt.%, pour point = 30 °C, density = 819.4 kg/m^3 at 30 °C, viscosity = 3.04 cStoke at 30 °C and Reid vapour pressure = 100.6 kPa.

2.3. Experimental method

Crude oil was mixed with the distilled water and stirred for 24 h. The mixture showed a uniform yellowish color. During preparation of emulsion, emulsion was left for 30 min to see any separation and it was stable. The pH of the oil–water emulsion was measured with a digital pH meter. The pH of the resulting base emulsion was 6.65. For lowering the pH of the effluent dilute H_2SO_4 and for increasing the pH dilute NaOH were used. Vessel was filled with the crude oil–water emulsion. Electrodes were submerged and the current was passed by the regulated DC power supply. Voltage and current were maintained at a fixed value with the help of knob. Samples of 10 ml of oil–water emulsion were withdrawn from the vessel from a depth of 50 mm below the free surface of oil–water emulsion at regular time intervals. After electrolysis the sludge at the top of the vessel is skimmed off. A sample of the supernatant was used for the determination of the residual oil concentration, using CCl_4 as an extractant. If the supernatant was found to have more than the permissible oil concentration of 10 mg/l, then this can be further treated in the second stage to meet the permissible limit. In the present case electro-coagulation is not occurring.

2.4. Analytical measurement

The determination of the concentration of oil was done by finding out the absorbance characteristic wavelength using UV/VIS spectrophotometer (Perkin Elmer 35). A standard solution of oil was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} furfural was found to be 430 nm. Calibration curve was plotted between the absorbance and the concentration of oil solution. The linearity of calibration curve indicates the applicability of the Lambert–Beer's Law. The limit of detection for oil concentration was 250 mg/l and it was accurate to two decimal point.

3. Results and discussion

The treatment process has to ensure that the oil concentrations in the treated emulsiont are within the permissible limit of 10 mg/l prescribed by the Central Pollution Control Board (CPCB), Delhi, INDIA. The effect of various parameters like, voltage, salinity, pH, oil concentration, flotation time on oil removal using electroflotation has been studied.

3.1. Effect of voltage

The effect of voltage is shown in Figs. 2–4 for 50, 70 and 100 mg/l of oil concentration, respectively. Two fully submerged electrodes with 15 mm spacing were used. With increase in volt-

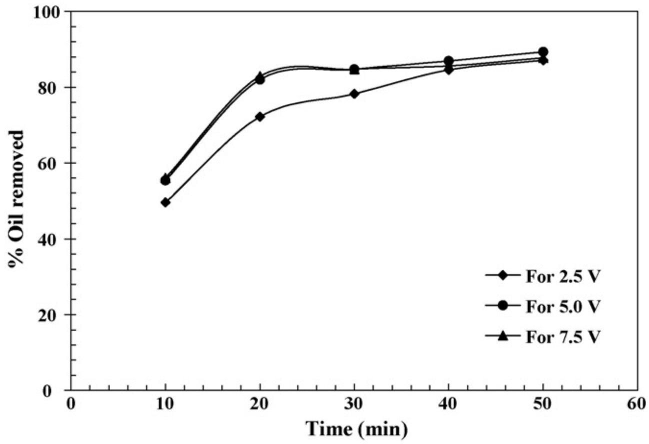

Fig. 2. Effect of voltage on oil removed for 50 mg/l concentration of oil.

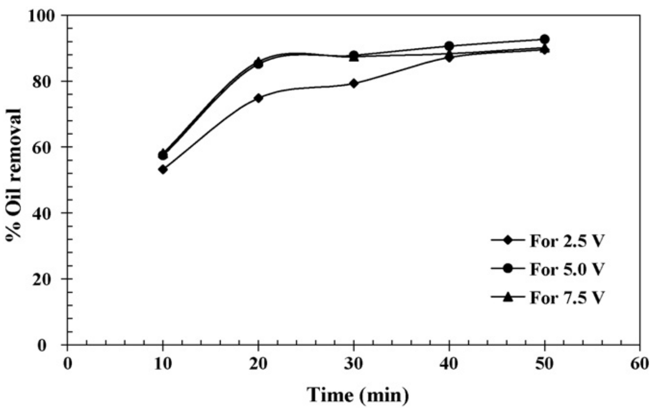

Fig. 3. Effect of voltage on oil removed for 70 mg/l concentration of oil.

