OIL FIELD EFFLUENT WATER TREATMENT FOR SAFE DISPOSAL BY ELECTROFLOTATION

A DISSERTATION
Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By
RUPESH M. BANDE

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)
JUNE, 2006

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"OIL FIELD EFFLUENT WATER TREATMENT FOR SAFE DISPOSAL BY ELECTROFLOTATION"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2005 to June 2006 under supervision of **Dr. B. Prasad**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: June 30, 2006

Place: Roorkee

(RUPESH M. BANDE)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

Dr. B. Prasad
Associate Professor
Department of Chemical Engineering
Indian Institute of Technology Roorkee
Roorkee - 247667 (India).

ACKNOWLEDGEMENT

I express my deep sense of gratitude to my guide Dr. B. Prasad, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for his keen interest, constant guidance and encouragement throughout the course of this work, his experience, assiduity and deep insight of the subject held this work always on a smooth and steady course. Useful criticism and constant help extended in the hours of need had been immensely useful.

Thanks are due to Dr. Shri Chand, Professor and Head, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for providing various facilities during this dissertation.

I would also like to thank Dr. I. M. Mishra, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for his useful guidance and encouragement provided to me during this dissertation.

I would like to express my special thank to Dr. K.C. Koshel, GGM- CHIEF LABS, ONGC, Dehradun and Shri Anurag Jain Chemical Lab, ONGC, Dehradun for their constant help and advice throughout my work. I am greatly indebted to my friends Ashwani, Ravi, Vishwanath and Rahul for their enthusiastic support, encouragement and help, made me come up with this report.

I thank all well wishers who in any manner directly or indirectly have put a helping hand in any part of this piece of work. I am thankful to Shri B. K. Arora (Senior Technical Assistant) and Shri Ayodhya Prasad (Senior Laboratory Attendant), Pollution Abatement Research Laboratory, Department of Chemical Engg., IIT Roorkee, Roorkee and Shri R. K. Sharma (Senior Technical Assistant), Thermodynamics Lab, Department of Metallurgy Engg., IIT Roorkee, Roorkee for the continuous help provided during the experimental work.

Above all, I want to express my heartiest gratitude to all my family members for their love, faith and support for me, which has always been a constant source of inspiration.

RUPESH M. BANDE

ABSTRACT

Large quantity of effluent is produced during the exploitation of an oil field which is separated at Process Platform. It is a tough emulsion, slightly turbid in nature and contains considerable amount of residual oil in the form of emulsion. It is hazardous to dispose such effluents without proper treatment. Free oil hinders the penetration of sunlight in river water distracting aquatic life and restricts natural cleansing of water in rivers or lakes. Bathing in contaminated oily water causes skin cancer. Free and emulsified oil can clog and coat the filters and ion exchange beds, decreases effectiveness of filtration and interface with backwashing. Various conventional methods like coagulation, flocculation, dissolved air flotation, etc. have not proved to be satisfactory, necessitating to work into alternative process of treatment for safe disposal.

Attempt has been made to evaluate the electroflotation techniques for treatment of oil field effluent. In this technique the process of electrolysis initiated in the effluent by passing direct current in it through perforated aluminum electrodes. This results into separation of oil which forms a layer on the surface of effluent system. The separated oil on the effluent surface can be easily skimmed out.

The batch process studies have been conducted to optimise electrical input in the effluent and it is observed that at 5.0 Volt & 0.4 Ampere current is optimum. Also oil removal efficiency is high at 4.72 pH. It has also been observed that decrease in salinity and increase in oil content of the effluent enhances the efficiency of the electroflotation process.

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CHAPTER 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 produced oil field water usually contains high concentration of oil, salinity, suspended solids and total dissolved solids and 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.

Major pollutant in oilfield waste water is oil which may range between 100-1000mg/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 to fauna. Oilfield water also contains suspended solids which include: clay, sand, scale corrosion product likes Iron Sulphide, Iron Oxide, Bacteria & Oil.

In offshore areas the governing regulatory body specifies maximum hydrocarbon content in the water that is discharged overboard, generally in the range from 20mg/l to 72mg/l depending on the specific location. In most onshore surface water can not be disposed off due to possible salt contamination and must be injected into an acceptable disposal formation or disposed off by evaporation. In either case it will be necessary to treat the produced water to lower its hydrocarbon content below that normally obtained from free water knockouts and oil treaters. The effluent injected into the formation may result in decreased injectivity due to pore plugging caused by oil, and suspended solids. Burning of oil in evaporation pits may cause adverse impact on air quality besides loss of revenue in oil sales. Therefore it is desirable to treat the effluent suitably prior to inland or subsurface disposal.

1.1 METHOD OF WATER REUSE FOR DISPOSAL

There are three methods of reuse or disposal of oil field waters.

1.1.1 Reinjection

Produced oil field waters are usually disposed of by reinjection into a disposal well or injection well for water flooding. The amount and rate of water injection is greatly influenced by the amount of suspended solids and oil present in the water. Suspended solids or oil can plug the pore spaces in the formation or build-up an impermeable filter cake on the face of the reservoir rock that would impede 'water injection. The character of the reservoir rock largely influences the quality of water that can be injected. A reservoir rock with small pore sizes and low porosity requires water of very low suspended solids. Conversely, a high porosity reservoir having large pores and void would take water containing a considerable amount of suspended solids. Suspended solids are often present in water in a finely divided state and in amounts small enough so that their presence is not easily detected by looking at the water. Yet when large volumes of water are injected, even small counts of suspended solids can form an appreciable filter cake or deposit in an injection well bore and increase the injection well pressure.

1.1.2 Discharge into other Bodies of Water

Due to the high salt content of produced water, almost no oil field water is discharged into fresh water lakes, rivers or streams. The water must be analyzed for oil content and meet the Environment Protection Standards.

1.1.3 Use in Generation of Steam

Only a small part of oil field brines are used in Generators. The water used to generate steam must be of very high purity. Dissolved salts as well as suspended solids and oil must be removed from water used to feed steam generators.

1.2 OIL WATER EMULSIONS

Emulsions are suspensions of droplets, greater than 0.1 μm, consisting of two completely immiscible liquids, one of which is dispersed throughout the other. Emulsification of oil caused by the uptake of water by the oil, results in a fluid with increased viscosity.

Emulsions consist of three phases, namely (i) the finely divided droplets, (ii) the external or continuous phase, which is the matrix that keeps droplets in suspensions, and (iii) the interface which consists of an emulsifier or stabilizer that keeps the emulsions stable, binding the internal and external phases together and preventing droplets from approaching each other and coalescing.

Emulsions are frequently quite persistent in the environment and resist their decomposition in to their original constituents of oil and water.

1.3 TYPES OF EMULSIONS

1.3.1 According to existence of oil in water

According to existence of oil in water emulsions are divided in to four categories which are as follows in Table 1.1:

Table 1.1. 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

Source: Shrivastava, 2002.

1.3.2 According to stability of emulsions

Stability is widely referred as the persistence of an emulsion in the environment, and has been identified as an important characteristic of oil-water emulsions. Some emulsions quickly decompose into separate oil and water phases once removed, while more stable emulsions can persist for days to year. Viscosity of an emulsion is correlated with its stability.

Classification of emulsions according to stability is as follows:

a) **Unstable emulsions:** Persist for only few hours after mixing stops. These emulsions readily separate into oil and water due to insufficient water to water particle interaction. However, the oil may retain small amount of water, especially if the oil is viscous.

b) **Stable emulsions:** Persist for longer periods and they show viscoelastic properties and there viscosities are at least three times more than that of starting oil. In addition, some, if not most stable emulsions increase in viscosity over time.

c) **Meso stable emulsions:** These are most commonly formed and may lack of surfactants or excess of destabilizing agents such as aromatics. Meso-stable emulsions have properties between stable and unstable emulsions. The viscosity of oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may also degrade to form layers of oil and stable emulsions (NRT Committee, 1997).

The stability of an emulsion is also influenced by its physical and electrical properties (Liu et al, 1996).

Physical properties include interfacial tensions between the phases and the viscosity. Viscosity measurement provides considerable information about the structure of the emulsions and their stability. The viscosity of the continuous or external phase is of prime importance in overall emulsion viscosity. The formation of an emulsion is a function of the boundary tensions between the two liquid phases, determining the type of emulsion as either w/o or o/w. Miscibility determines the emulsions type. O/w emulsions are readily miscible with water.

Modification of the interfacial tension by the presence of the surfactants can produce smaller droplets for the mixing energy. In the equation-

$$W = \sigma.A$$

A reduction in σ (the interfacial tension), with W (the mixing energy), held constant, result in a proportional increases in A (the surface area), and hence overall reduction in droplet size.

Electrical properties include conductivity and dielectric properties. Oil is an insulator, i.e. o/w emulsions conduct an electric current, whereas w/o do not. The dielectric properties of emulsions systems are different from the average of the individual phases. The dielectric constant is important because of its intimate relationship to emulsion stability. The dielectric properties of an emulsion can be measured in a single parameter defined as Zeta Potential.

1.4 ZETA POTENTIAL

Zeta potential is the charge that develops at the interface between a solid surface and its liquid medium. This potential, which is measured in Mill Volts, may arise by any of several mechanisms. Among these are the dissociation of ionogenic groups in the particle surface and the differential adsorption of solution ions into the surface region. The net charge at the particle surface affects the ion distribution in the nearby region, increasing the concentration of counterions close to the surface. Thus, an electrical double layer is formed in the region of the particle-liquid interface.

This double layer (upper part of figure) consists of two parts: an inner region that includes ions bound relatively tightly to the surface, and an outer region where a balance of electrostatic forces and random thermal motion determines the ion distribution. The potential in this region, therefore, decays with increasing distance from the surface until, at sufficient distance; it reaches the bulk solution value, conventionally taken to be zero. This decay is shown by the lower part of the figure and the indication is given that the zeta potential is the value at the surface of shear.

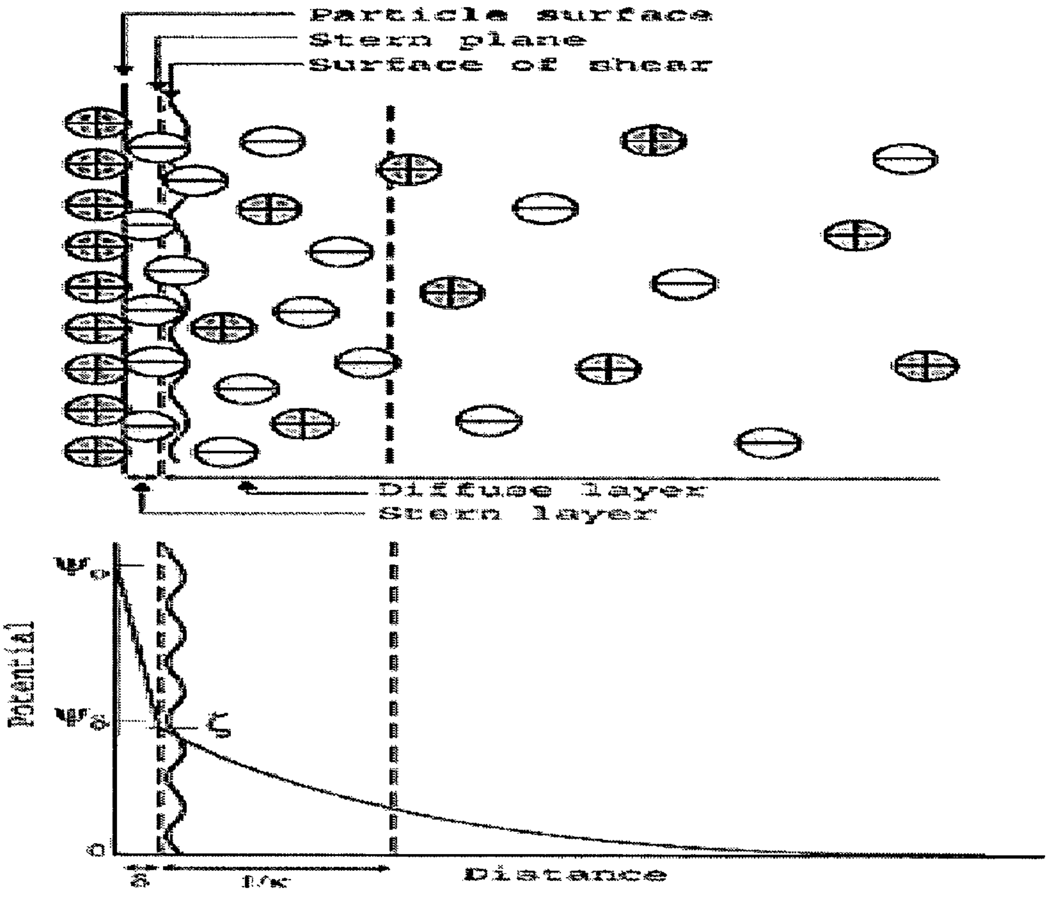


Fig 1.1. Zeta potential

In an electric field, as in micro electrophoresis, each particle and its most closely associated ions move through the solution as a unit, and the potential at the surface of shear between this unit and the surrounding medium is known as the zeta potential. When a layer of macromolecules is adsorbed on the particle's surface, it shifts the shear plane further from the surface and alters the zeta potential.