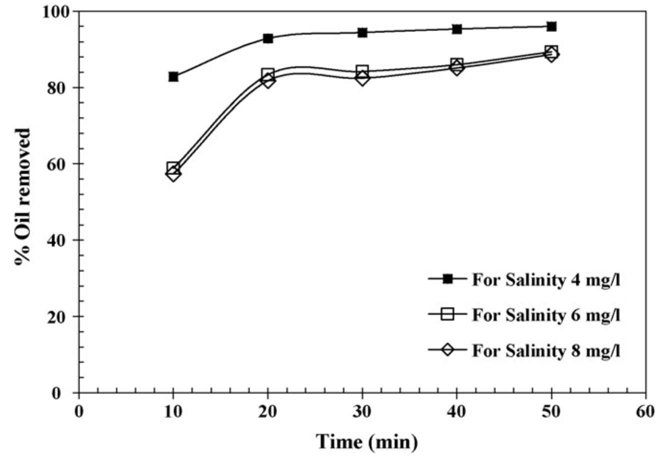

Fig. 5. Effect of salinity on oil removed for 50 mg/l concentration of oil.

age from 2.5 to 5.0 V the percentage amount of oil removed also increased. For voltage 2.5, 5 and 7.5 V corresponding currents was 0.2, 0.4 and 0.9 A, respectively. For example, 77.51–89.24% of oil was removed in the first 20 min for 100 mg/l concentration of oil. On further increasing voltage beyond 5 V the amount of oil removed was almost same for same time of treatment at 7.5 V. Increasing voltage enhances the generation of hydrogen and oxygen gases formed at electrode surfaces. This leads to an increase in the number of gas bubbles inside the cell. Consequently, the attachment step between gas bubbles and oil drops is enhanced, and more oil drops are carried out by gas bubbles. Hence, the oil removal was increased. However, further increase in voltage beyond optimum value increases excessively the number of bubbles generated. Increasing the voltage, increased in current, hence the generation bubbles increased and so the oil removal.

The electrical energy consumption increases with increasing current. Since the current is a key variable in controlling the performance of the electroflotation, it is desirable to decrease cell voltage rather than decrease current to minimize the energy consumption. The energy consumption was in the range of 0.17–2.25 kWh/m^3 for 40 min of process time.

3.2. *Effect of salinity (NaCl)*

Here the salinity is changed using NaCl, hence the salinity is equivalent to the concentration of NaCl. Figs. 5–7 indicate the effect of salinity on electroflotation for oil removal. Two fully submerged electrodes with 15 mm spacing with voltage of 5.0 V

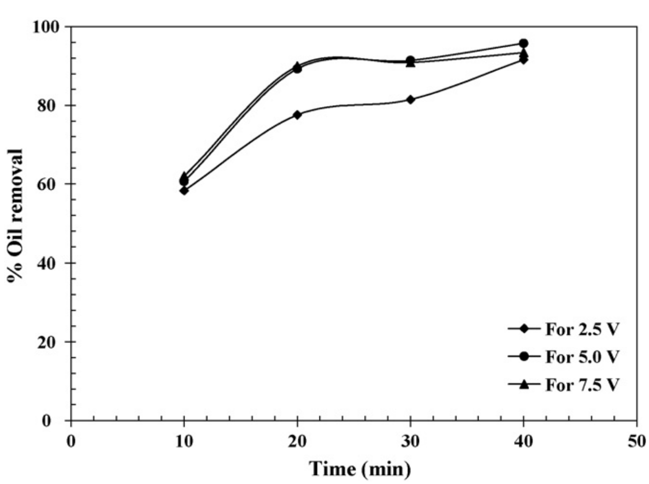

Fig. 4. Effect of voltage on oil removed for 100 mg/l concentration of oil.