Zeta potential is therefore a function of the surface charge of the particle, any adsorbed layer at the interface, and the nature and composition of the surrounding suspension medium. It can be experimentally determined and, because it reflects the effective charge on the particles and is therefore related to the electrostatic repulsion between them, the zeta potential has proven to be extremely relevant to the practical study and control of colloidal stability and flocculation processes [www.btc.com].

1.5 MINIMAL NATIONAL STANDARDS (MINAS) FOR INDUSTRIAL EFFLUENTS

The Central Pollution Control Board (CPCB), Delhi, under powers vested in it through the water (Prevention and control of pollution) Act, 1974, has prescribed effluent standards for various quality parameters. For oil and greases, the standard limit is 10 mg/l. Taking in to account the treatability of the effluent from the technical feasibility point of view, the cost of treatment and cost burden that can be boomed by industry, CPCB has noticed industry specific MINAS. The MINAS will be binding for all industrial units throughout the country. Table 1.2 gives the effluent Criteria for Industries.

Table 1.2. Effluent Criteria for Industries

Parameter	**Limit for disposal to sewers**	**Flow Limit for disposal to open drains (KLD)**		**Limits for disposal on land**
		up to 25	**more than 25**	
Oil and grease	10 mg/l	0.25 Kg/day	10 mg/l	10 mg/l

Source: CPCB Book

1.6 EFFECT OF OIL EFFLUENTS ON WATER BODIES

Oils discharged into the water bodies/on soils cause adverse impact. Oil present in the waste process water also creates problem. Oil in the river or lakes affect fish also on human health causing cancer. It also effect on industries and water treatment process. Table 1.3 gives effects of oil discharged effluents (Eckenfelder, 1996).

Table 1.3. 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.		

1.7 TREATMENT OF OIL WATER EMULSIONS

Treatment of oily waste water may result in –

- **(i)** Improved oil/water separation
- **(ii)** Improved water clarity
- **(iii)** Oil recovery
- **(iv)** Water reuse
- **(v)** Protection of downstream facilities
- **(vi)** Environmental permit compliance

Table 1.4. Treatment types of oil-water emulsions

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.

Source: Cheremissionoff et al., 1976

1.8 REMOVAL OR SEPARATION OF OIL EMULSIONS

Emulsions are stable mixture of two immiscible liquids. Emulsions are stabilized by an emulsifying agent, which is a film of surface-active agents that reduces the interfacial tensions between the oil and water. The film of emulsifiers can be changed by heat, chemicals, mechanical device or a combination of the three.

(i) Heat is usually required to resolve oil water emulsions. Typical treatment temperature range is 10 to 85 ^{0} C.

(ii) Chemical applications consist of three major areas: demulsification and the pH adjustment. Demulsification formulations are utilized to chemically separate, or aid in the separation of the two phases comprising the emulsified waste oil. These formulations are designed to resolve the emulsion without over-treatment characteristics.

(iii) Agitation is usually essential to disperse the chemical treatment and to obtain uniform heating. A number of methods exist to provide agitation.

(iv) Retention time allows time for the treatment process to work. A minimum period of 8 to 24 hours is recommended.

The separation in to two components phases follows three stages:

(i) Droplets migrate to the interface between the oil and water bulk phases.

(ii) At the interface droplets coalesce and are taken up into the bulk oil phases.

(iii) The separated oil is removed from the water surface.

1.8.1 Migration to the bulk oil-water interface

Due to density difference, oil droplets experience a buoyancy force accelerating them towards the surface. However as the velocity increases, the drag on the droplets as they move through the water counteract this force until a point is reached when the two forces are exactly balanced. The velocity that individual droplets attain at this equilibrium is known as the terminal ascent velocity and is given by Stoke's law:

$$U_t = \Delta\rho . g . d^2 / 18 . \mu_c$$

Where, U_t = Terminal ascent velocity of a droplet with diameter d.

$\Delta\rho$ = Differential density between oil and water

μ_c = Continuous phase viscosity

g = Acceleration due to gravity.

This equation can be used to calculate the time required for droplets of a given size to migrate to the surface.

For dispersed phase concentration greater than 1 %, interaction between droplets causes the oil to separate more quickly than predicted by Stoke's law. This is because groups of droplets rise together as a cloud, and small droplets are carried up in the wake of faster moving larger droplets.

1.8.2 Coalescence

This is the step in the process, which determines the overall rate at which separation proceeds. Some factors which influence the coalescence are:

- **(i)** Differential density: Increased Differential density speeds coalescence.
- **(ii)** Phase viscosity: Coalescence proceeds more quickly than, with low viscosity for both the dispersed and continuous phases.
- **(iii)** Temperature: Coalescence rate increases at elevated temperatures primarily because of the associated reduction in viscosity for both the continuous and dispersed phases.
- **(iv)** Interfacial tension: A high interfacial tension promotes coalescence. An interfacial tension in oil-water system is sensitive to pH, reaching a maximum at neutral pH.
- **(v)** Surface active agents: Surfactants stabilize the film by binding the two phases across the interface.
- **(vi)** Electric double layer: The presence of an electric double layer prevents the close approach to adjacent droplets and so stabilizes the film.

1.9 OIL WATER SEPARATION TECHNOLOGY

Many techniques are available, including a variety of filters, chemical dosing, and reverse osmosis for separation of oil-water emulsions. For a technique to be successful it needs to satisfy a number of criterion, including: -

- **(i)** It must be cost effective, producing results, which are cheaper than dumping and purchasing more water. Both the capital and operating costs must be low and the results as good as tap water for the technique to be successful.
- **(ii)** It must remove the contaminants producing water, which can be reused in the same application, or as a replacement for water in another application.
- **(iii)** It must not in itself produce great amounts of waste.
- **(iv)** It must operate reliably and have low downtimes.

There are many techniques for oil water separation.

1.9.1 Gravity separation

It is primary and most common treatment, based on the specific gravity difference between water and immiscible oil globules, and used to remove free oil to the surface of a water body for subsequent skimming and removal.

The rise in rate of these oil globules is described by Stokes law:

$$V_R = \frac{gD^2(\rho_w - \rho_o)}{18\mu}$$

Where, V_R =Rise velocity

g = Gravity constant

D = Oil globule diameter

ρ_w = Water density

ρ_o = Oil density

μ = Fluid viscosity

The effectiveness of a gravity separator depends upon proper hydraulic design and the period of wastewater detention for a given rise velocity. Longer retention time generally increases separation efficiency. The effective removal of oil droplets with a given rise velocity is a function of the system geometry. The liquid detention time must be sufficient to oil droplets rising at a given velocity to come to the fluid boundary where they can be removed by skimming (Cheremissionoff et al., 1976).

1.9.2 Filtration

Filtration systems have been applied to the separation of free and emulsified oil from water streams. Broad spectrums of material ranging from anthracite, plastics, sand, and graphite have been used as filter media. Addition of polyelectrolyte has been shown to improve the performance of this process significantly. But this is not useful for handling large volume of water.

1.9.3 Air flotation

Oil droplets and light solids can be removed from water by introducing small bubbles of air or gas into the water. There are two main types of air flotation process such as:

1.9.3.1 Induced air Flotation

Air or gas is drawn into the liquid by an editor-rotor and is shared in to bubbles (102-103 μm). This process further may be considerably enhanced by the use of an organic polyelectrolyte flotation reagent. Inorganic coagulates are generally unsuitable for this process.

1.9.3.2 Dissolved Air Flotation

Low concentration of oil can be removed by dissolved air flotation. In this process, an effluent volume is pressurized in the presence of excess air, causing addition air to go in to solution in accordance with Henry's law. When this water is discharged to the inlet chamber of flotation unit at close to the atmospheric pressure, the dissolved air comes out of the solution in the form of tiny air bubbles, which attach themselves to become enmeshed in suspended oil globules (Orthomer, 1988).

1.9.4 Carbon Adsorption

Activated carbon adsorption has very limited use in the removal of free oil but still it is in practice. Wastewater used to activated carbon adsorption units must be pretreated to prevent clogging and coating of activated carbon with free oil.

1.9.5 Chemical coagulation

Chemical coagulation has been used for decades to destabilize suspensions and to effects precipitation of soluble metal species, as well as other in organic species from aqueous streams, thereby permitting their removal through sedimentation or filtration, alum, lime and/or polymers have been the chemical coagulants used. These processes, however, tend to generate large volumes of sludge with high bound water content that can be slow to filter and difficult to dewater.

In the destabilization of oily particles, chemical demulsifies provide the opposite charge to the emulsion, allowing the accumulated electrical charge on the interface of the emulsified oil droplets to be neutralized. Normally, cationic demulsifies, which exhibit a positive charge when dissociated in water, are used to destabilize oil-water emulsions. Coalescence occurs when the zeta potential of oil particles approaches zero. The process of destabilization is known as coagulation and agglomeration of neutralized particles to form the bigger flocs is known as flocculation. Although the exact method by which coagulation is accomplished can not be determined, four mechanisms are thought to occur. These include ionic layer compression, adsorption and charge neutralization, entrapment in a flocculent mass, and adsorption and intraparticle bridging.

1.9.6 Electrocoagulation (EC)

Electrocoagulation is a technique involving the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with pollutants in the water, in a similar manner to the addition of coagulating chemicals such as alum and ferric chloride, and allow the easier removal of the pollutants. The electrolytic addition of these ions has a number of advantages over their addition chemically. There is no addition of anions meaning no increase in salinity of the treated water. The system produces half to one third of the sludge. Greater activity means less metal ions required and a wider range of pollutants can be removed. In electroflocculation, the pollutants are removed by the bubbles, which are generated during the process, capturing the coagulated pollutants and floating to the surface. (Robinson, 1999 & 2000).

1.9.7 Electroflotation (EF)

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. Electroflotation was first proposed by Elmore in 1904 for flotation of valuable minerals from ores of hydrogen and oxygen gases generated from water

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. Waste petroleum industries usually have large volumes of small oil concentrations in their effluents, which form stable oil-water emulsions. Oil effluents can result also from the remaining of oil spill disasters in sea waters. Currently several water desalination plants face problems in filters' units due to presence of oil emulsions in their intake water sources.

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 [Honsy (1996)].

Table 1.5. Summary of oil removal processes

Process	Advantages	Disadvantages
Gravity separator • API • Corrugated plate separator	Economical and simple operation	Limited efficiency Susceptible to warmer conditions
Air Flotation: • Dissolved Air Flotation • Induced Air Flotation	Handles high solids shock loads	Sludge disposal problem when coagulant is used 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 & 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.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL STUDIES

Singh (1991) studied about the formation and treatment of only wastewater in mineral oil production and different parameters responsible for the stability of oily wastewater. This paper deals with the surface science of the subject and oily wastewater. This paper deals with the surface science of the subject oil removal methods and their advantages and disadvantages. The literature survey proved that air flotation was one of the most promising techniques in this regard. He found dissolved air flotation to be more suitable than induced air flotation due to smaller bubble size.