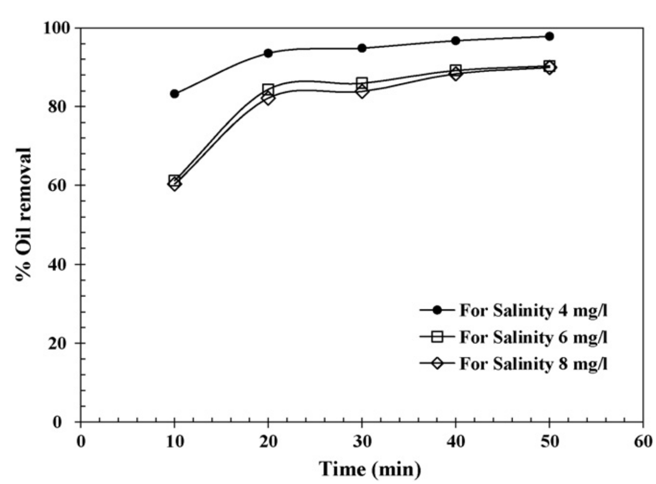

Fig. 6. Effect of salinity on oil removed for 70 mg/l concentration of oil.

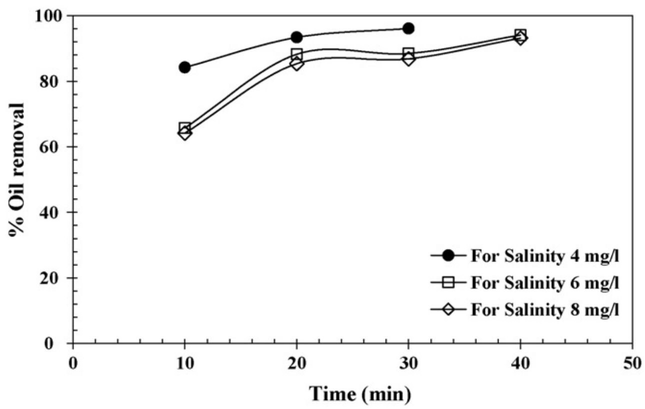

Fig. 7. Effect of salinity on oil removed for 100 mg/l concentration of oil.

and current, 0.4 A were used. From Figs. 2–6 (for 5.0 V), it was found that the addition of NaCl significantly enhanced the oil removal but further increase in NaCl decreased the oil removal. The results show that as the salinity of the effluent is decreased from 8 to 4 mg/l, the amount of oil removal increased and the period of treatment and electricity consumption decrease. It is possible to remove 96.14% oil within 30 min at 4 mg/l salinity of effluent for 100 mg/l concentration of oil; moreover, 84.25% oil was removed within 10 min of treatment time. The NaCl presence decreases the size of gas bubbles, especially hydrogen gas. Since the buoyancy of smaller bubbles is lower than larger bubbles, they rise slowly to the surface with high opportunities for collision with oil drops. This leads to an improvement in the oil removal process.

3.3. Effect of pH

To study the effect of pH on removal of oil, 50 mg of oil concentration, two fully submerged electrodes with 15 mm spacing and 5.0 V, 0.4 A were used. pH of effluent was changed to desired value using H_2SO_4 or NaOH. On decreasing the pH of the effluent from its original value of 6.65, the rate of amount oil removal increased and increasing pH of the effluent from its original value 6.65 the rate of amount removal decreased. At pH 4.72 the amount oil removal was 91.46% within 40 min. With decreased in pH of the effluent the treatment time also decreased. The electricity consumption also decreased with decrease of pH. However, on increasing pH of the effluent the process of oil removal decreases and time of treatment and electricity consumption increased. Fig. 8 indicates that the amount of oil removal is almost same in the 6.65–7.28 pH range. The rate of removal of oil at all pH values was very sharp during first 20 min and slow down there after.

3.4. Effect of oil concentration

The effect of oil concentration on removal of oil is shown in Fig. 9. Increasing concentrations from 50 to 100 mg/l enhanced the percentage oil removal. For example, the percentage oil removals, after 40 min, are 84.57, 87.15 and 91.58 for initial oil concentrations 50, 70 and 100 mg/l, respectively. The enhancement in oil removal may be due to an increase in the chance of gas bubbles to attach to floating oil drops in the emulsion. The results show that for all the initial oil concentrations; the percentage removal starts to stabilize after specific time (40 min). The oil drops inside the emulsion have several sizes, once the largest drops are removed; the efficiency of the process slows down. Literature indicated that smaller oil drops cannot be removed from waste emulsions by electroflotation unless their size is increased [11]. This leads to an enhancement in collision probability between oil drop and gas bubble.