Benali (1992) studied the Rheological and Granulometrical of a cutting oil emulsions. Cutting oil emulsions are frequently used for lubrication and drilling of cutting tools. Rhelogical behavior of emulsions had been investigated using a controlled stress rheometer while granulometrical investigation had been performed using an optical microscope and a coulter particle size analyzer. Cutting oil emulsions behaves as non -Newtonian fluids characterized by a generalized behavior at low oil concentration, a plastic behavior at medium oil concentration, and a viscoelastic behavior at high oil concentration (from 70 to 90 %). For low oil concentration, the viscosity of emulsions increases with the decrease of the mean diameter of the droplets. For a constant shear rate, this is according to theory. Whereas, for high oil concentration, the mean diameter increases sharply with the increase of the oil concentration. This was due probably to interfacial films and particle interaction effects.

Brain et al. (1997) studied the treatment of oily wastes using high-shear rotary ultrafiltration. The high-shear rotary ultrafiltration (UF) system uses membrane rotation to provide the turbulence required to minimize concentration polarization and flux decline. The high-shear UF system was effective in concentrating oily wastes from about 5% to as high as 65%. The decoupling of turbulence promotion from feed pressurization/recirculation by rotating the membrane was the primary reason for the improvement in performance over the observed with conventional UF system. Transitional and gel layer oil concentrations (20% and 50-59%, respectively) were higher than values reported in the literature. Permeate flux was dependent on the temperature and rotational speed. Flux increased by about 45% when the temperature was increased from 43 to 60 °C. A larger decrease in waste viscosity, over that predicted for water alone, and increased oil droplet diffusivity were hypothesized as reasons for the stronger than expected flux-temperature relationship. The flux-rotational speed (ω) relationship was described by $J = f(\omega)^{0.90}$ however, the gel layer exhibited stability with increasing ω. The ceramic membrane was superior to the polymeric membrane in regards to permeate flux and quality as well as cleaning and durability.

Lin and Lan (1998) studied the treatment of waste oil/water emulsion by ultrafiltration and ion exchange. The present work investigates the treatment of waste drawing oil which is a high-strength waste oil/water emulsion commonly used in the cable and wire industries. Semi-batch ultrafiltration (UF) and ion exchange processes were employed to treat the waste oil/water emulsion. Experiments were conducted to examine the performance characteristics of the UF membranes of hydrophilic and hydrophobic types and of different pore sizes. Ion exchange treatment using synthetic strong acid cationic and strong base anionic resins was used as the polishing step to further lower the permeate COD and copper concentration and to improve the turbidity and conductivity. The test results have shown very good performances of combined UF and ion exchange processes. The water quality of permeates from the combined treatment processes have been consistently excellent which permit direct discharge or can be considered for re-use. An economic evaluation and a simple flow chart of the treatment system are also presented to show its advantage over the current practice of waste drawing oil disposal.

Cumming et al. (1999) studied the rejection of oil using an asymmetric metal microfilter to separate oil in water dispersion. Dispersed oil drops need to be reduced to very low concentration before water can be discharged into the environment.

Conventional equipment to achieve separation includes; settling tanks, hydrocyclones and centrifuges. However, these devices are not effective at removing oil drops with small diameters and filtration may have to be used. The rejection (retention by the filter) of oil drops dispersed in water by an asymmetric surface filter has been measured. The filter medium has conical pores that pass from the filtering side to the filtrate side with no internal tortuosity. The filter tube was cylindrical with a central rod supporting an annular helix of 14 mm pitch and the oil in water emulsion was pumped through the tube giving rise to a retentive (concentrated suspension of oil in water) and a permeate (filtrate almost clear of oil). The oil emulsion was stabilized by polyvinyl alcohol at a concentration of 0.2 g/l to give drops of between 1-40 μm in diameter. This is the emulsion size associated with produced water from oil reservoirs. The percentage retention of the oil drops by the filter, at a given drop diameter, was determined using a Coulter Multisizer in conjunction with a metal tracer added to the oil. The Filters were tested at a fixed rate of permeate flux and gave similar rejections whether the more open end or tighter end of the pores faced the challenge emulsion. The latter case required an increase in the transmembrane pressure from 0.18 to 0.2 bar, this pressure remained constant throughout the experiments. Thus, the microfiltrations were performed under conditions of constant flux and pressure. Using a feed of larger oil drops significantly changed the rejection; a coarse emulsion had a rejection of 89% at 2 μm whilst a finer emulsion gave a 50% cut-off at 5μm.

Scholz et al. (2000) studied the treatment of oil-contaminated wastewater in a membrane bioreactor. Activated sludge processes are frequently applied to treat industrial effluents. The membrane-bioreactor (MBR) is a modification of this conventional process, where the activated sludge is concentrated in a bioreactor, which is connected to a cross-flow ultrafiltration membrane unit. Trials in a MBR with a high-activated sludge concentration of up to 48 g l^{-1} showed that oily wastewater also containing surfactants was biodegraded with high efficiency. During the different loading stages of the MBR operation a removal rate of 99.99% could be achieved for fuel-oil as well as lubricating oil at a hydraulic retention time of 13.3 h.

The maximum biodegradation of fuel oil amounted to 0.82 g hydrocarbons degraded per day, and g MLVSS and average values of 0.26-0.54 g hydrocarbon g^{-1} MLVSS $_{d}^{-1}$ could be achieved. The average removal of COD and TOC during the experiment was 94-96% for fuel oil 97, and 98% for lubricating oil, respectively.

Due to the high removal efficiency of oily pollutants and the complete retention of suspended solids by the ultrafiltration unit, the MBR system shows good potential for application in industry for process wastewater recycling purposes.

Campos et al. (2002) studied the oilfield wastewater treatment by combined micro filtration and biological processes. After coarse filtration, this high saline wastewater was micro filtrated through mixed cellulose ester (MCE) membranes, resulting in average removals of COD, TOC, O&G and phenols of 35%, 25%, 92% and 35%, respectively. The permeate effluent was fed into a 1-L air-lift reactor containing polystyrene particle of 2 mm diameter, used as support material. This reactor was operated for 210 days, at three hydraulic retention times (HRT): 48, 24 and 12 h. Even when operated at the lowest HRT (12h), removal efficiencies of 65% COD, 80% TOC, 65% phenols and 40% ammonium were attained. The final effluent presented COD and TOC values of 230 and 55 mg/L, respectively. Results obtained by gas chromatography analyses and toxicity tests with Artemia Salina showed that a significant improvement in the effluent's quality was achieved after treatment by the combined (microfiltration/biogical) process.

Sharmani et al. (2002) studied the destabilization of oil water emulsions and separation by dissolved air flotation. The roles of aluminum and ferric sulfate as destabilizing agents for oil water emulsions that have been emulsified by a non ionic surfactant was investigated in terms of oil removal. The effect of coagulant dose, pH, and duration and intensity of both slow and fast mixing was considered. Electrokinetic measurement indicates that oil droplets have a negative zeta potential that is weakly dependent on pH. The chosen coagulant was shown to be effective in reducing the zeta potential of oil droplets, and charge reversal was observed for aluminum sulfate. Oil removal up to 99.3 % at pH 8 and 99.94 at pH 7 was seen for aluminum sulfate and ferric sulfate respectively. Rapid mixing times of around 20 seconds and flocculation time ranging from 15-20 minutes to be optimal for dissolved air flotation (DAF) separation. It was concluded that relatively low mixing speeds for coagulation and flocculation are essential for efficient operation. The initial oil concentration was 1630 ppm. At pH 7, a reduction of residual oil concentration to 82 ppm is observed, when 20 mg/l aluminum sulfate was used, However ineffective oil removal, only 31 % at pH 9.

For ferric sulfate, the maximum reduction of residual oil concentration was observed at pH 7, where almost 99.94 % of oil removal is removed at doses of 120 mg/l. Ferric is slightly more efficient than aluminum sulfate in terms of the oil removal.

2.2 ELECTROFLOTATION

Ho and Chan (1986) studied the electroflotation of palm oil mill effluent (POME) using lead dioxide-coated titanium anode on a laboratory scale .He was found the anode to be corrosion-resistant under the conditions of the experiment. He was determined the feasibility of the process by monitoring the effluent quality as a function of electrolysis time. He was observed Simultaneous flotation of suspended particles and anodic destruction of soluble substances in POME. About 40% of the COD of the dissolved substances of POME could be anodically destroyed together with 86% of suspended particles, made up of mainly plant cell debris, floated off. He envisaged the electroflotation process could form the first stage of a treatment system with aerobic or physicochemical process as secondary treatment step.

Ketkar et al. (1991) studied the electroflotation of quartz fines. He studied the effect of change in diameters of hydrogen and oxygen gas bubbles on the recovery of quartz fines. He founded a change in electrode surface geometry and current density changes the bubbles diameters as well as bubble flux thereby affecting flotation recoveries.

Honsy (1996) studied the separation of oil from oil-water emulsion by electroflotation technique. He used a set of electrode, a lead anode and stainless steel screen cathode 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 are electrical current, oil concentration, flotation time and flocculant agent concentrations. He was obtained a well-fitted empirical correlation represents the change in percentage oil removal with wide range of operating conditions. The oil separation reached 65% at optimum conditions; 75% in the presence of NaCl (3.5% by wt. of 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/m3 according to experimental conditions. An equation relates the $\boldsymbol{K}$ with I was obtained. The general form of the equation is $\boldsymbol{K} =$ constant $(I)^n$; where the n values are 0.64 and 0.62 for solutions with and without NaCI, respectively. The previous relation is valid only for current values from 0.3 to 1.2 A. The effect of emulsion flow rate on the separation process was determined on continuous scale.

Calvin (1997) studied the electroflotation of ground water decontamination using platinum-clad columbium screen as anode, and a stainless steel screen as cathode. A rock salt solution was used as the electrolyte, generating hypochlorite to oxidize cyanide, and hydroxides to from metal hydroxide precipitates which were carried to the top of the electroflotation device by rising gas bubbles. The device was used successfully to remove Ni, Zn, Pb, Cu, CN in polluted groundwater obtained from directly under a contaminated site, meeting the pretreatment standards of the pollutant for the local POWT sewer system. The cost of an electroflotation device plus a sand filter compares favorably with a conventional treatment system using cyanide oxidation/ alkaline precipitation/ polymer aided clarification.

Oussedik and Khelifa (2001) studied the reduction of copper ions concentration in wastewaters of galvanoplastic industry by electroflotation. This work consisted of studying the electrofiotation process of solution containing copper ions which is a harmful metal, According to the results obtained, it has been noticed that these factors: concentration of eliminated ion, concentration of additives, density of current and pH of solution have a direct action on the processes of reduction of copper concentration.

According to these results he have tried to treat a solution polluted by this metal with an efficiency elimination optimal of 90%.

Mostefa and Tir (2004) studied coupling flocculation with electroflotation for waste oil/water emulsion treatment is adequate for the separation of oil from oily wastewater. Flocculation plays an important role in the improvement of this process due to its ability to remove organocolloids. He examined the evaluation of the most important operating parameters. An experimental design was applied in order to estimate the effect of operating conditions on the performance of the coupling of flocculation with electroflotation by measuring chemical oxygen demand, turbidity and conductivity. Three various flocculants were considered. The efficiency of oil separation reached 99% for a concentrated emulsion of 4% (wt.) at optimum conditions and at an optimum concentration of flocculant agents.

Khelifa et al. (2005) studied the treatment of metal finishing effluents by the electroflotation technique. Metal finishing water contains an appreciable quantity of heavy metals such as nickel, copper, zinc, cobalt, etc.The techniques used to depress the pollution caused by the effluents of the metal finishing industry are costly and not easily controllable. Electroflotation (EF) serves as an efficient and promising alternative due to its simplicity and cost-effectiveness. The effects of the following parameters were examined: current density, pH, heavy metal concentration, supporting electrolyte concentration, and the nature of the electrodes. By optimizing the operation, heavy metal removal reached 98-99%, and maintained final and global concentration to a value lower than the World Health Organization standard, which is 1 mg/L for nickel and copper.

Marcos et al. (2005) studied the application of electrochemical technology to the remediation of oily wastewater. The successful application of electrochemical technology, employing a dimensionally stable anode (DSA_), for the remediation of wastewater from the oil extraction industry has been demonstrated. Samples from the oil–water separation box of an effluent treatment plant were submitted to voltammetry, chronoamperometry and electrolysis studies using a DSA anode of nominal composition Ti/ $Ru_{0.34}Ti_{0.66}O_2$. Electrolysis of the oily wastewater lead to a time-dependent reduction in chemical oxygen demand (COD) in the sample that could be attributed to: (i) the direct oxidation of oil components at the electrode, by the metal oxide itself or by OH_ radicals available at the electrode surface, (ii) the indirect oxidation of oil components by intermediate oxidising agents formed in parallel reactions (ex. ClO^{-}), and (iii) the aggregation of suspended oil droplets by electroflotation. The largest reduction (57%) in COD was obtained following electrolysis of an oily sample for 70 h at 50 ^{0}C with a current density of 100 mA cm^{2}. The stability of DSA electrodes for use in oily wastewater remediation has been assessed.

Gao et al. (2005) removal of chromium from wastewater by combined electrocoagulation–electroflotation without a filter. A combined electrocoagulation and electroflotation process was designed to reduce Cr^{6+} to Cr^{3+} first and then to remove the total Cr from wastewater to a value below 0.5 mg/L. Acidic condition was employed in the reduction of Cr^{6+} and neutral conditions were found to be beneficial for the coagulation of the precipitates of $Cr(OH)_3$ and $Fe(OH)_3$. The formation of $Fe(OH)_3$ was ensured by sparging compressed air in the coagulation unit through a draft tube. The air not only oxidizes Fe^{2+} produced electrically, but also helps to mix the water for a better coagulation of the particles. The two-stage electroflotation arrangement can separate the solids from the wastewater to a value of less than 3 mg/L with total Cr less than 0.5 mg/L. The residence time required is about 1.2 h. The optimal conditions for the treatment are: charge loading about 2.5 Faradays/m^3 water, pH value in the coagulation unit is 5–8. The power consumption is less than 1 kWh/m^3 water at the conductivity of 1.5 mS/cm. When aluminum ions are either added or produced in situ in the coagulation unit, the treated wastewater can be discharged without any filtration.

Casqueira et al. (2006) studied the removal of zinc from liquid streams by electroflotation. The removal of heavy metals from dilute aqueous solutions (in the range of 10^{-7}–10^{-4} mol dm^{-3}) is often not acceptable using classical methods, which do not achieve levels in accordance with environmental quality standards. Electroflotation has certain desirable characteristics, compared to dissolved and dispersed air .otation, particularly in regard to the small bubble size distribution of the process.The aim of this work was to develop an electroflotation (EF)/electrocoagulation (EC) cell to study this combined process and the influence of some relevant parameters/variables, such as collector concentration, tension and current density variation, on the removal of zinc from synthetic solutions containing 20 mg l^{-1} of the metal. A platinum gore (5 mm) anode and stainless steel mesh cathode were used in the electroflotation cell. The work showed that it was possible to remove zinc by electroflotation, 96% removal being achieved using sodium dodecyl sulfate (SDS) as collector in the stoichiometric ratio 1:3, current density of around 8 mA/cm2 and an inlet pH of about 7.0.

OBJECTIVES OF THIS STUDY

The literature review presented earlier shows that the effect of several operating and system parameters on the Electrocflotation efficiency and thereby the removal of oil from the oil-water effluent has not studied in detail. In view of the above, the present work is undertaken. The aims and objectives of the work are as follows:

1. Removal of oil from Oil-Water Effluent using Electroflotation technique in batch and flow systems.
2. The effect of the following parameters on oil removal from oil-water effluent.
    a) pH
    b) concentration of oil
    c) voltage
    d) flotation time
    e) salinity

CHAPTER 3

ELECTROFLOTATION FUNDAMENTALS

3.1 ELECTROFLOTATION PHENOMENON

The physical process of gas evolution can be divided into three stages: nucleation, growth and detachment. Bubbles nucleate at electrode surfaces from solutions highly supersaturated with product gas and grow by diffusion of dissolved gas to the bubble surface or by coalescence at the electrode with other bubbles. They detach from the electrode when buoyancy or liquid shearing forces pulling the bubbles away overcome the forces binding them. Surface in homogeneities such as cracks are generally considered high energy nucleation sites due to the availability of atomic ledges as high energy anchorage points. For bubble generation in vacuum or pressure release flotation (analogous to precipitation) the above phenomenon is important. During the electrolysis it is generally agreed that the preferred nucleation sites are at surface inhomogeneities such as fissures, cracks and scratches as well as local inhomogeneities resulting in donor acceptor and low over potential sites. The dependence of the voltage gradient at the tip of a needle electrode upon its curvature is a well known phenomenon. Occurrence of such sharp points on an electrode and the consequent presence of high local potential gradient sites cannot be pulled out. The importance of the role of voltage gradients towards nucleation is clear from the observation that on wire and mesh electrodes bubble size depends largely on electrode curvature (and thus potential gradient) almost independent of the current density. However bubble growth rates are not strongly dependent on the diameter of wire electrodes.

3.2 REACTION TYPES INVOLVED IN THE EF PROCESS

The basic principle of such process lies on water electrolysis. Subsequently, it is not surprising that it will be determined among other variables on pH and temperature. To state the reactions taking part, they can be assumed at first instance as follows, [Koshla et al., 1991].

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$$

$$2H_3O^+ + 2e^- \rightarrow 2H_2 + H_2O$$

The protonated water shows to be equivalent in both consumption and generation of positively charged specie. Half-reaction [1] is proposed to be achieved in the anode while the second, at the cathode. Venkatachalam (1992) has performed a rather complete analysis about the experimental consequences of producing gas through electrolysis.

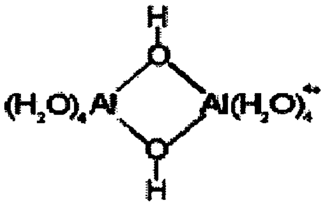
The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ according to the following reactions:

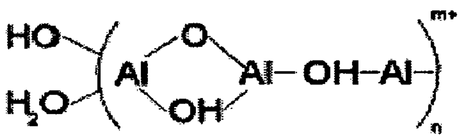
$$Al \rightarrow Al^{3+}(aq) + 3e^-$$

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

$$Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+ (aq)$$

Depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. Examination of the pE–pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed. For example, the structures of dimeric and polymeric Al^{3+} hydroxo complexes are shown below:





These gelatinous charged hydroxo cationic complexes could effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate. (Mollah et al., 2001)

The advantages of this are that the aluminum is much more active, requiring less metal for the removal of the same pollutants, and they can remove more material. In applying the aluminum via a sacrificial anode, the cathode releases hydrogen gas, which can operate like the air bubbles in a dissolved air flotation unit. This system automatically adds its own flocculating agent and generates its own gas bubbles, in a controlled manner, enabling suspended solids, oils/greases and other pollutants to be removed cheaply. In electrocoagulation, sacrificial electrodes are used and the passage of an electric current through the water from the electrodes causes the metal to go into solution as the ions, via the anode reactions:

$$Al - 3e^- \longrightarrow Al^{3+} \text{------------------------} (1.1)$$

At the cathode, the reaction is more typically

$$2H_2O + 2e^- \longrightarrow 2\ OH^- + H_2 \text{---------------} (1.2)$$

In this manner, the same effect is achieved as would be done using chemical dosing, but without the addition of any anions, leaving the residual salinity of the water practically unaltered. The cathode reaction results in a slight increase in the pH of the treated water, usually about 1 pH unit, depending upon the starting pH and the degree of treatment required. The pollutants are then removed in a similar manner to that associated with chemical coagulation, namely filters, settling or similar. Electroflocculation is a term used to describe the use of electrocoagulation to coagulate the pollutants, plus the cathode bubble generation to float the pollutants to the surface. In this regard, electroflocculation is similar to dissolved air flotation (DAF), with one major difference that there are no chemicals to be added and consequently no increase in the salinity of the treated water. The electroflocculation process generates the coagulating ions and the gas bubbles in one action, without the need for additional compressed air/bubble generation equipment. Best results are achieved with a pH in the range $3.5 < pH < 9$.

In its operation, the system generates a floc, which floats to the surface. When done correctly, this floc forms a thick stable layer on the surface of the water.

Provided the water is not disturbed very much, this layer will float there for many hours. During this time, it should be removed, taking with it most of the removed pollutants. There are several methods of doing this, including floating them above the surface of a weir by raising the level of the water, or scraping them off mechanically. One of the limitations of the removal efficiency of this technique is the efficiency with which this surface floc can be removed.

The process adds aluminum to the water as well as raising the pH slightly due to the generation of hydroxide radicals through reaction (1.2). The amount of aluminum added depends upon the nature of the water being treated. However typical amounts added, as determined from calculations based upon the passage of current and the reaction at the anode, reaction (1.1), suggest that amounts of between 10 and 50 mg/L are used. Beyond that amount, the process starts to be too expensive for many applications. The insolubility of aluminum and the nature of the coagulating reaction mean that most of the aluminum is used in the coagulating process and the aluminum levels in solution are not often beyond the 2 mg/l level.

The application of a voltage and the subsequent passage of an electric current through water containing emulsified fats, oil and/or greases (FOGs), causes them to be released from emulsion. The gas bubbles produced combine with the natural buoyancy of the FOGs and the coagulating effect of the metal, to raise the FOGs to the surface, from where they can be floated off and removed. Removal rates of greater than 99% have been achieved from a single stage process. When combined with a two-stage process, removal rates of greater than 99.95% have been consistently achieved in industrial applications treating up to 10,000 liters per day. As well as reductions in the FOG concentrations, the COD level has been reduced by over 96% (Robinson, 1999 & 2000).

3.3 FACTORS AFFECTING ELECTROFLOTATION

The performance of an electroflotation system is reflected by the pollutant removal efficiency and the power and/or chemical consumptions. The rate of flotation depends on following factors:

3.3.1 Size

The rate of the flotation process is affected greatly by the size of floating particles. The flotation process is also affected by the bubble size of the hydrogen and oxygen gases formed at electrode surfaces. There are several factors influence bubble size such as:

- (i) Current density
- (ii) Temperature of electrode surface
- (iii) Curvature of electrode surface
- (iv) Type of electrode material
- (v) pH of the medium

3.3.2 Charge

The rate of flotation strongly depends upon the charge of both particle and bubble. However, the measurement of the charge on a small gas bubble is not easy to determine and only a few investigators measured bubble zeta potentials. Maximum rate of flotation was achieved when the zeta potentials of bubbles and particles were in opposite sign.

3.3.3 Volume

The success of flotation process depends upon the presence of sufficient volume of gas bubbles relative to the floating particles. However, large volume of gas bubbles could lead to coalescence of bubbles instead of attachment to floating particles. This criterion is difficult to adjust in conventional flotation processes; however, it is relatively easier to adjust in an electroflotation process.

3.3.4 Motion

The motion of the bubble inside the cell is important to the flotation process. The trajectory of the bubbles affected by the hydrodynamics and electrodes position in the cell [Honsy (1996)].

3.3.5 pH Effect

The size variation of the bubbles depends on water pH as well as the electrode material as shown in Table 3.1. The hydrogen bubbles are smallest at neutral pH. For oxygen bubbles, their sizes increase with pH. It should be noted, however, the cathode materials affect the size of the hydrogen bubbles, and so do the anode materials. The bubble sizes obey a log-normal distribution. Using buffer solution, Llerena et al. found that the recovery of sphalerite is optimal at pH between 3 and 4. They also documented that during this pH range, the hydrogen bubbles are the smallest, about 16±2 μm. Decrease or increase pH from 3 to 4 results in the increase of hydrogen bubbles. At pH of 6, the mean of hydrogen bubbles is 27 μm. At pH of 2, the hydrogen bubbles are about 23 μm when the current density was all fixed at 500 A/m^2 using a 304 SS wire. Oxygen and hydrogen were separated in their research and it was found that the increase of pH in the cathode chamber and pH decrease in the anode chamber is very quick when no buffer solutions were used. The recovery efficiency of oxygen is about half of that of hydrogen proportional to the amount of gas generated at a given current. This was also confirmed by O_2 and H_2 gas sparging [Chen (2004)].

3.3.6 Current Density

The gas bubbles depend also on the current density. The surface condition affects the particle size, too. The polished mirror surface of the stainless steel plate gives the finest bubbles, Table 3.2 and Table 3.3. Besides size of bubble, the bubble flux, defined as the number of gas bubbles available per second per unit cross-section area of the flotation cell, also plays a role in mineral flotation, recovery of different sized particles. A decrease of gas bubble sizes was found with the increase of current intensity, Table 3.2 and Table 3.3. Burns et al. found that such a decrease of bubble size with increase in current density was true only at the low end of current densities.