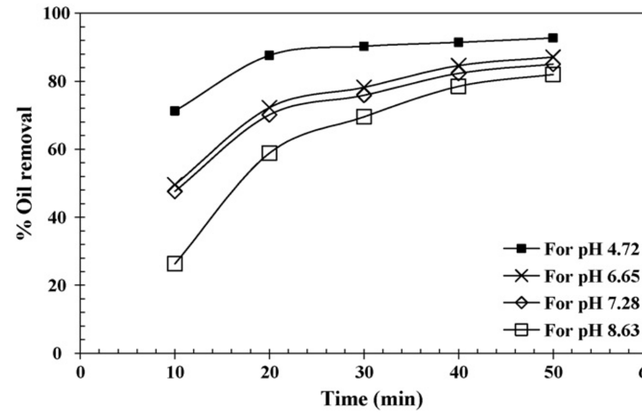

Fig. 8. Effect of pH on oil removed for 50 mg/l of concentration of oil.

3.5. Effect of flotation time

Fig. 10 shows the variation in oil concentration with flotation time. For example, at initial concentration equal to 50 mg/l. For flotation time of 30, 40, and 50 min at 5.0 V, the oil concentrations are 7.64, 6.54, and 5.34 mg/l, respectively. The oil removal values are 84.72%, 86.92%, and 89.32% for 30, 40, and 50 min, respectively. The corresponding energy increases by a factor of 1.66 (fro time from 30 to 50 min) while the oil removal enhances by a factor that does not exceed 1.06. The trend of the present results is similar to Hosny [11].

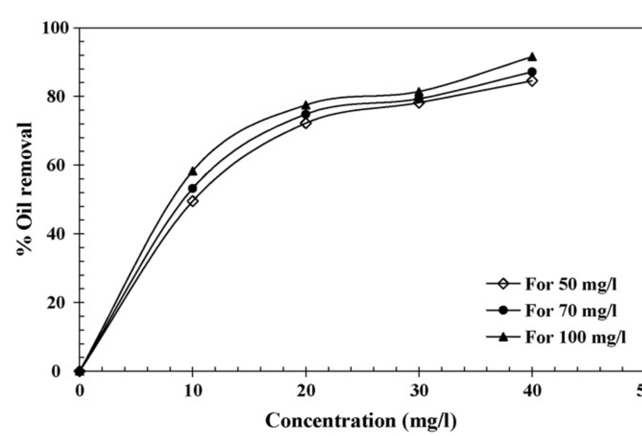

Fig. 9. Effect of concentration on amount of oil removed at 2.5 V.

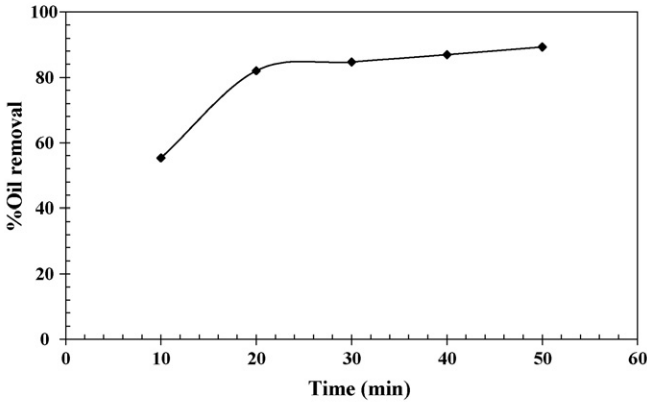

Fig. 10. Effect of flotation time on amount of oil removed at 5.0 V for 50 mg/l of oil concentration.

4. Conclusion

Electroflotation is an excellent technique for oil removal from waste water. The byproduct hydrogen gas was generated, though, in small quantities, could be utilized for other purposes. Twenty minute treatment of the effluent with 5.0 V and 0.4 A current is sufficient to bring down oil content within permissible limit of 10 mg/l for surface disposal. The rate of oil removal from the effluent with electroflotation treatment increases with decrease of effluent pH, under higher pH condition the process is less effective. More than 90% oil could be removed at pH 4.72 in 30 min treatment time. Destabilization of the effluent was faster at low salinity (4.0 mg/l) of effluent. Oil removal increases with the addition of NaCl and then decreases. The electroflotation technique could remove almost all the oil within 10 min from the low salinity effluent. The technique is more efficient in case of effluents with higher oil content.

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