When the current density is higher than 200 A/m^2, no clear trend can be observed with gas bubbles ranging from 20 to 38 μm, Table 3.1 [Chen (2004)].

Table 3.1. The range of gas bubbles at different pH and electrode materials.

pH	Hydrogen (μm)			Oxygen (μm)
	Pt	Fe	C	Pt
2	45-90	20-80	18-60	15-30
7	5-30	5-45	5-80	17-50
12	17-45	17-60	17-60	30-70

Table 3.2. For Hydrogen Gas bubbles diameter.

Electrode	Current density (A/m^2)				
	125	200	250	300	375
SS Plate	34	32	29	26	22
200 Mesh	39	35	32	31	28
100 Mesh	45	40	38	30	32
60 Mesh	49	45	42	40	37

Table 3.3. For Oxygen Gas bubbles diameter.

Electrode	Current density (A/m^2)		
	125	250	375
Pt Plate	48	46	42
200 Mesh	50	45	38

Table 3.4. The mean gas bubble size at different conditions (polished graphite electrodes, Na2SO4).

Ionic strength	Current density (A/m^2)	Gas	Mean size (µm)
0.1	52	O_2	18.6
	98.5		21.2
	129.2		23.3
	295.4		20.0
	492.3		28.7
	689.2		20.7
	886.1		31.7
	55.4	H_2	29.7
	98.5		37.7
	196.9		19.3
0.01	33.8	O_2	27
	46.2		24.7
	58.5		22.0
	36.9	H_2	37.6
	43.1		37.3
	55.4		22.0

3.3.7 Arrangement of the Electrodes

Usually, an anode is installed at the bottom; while a stainless steel screen cathode is fixed at 10–50mm above the anode Fig 3.1. An electrode arrangement cannot ensure quick dispersion of the oxygen bubbles generated at the bottom anode into wastewater flow, affecting flotation efficiency. Moreover, if the conductivity of wastewater is low, energy consumption will be unacceptably high due to the large inter-electrode spacing required for preventing the short-circuit between the upper flexible screen cathode and the bottom anode.

Chen et al. proposed and tested the novel arrangement of electrodes with anode and cathode placed on the same plane as shown in Fig 3.2. Effective flotation was obtained because of quick dispersion of the small bubbles generated into the wastewater flow. Quick bubble dispersion is essentially as important as the generation of tiny bubbles. For a conventional electrode system, only the upper screen cathode faces the wastewater flow, while the bottom anode does not interact with the flow directly. Therefore, the oxygen bubbles generated at the bottom anode cannot be dispersed immediately into the wastewater being treated. Consequently, some oxygen bubbles may coalesce to form useless large bubbles. This not only decreases the availability of the effective small bubbles, but also increases the possibility of breaking the flocs formed previously, affecting the flotation efficiency. When the anode and the cathode are leveled, such an open configuration allows both the cathode and the anode 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. Another arrangement of the electrodes is shown in Fig 3.3. It has the advantage of the uniform property of the surface of an electrode. It is also very much efficient.

Meanwhile, the open configuration has been proven quite effective in the flotation of oil and suspended solids. Significant electrolysis energy saving has also been obtained due to the small inter-electrode gap used in the novel electrode system. It is useful to point out that the electrolysis voltage required in an EF process is mainly from the ohmic potential drop of the solution resistance, especial y when the conductivity is low and the current density is high. Since the ohmic potential drop is proportional to the inter-electrode distance, reducing this distance is of great importance for reducing the electrolysis energy consumption. For a conventional electrode system, due to the easy short-circuit between the upper flexible screen electrode and the bottom electrode, use of a very small spacing is technically difficult. But for the electrode system shown in Fig 3.2 and Fig 3.3, the inter-electrode gap can be as small as 2 mm [Chen (2004)].

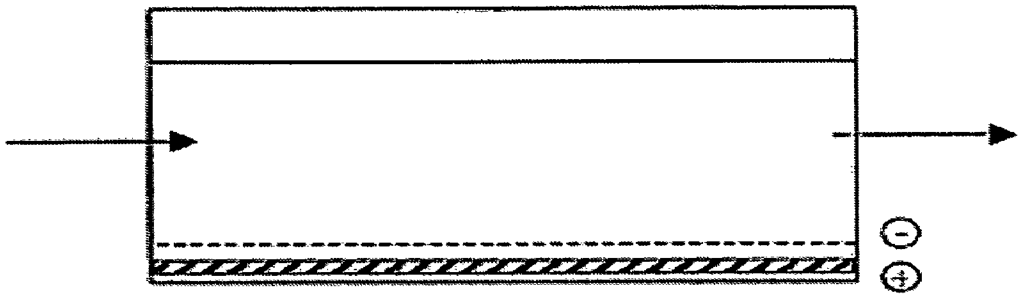


Fig. 3.1. Conventional electrode arrangement for electroflotation

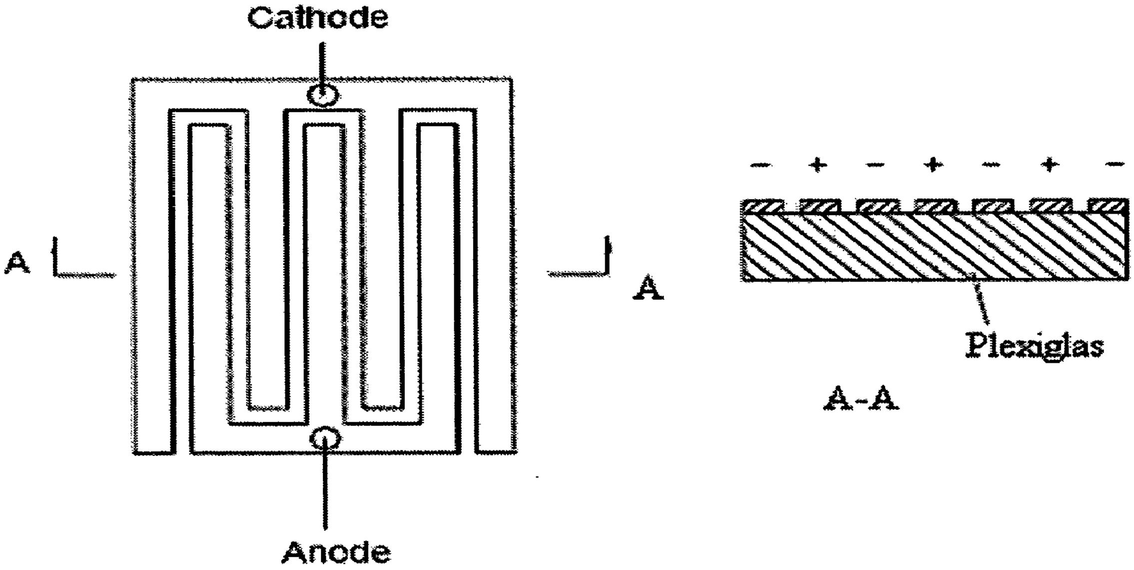
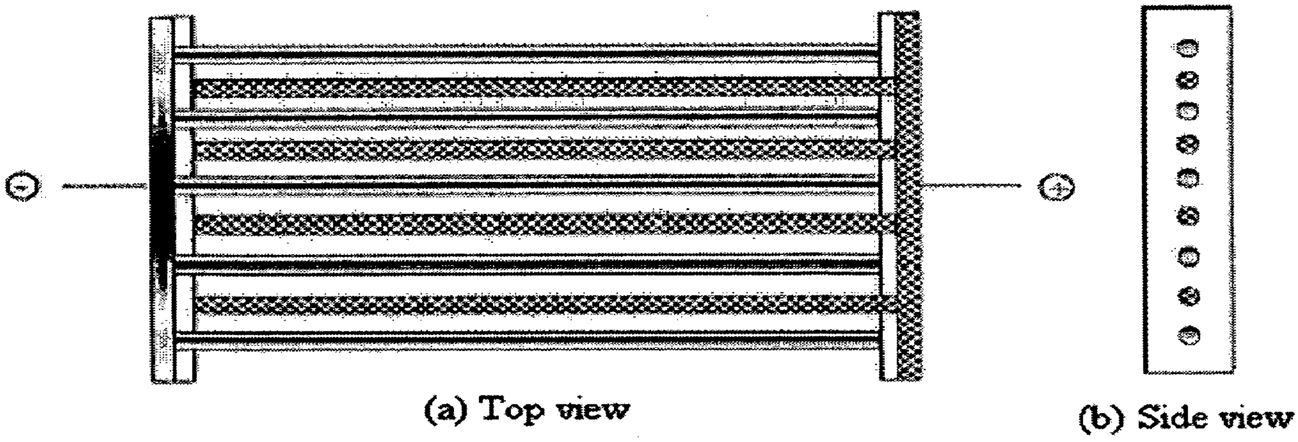


Fig 3.2. Novel electrodes arrangement for electroflotation



(a) Top view

(b) Side view

Fig. 3.3. Alternative electrodes arrangement for electroflotation

3.4 COMPARISON WITH OTHER FLOTATION TECHNOLOGIES

The effective electroflotation obtained is primarily attributed to the generation of uniform and tiny bubbles. It is well known that the separation efficiency of a flotation process depends strongly on bubble sizes. This is because smaller bubbles provide larger surface area for particle attachment. The sizes of the bubbles generated by electroflotation were found to be log-normally distributed with over 90% of the bubbles in the range of 15–45μm for titanium-based anode. In contrast, typical bubble sizes range from 50 to 70 μm for DAF. Burns et al. reported that values of gas bubble size vary from 46.4 to 57.5 μm with the pressure decrease from 635 to 414 kPa for DAF. The electrostatic spraying of air gives gas bubbles range from 10 to 180 μm with mean diameter being 33–41μm. Impeller flotation (IF) produces much smaller gas bubbles but its pollutant removal efficiency is not good probably due to the quick coalesce of the tiny bubbles to form larger ones soon after they are generated. Table 3.5 summaries the comparison of different flotation processes for treating oily wastewater. IC, OC and F in the table denote inorganic coagulants, organic coagulants and flocculants, respectively. Electroflotation clearly shows advantages over either DAF, settling or IF. When the conductivity is low, direct application of EF consumes large amount of electricity. For this case, addition of table salt (NaCl) is helpful [Chen (2004)].

Table 3.5. Comparison with Other Flotation Technologies

Treatment Type	EF	DF	IF	Settling
Bubble size (μm)	1-30	50-100	0.5-2	
Specific electricity consumption (W/m^3)	30-50	50-60	100-150	50-100
Air consumption (m^3/m^3) water		0.02-0.06	1	
Chemical conditioning	IC	OC+F	OC	IC+F
Treatment time (min)	10-20	30-40	30-40	100-120
Sludge volume as % of treated water	0.05-0.1	0.3-0.4	3-5	7-10
Oil removal efficiency (%)	99-99.5	85-95	60-80	50-70
Suspended solid removal efficiency (%)	99-99.5	90-95	85-90	90-95

CHAPTER 4

EXPERIMENTATION

4.1 GENERAL

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 conc., pH, voltage, salinity, flotation time etc.

4.2 EXPERIMENTAL SET UP

A square cross section 2.04×10^{-3} m^3 vessel (200 x 85 x 120 mm) was used for electrofloatation. The vessel was fabricated from transparent perplexes material sheets of 5 mm thickness. Aluminum plates (150 x 72 x 2 mm thick (W x L x t)) perforated uniformly with 2mm drill bit to facilitate passage for upward movement of the oil droplets to the surface were used as the electrodes. A regulated DC power supply 15V/ 5A was used to apply potential between the anodes and cathodes.

4.3 WASTE WATER SAMPLE

Crude oil by ONGC was used as the wastewater for this study. Oil-water emulsion of different oil concentration was made by mixing the oil with the distilled water.

4.4 EXPERIMENTAL METHOD

Batch Process

The step by step procedure of conducting the experiments in the present study is outlined as under:

1. Crude oil was mixed with the distilled water and stirred for 24 hours. The mixture showed a uniform yellowish colour.
2. The pH of the oil-water emulsion was measured with a digital pH meter.
3. For lowering the pH of the effluent dilute H_2SO_4 & for increasing the pH dilute NaOH were used.

4. Vessel was filled with the crude o/w emulsion. Electrodes are submerged and the current was passed by the regulated DC power supply. Voltage and current were maintained to 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.
5. After electrolysis the sludge at the top of the vessel is skimmed off.
6. A sample of the supernatant was used for the determination of the residual oil concentration, using CCl_4 as an extractant.
7. If the supernatant was found to have more than the permissible oil concentration of 10 mg/l, then this was further treated in the second stage to meet the permissible limit.

4.5 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} for 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 (Fig. 4.1) indicates the applicability of the Lambert-Beer's Law.

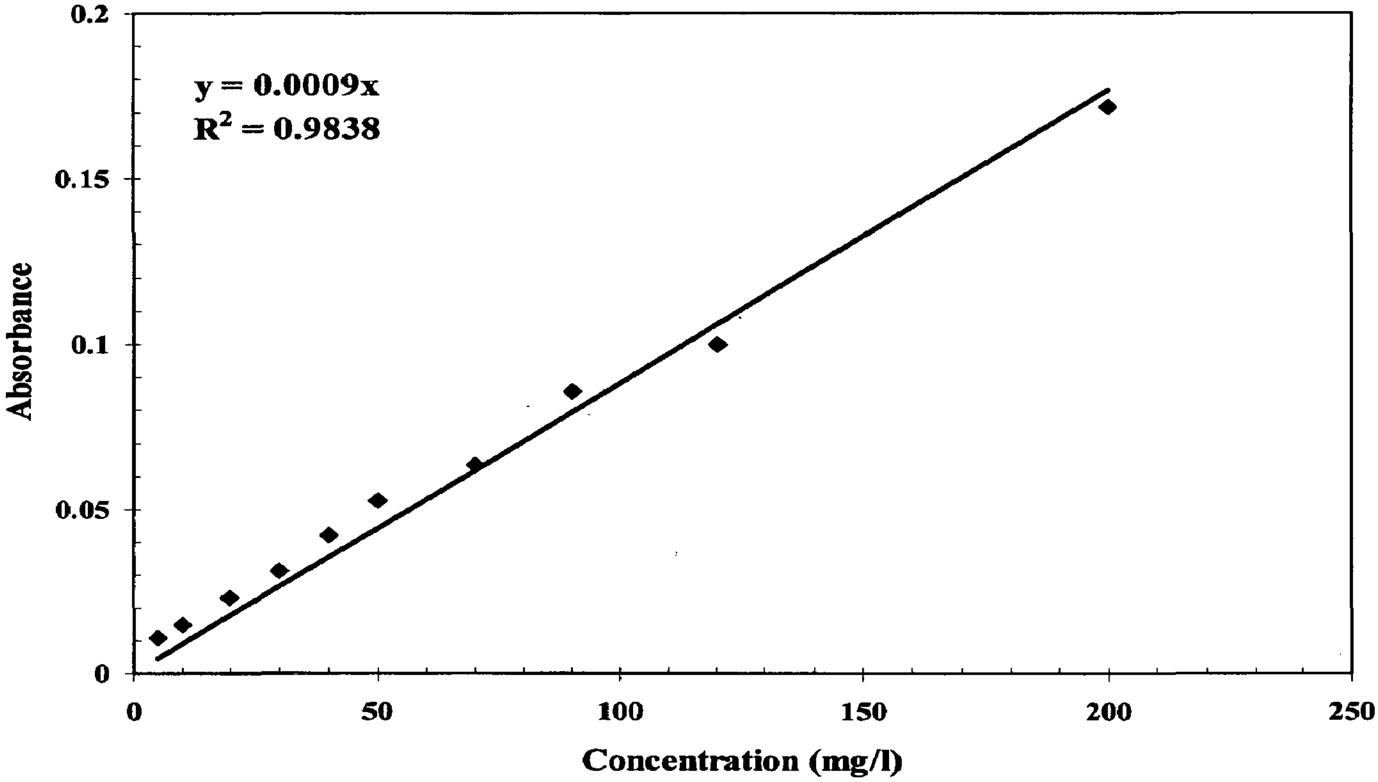


Fig. 4.1. Calibration graph for the calculation of oil concentration.

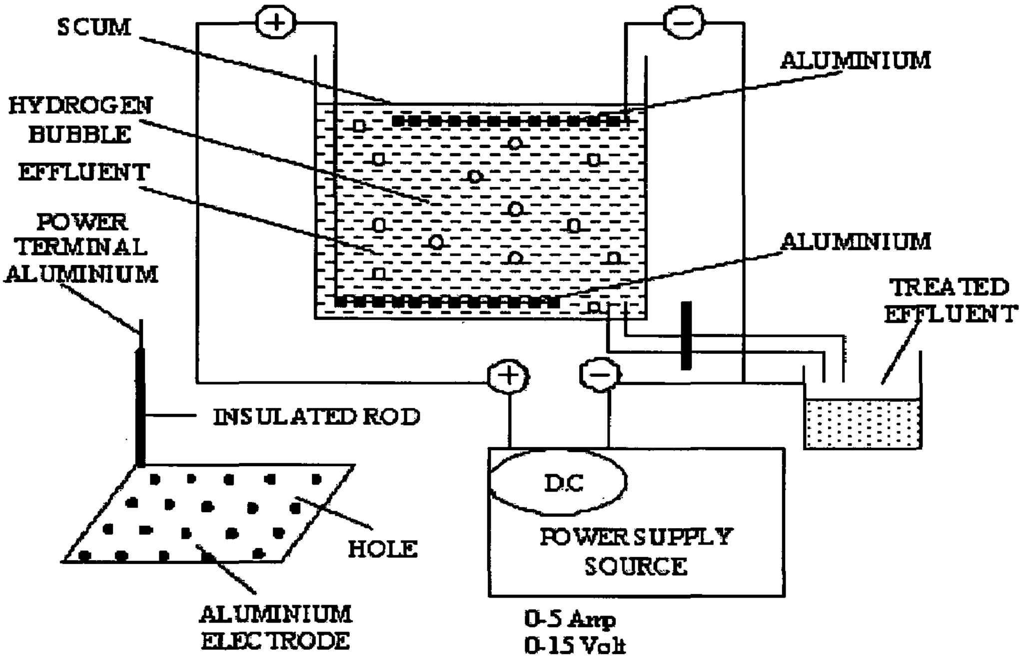


Fig. 4.2. Schematic diagram of the laboratory scale batch electroflotation System

CHAPTER 5

RESULTS AND DISCUSSION

The experimental results on the demulsification by electroflotation are presented in the following. The treatment process had to ensure that the oil concentrations in the supernatant are within the permissible limit of 10 mg/l prescribed by the Central Pollution Control Board (CPCB), Delhi. Therefore, the concentration of residual oil in the treated water is more important than the percentage of oil removed.

5.1 EFFECT OF VOLTAGE

The effect of voltage is shown in Fig.5.1, Fig.5.2 and Fig.5.3. With increase in voltage from 2.5 to 5.0 volts the % amount of oil removed also increased. For example 77.51 to 89.24% of oil was removed in first 20 minutes for 100mg/l concentration of oil. On further increasing voltage beyond % volts the amount of oil removed was almost same for same time of treatment at 7.5 volt.

Number of Electrodes: 2, Electrode Spacing: 15 mm, Electrode is fully ubmerged

Table 5.1. Effect of voltage for 50 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Voltage 2.5 V and 0.2 A				
1	10	25.22	49.55	8.33X 10^{-5}
2	20	13.89	72.22	16.7X 10^{-5}
3	30	10.89	78.22	25.0X 10^{-5}
4	40	7.71	84.57	33.3X 10^{-5}
5	50	6.46	87.08	41.7X 10^{-5}
Voltage 5.0 V and 0.4 A				
1	10	22.33	55.34	33.3X 10^{-5}
2	20	9	82	66.7X 10^{-5}
3	30	7.64	84.72	100.0X 10^{-5}
4	40	6.54	86.92	133.3X 10^{-5}
5	50	5.34	89.32	166.7X 10^{-5}
7.5 V and 0.9 A				
1	10	22	56	112.5X 10^{-5}
2	20	8.57	82.86	225X 10^{-5}
3	30	7.64	84.72	337.5X 10^{-5}
4	40	7.2	85.6	450X 10^{-5}
5	50	6.14	87.72	562.5X 10^{-5}

Table 5.2. Effect of voltage for 70 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Voltage 2.5 V and 0.2 A				
1	10	32.75	53.21	8.33X 10^{-5}
2	20	17.62	74.81	16.7X 10^{-5}
3	30	14.47	79.31	25.0X 10^{-5}
4	40	8.99	87.15	33.3X 10^{-5}
5	50	7.32	89.53	41.7X 10^{-5}
Voltage 5.0 V and 0.4 A				
1	10	29.75	57.5	33.3X 10^{-5}
2	20	10.36	85.2	66.7X 10^{-5}
3	30	8.54	87.8	100.0X 10^{-5}
4	40	6.58	90.6	133.3X 10^{-5}
5	50	5.11	92.7	166.7X 10^{-5}
Voltage 7.5 V and 0.9 A				
1	10	29.3	58.13	112.5X 10^{-5}
2	20	9.84	85.93	225X 10^{-5}
3	30	8.81	87.41	337.5X 10^{-5}
4	40	8.15	88.34	450X 10^{-5}
5	50	6.91	90.12	562.5X 10^{-5}

Table 5.3. Effect of voltage for 100 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Voltage 2.5 V and 0.2 A				
1	10	41.69	58.31	8.33X 10^{-5}
2	20	22.49	77.51	16.7X 10^{-5}
3	30	18.57	81.43	25.0X 10^{-5}
4	40	8.42	91.58	33.3X 10^{-5}
Voltage 5.0 V and 0.4A				
1	10	39.35	60.65	33.3X 10^{-5}
2	20	10.76	89.24	66.7X 10^{-5}
3	30	8.62	91.38	100.0X 10^{-5}
4	40	4.26	95.74	133.3X 10^{-5}
Voltage 7.5 V and 0.9A				
1	10	38.03	61.97	112.5X 10^{-5}
2	20	10.07	89.93	225X 10^{-5}
3	30	9.14	90.86	337.5X 10^{-5}
4	40	6.63	93.37	450X 10^{-5}

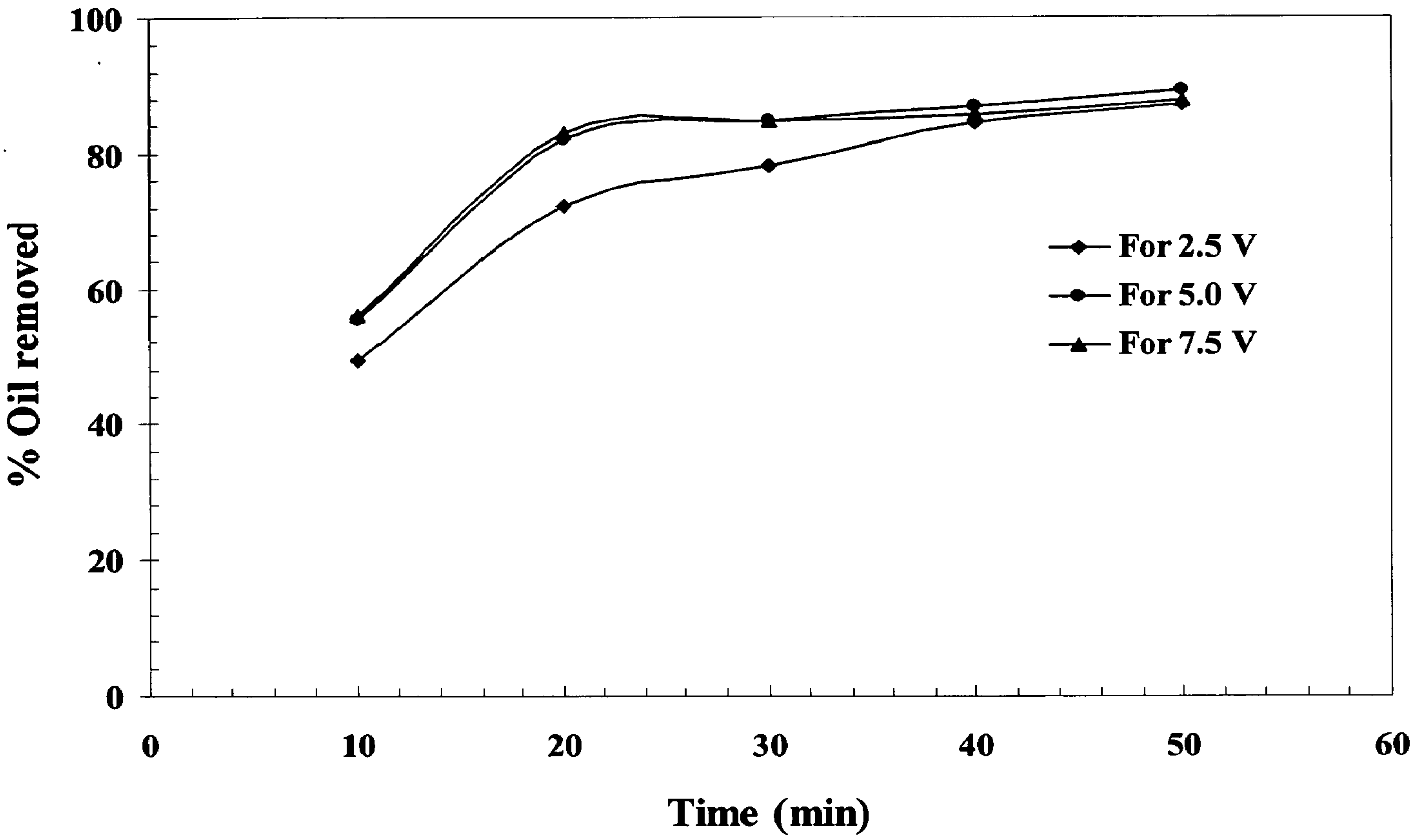


Fig.5.1. Effect of voltage on amount of oil removed for 50 mg/l concentration of oil

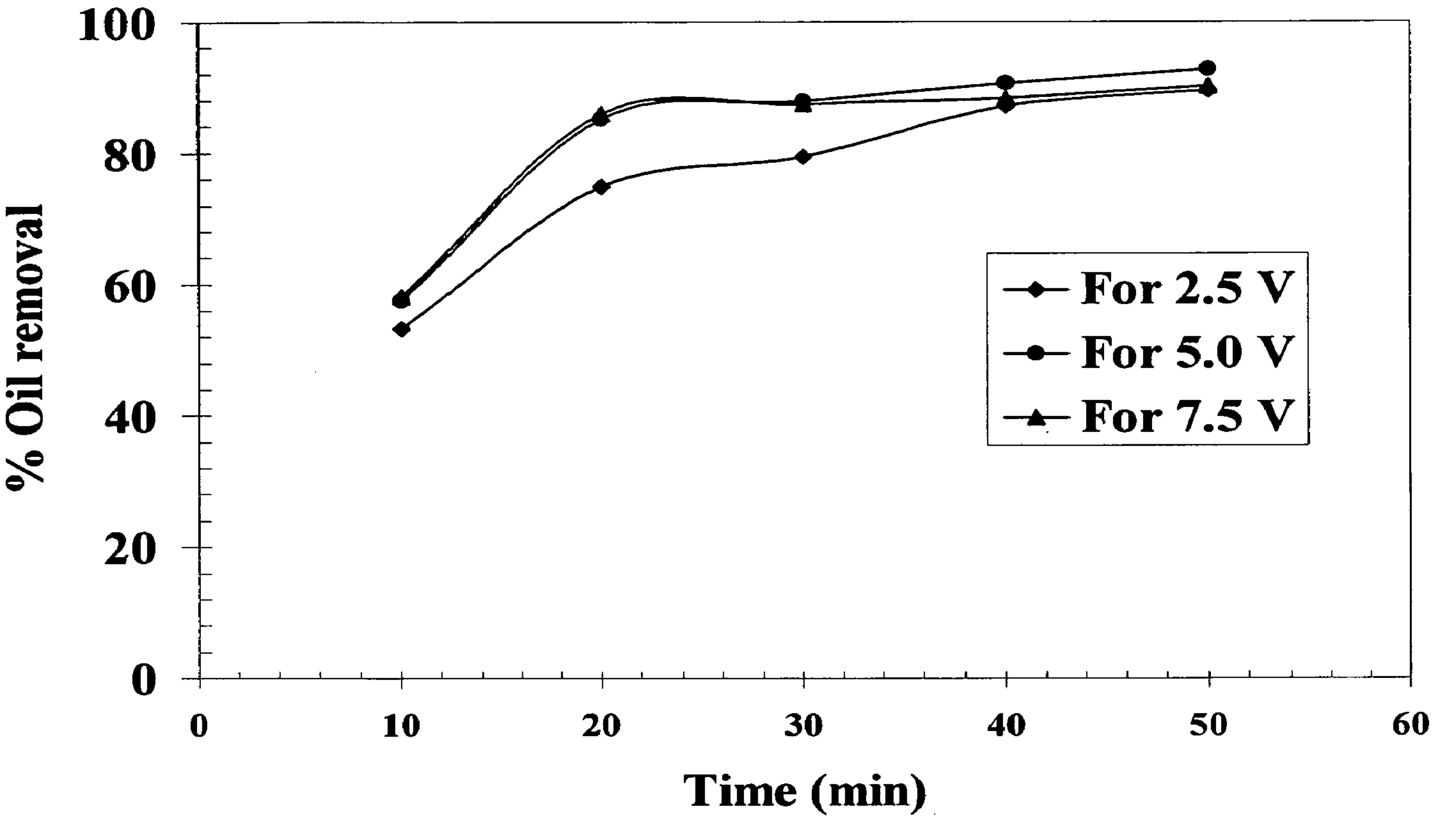


Fig.5.2. Effect of voltage on amount of oil removed for 70 mg/l concentration of oil

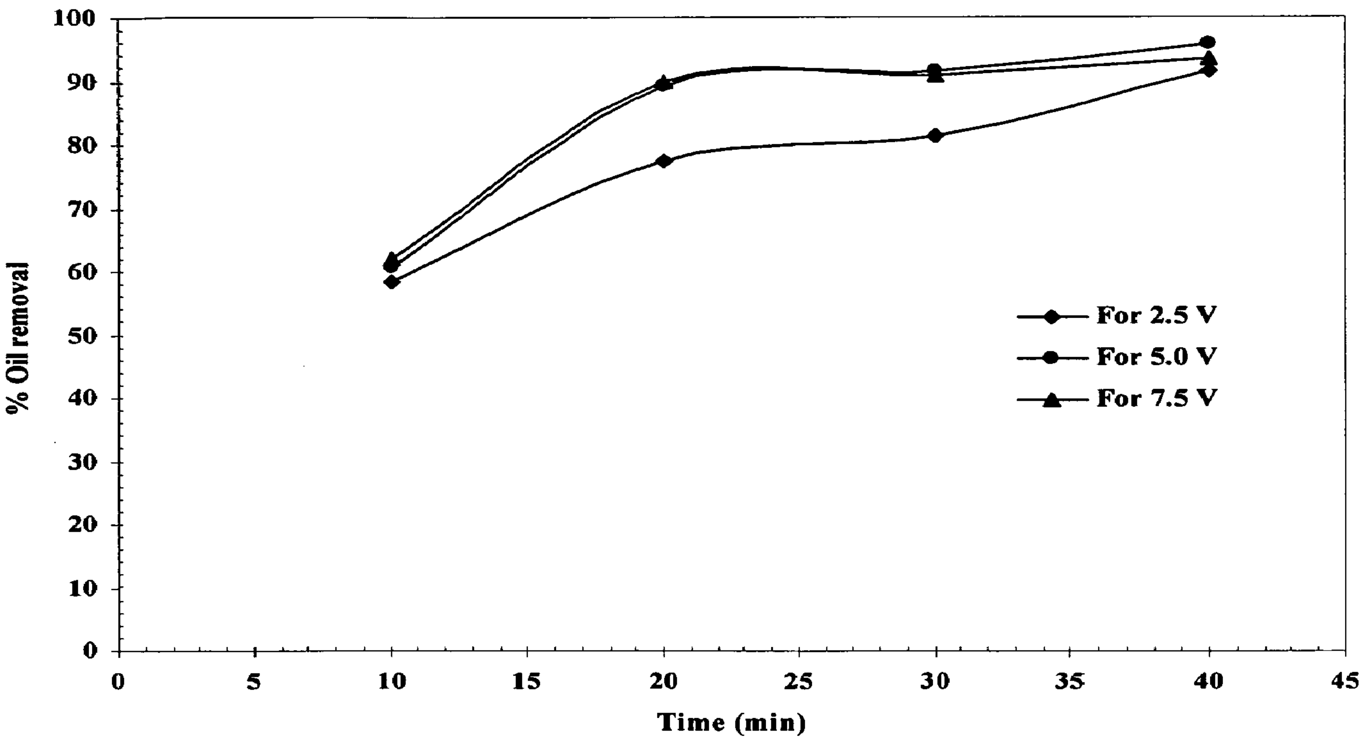


Fig. 5.3. Effect of voltage on amount of oil removed for 100 mg/l concentration of oil

5.2 EFFECT OF SALINITY

Fig.5.4, Fig.5.5 and Fig.5.6 indicates the salinity on electroflotation for oil removal. The results show that as the salinity of the effluent is decreased the amount of oil removal increase and period of treatment and electricity consumption decrease. It is possible to remove 96.14% oil within 30 minutes at 4 mg/l salinity of effluent for 100mg/l concentration of oil; moreover, 84.25% oil was removed within 10 minutes of treatment time. On increasing the salinity amount of oil removed decreased 93.17% oil was removed in 40 minutes.

Number of Electrodes: 2
Electrode Spacing: 15 mm
Electrode is fully submerged
Voltage applied: 5.0 V
Current supplied: 0.4 A

Table 5.4. Effect of salinity for 50 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Salinity 4 mg/l				
1	10	8.56	82.88	$33.3X\ 10^{-5}$
2	20	3.56	92.88	$66.7X\ 10^{-5}$
3	30	2.78	94.44	$100.0X\ 10^{-5}$
4	40	2.33	95.34	$133.3X\ 10^{-5}$
5	50	2	96	$166.7X\ 10^{-5}$
Salinity 6 mg/l				
1	10	20.56	58.88	$33.3X\ 10^{-5}$
2	20	8.33	83.34	$66.7X\ 10^{-5}$
3	30	7.89	84.22	$100.0X\ 10^{-5}$
4	40	7	86	$133.3X\ 10^{-5}$
5	50	5.33	89.34	$166.7X\ 10^{-5}$
Salinity 8 mg/l				
1	10	21.33	57.34	$33.3X\ 10^{-5}$
2	20	9.11	81.78	$66.7X\ 10^{-5}$
3	30	8.78	82.44	$100.0X\ 10^{-5}$
4	40	7.45	85.1	$133.3X\ 10^{-5}$
5	50	5.67	88.66	$166.7X\ 10^{-5}$

Table 5.5. Effect of salinity for 70 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Salinity 4 mg/l				
1	10	11.74	83.22	33.3X 10^{-5}
2	20	4.52	93.54	66.7X 10^{-5}
3	30	3.63	94.81	100.0X 10^{-5}
4	40	2.28	96.73	133.3X 10^{-5}
Salinity 6 mg/l				
1	10	27.13	61.23	33.3X 10^{-5}
2	20	10.96	84.33	66.7X 10^{-5}
3	30	9.85	85.92	100.0X 10^{-5}
4	40	7.59	89.16	133.3X 10^{-5}
5	50	6.77	90.32	166.7X 10^{-5}
Salinity 8 mg/l				
1	10	27.77	60.31	33.3X 10^{-5}
2	20	12.49	82.15	66.7X 10^{-5}
3	30	11.32	83.82	100.0X 10^{-5}
4	40	8.17	88.32	133.3X 10^{-5}
5	50	7.05	89.92	166.7X 10^{-5}

Table 5.6. Effect of salinity for 100 mg/l oil concentration

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
Salinity 4 mg/l				
1	10	15.75	84.25	33.3X 10^{-5}
2	20	6.57	93.43	66.7X 10^{-5}
3	30	3.86	96.14	100.0X 10^{-5}
Salinity 6 mg/l				
1	10	34.24	65.76	33.3X 10^{-5}
2	20	11.73	88.27	66.7X 10^{-5}
3	30	11.51	88.49	100.0X 10^{-5}
4	40	5.89	94.11	133.3X 10^{-5}
Salinity 8 mg/l				
1	10	35.85	64.15	33.3X 10^{-5}
2	20	14.62	85.38	66.7X 10^{-5}
3	30	13.18	86.82	100.0X 10^{-5}
4	40	6.83	93.17	133.3X 10^{-5}

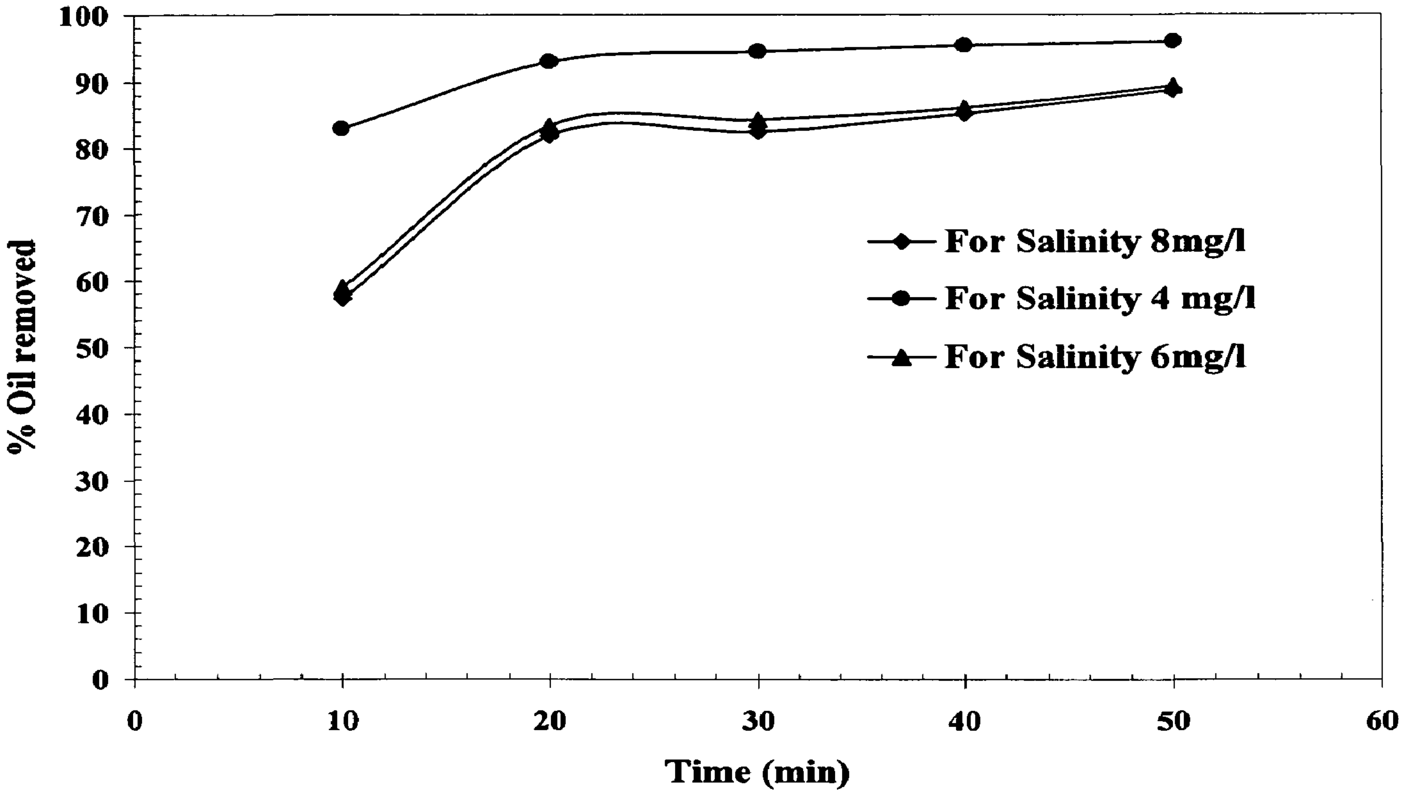


Fig. 5.4. Effect of Salinity on amount of oil removed for 50 mg/l concentration of oil

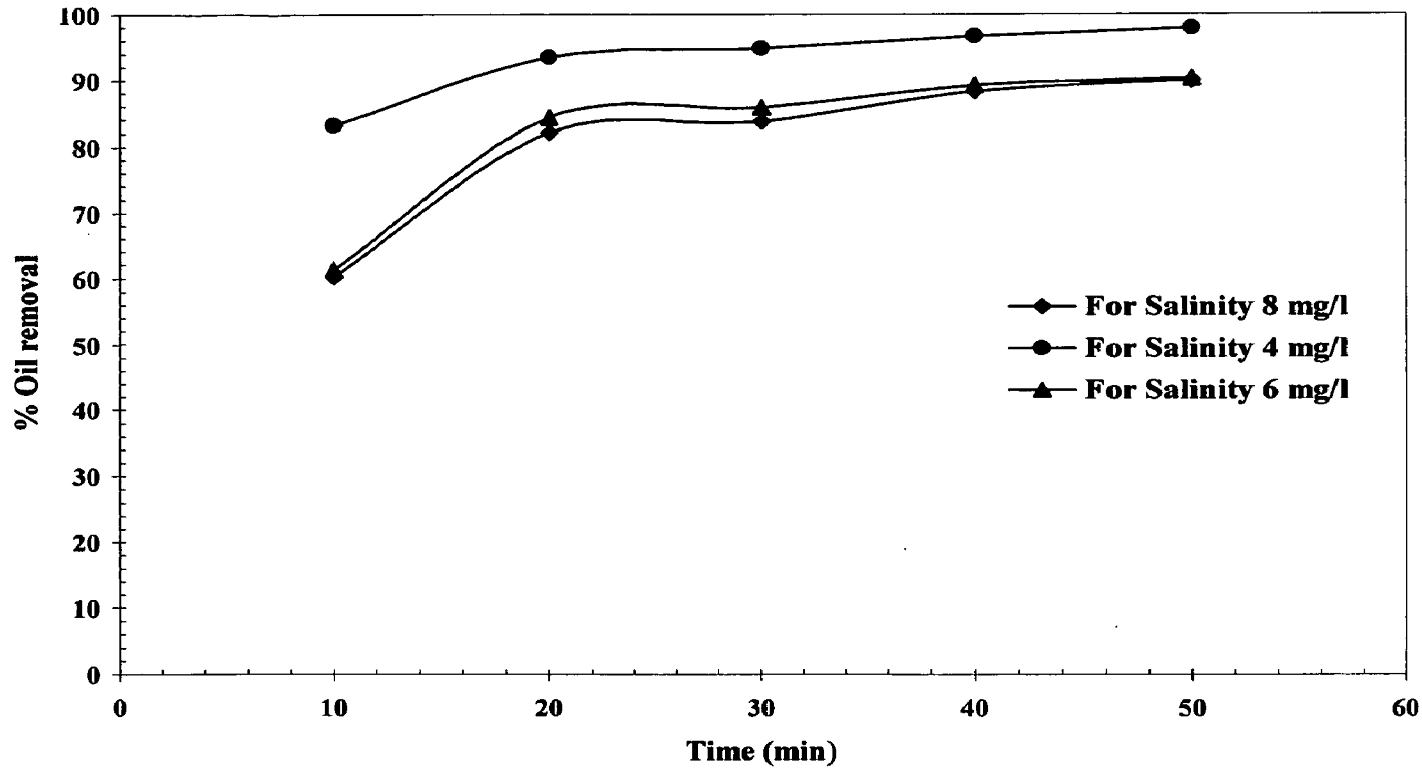


Fig. 5.5. Effect of Salinity on amount of oil removed for 70 mg/l concentration of oil

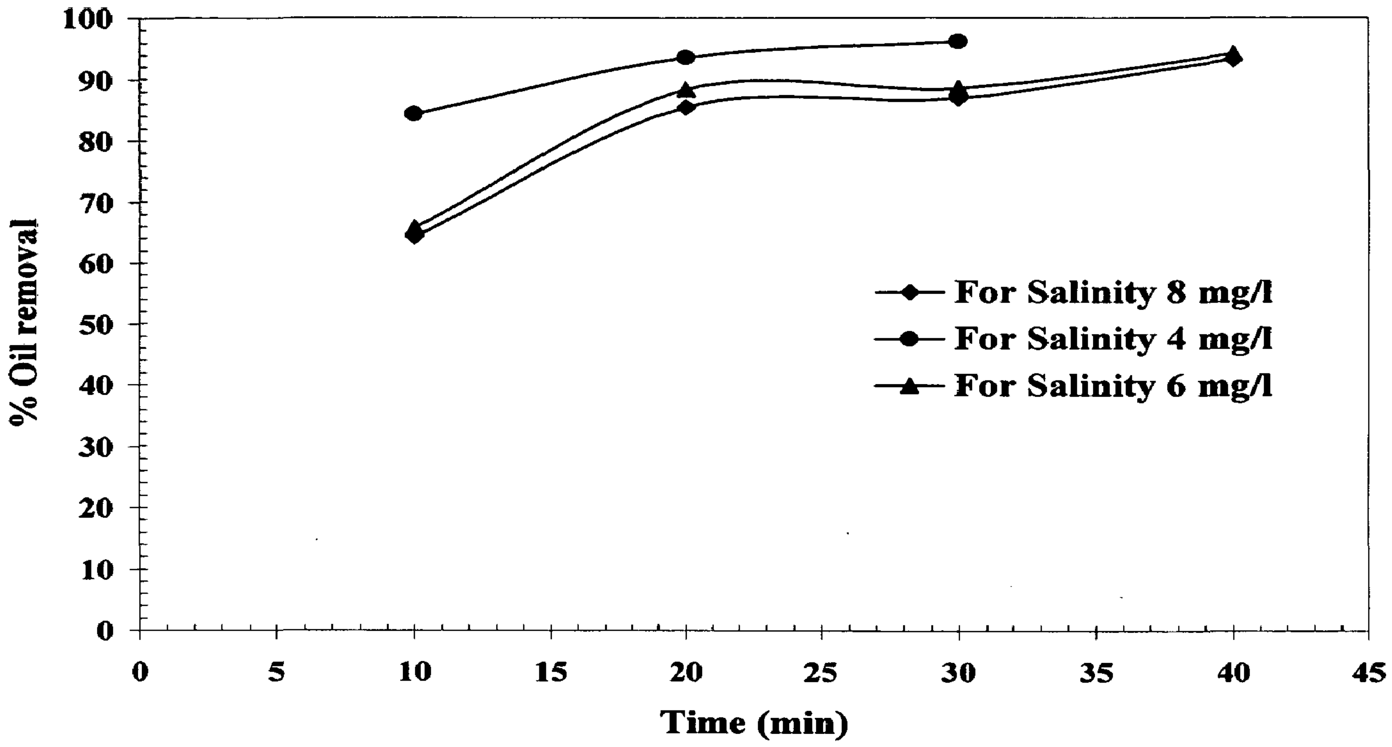


Fig.5.6. Effect of Salinity on amount of oil removed for 100 mg/l concentration of oil

5.3 EFFECT OF pH

The effect of pH on the electroflotation of effluent is shown in Fig.5.7. I t is clear from the results that on decreasing pH of the effluent from its original value 6.65 the rate of amount oil removal increases and increasing pH of the effluent from its original value 6.65 the rate of amount removal decreases. At pH 4.72 the amount oil removal is 91.46%bwithin 40 minutes. With decrease in pH of the effluent the treatment time also decreases. The electricity consumption also decreases with decrease of pH. However, on increasing pH of the effluent the process of oil removal decreases and time of treatment and electricity consumption increases. Fig.5.7 indicates that the amount of oil removal is almost same in the 6.65 to 7.28 pH range. The rate removal oil at all pH values is very sharp during first 20 minutes and slows down there after.

Oil concentration: 50 mg/l
Number of Electrodes: 2
Electrode Spacing: 15 mm
Electrode is fully submerged
Voltage applied: 5.0 V
Current supplied: 0.4 Amp
pH of effluent was increased by dilute H_2SO_4 and increased by dilute NaOH to desired value.

Table 5.7. Effect of pH

S.No.	Treatment time (min.)	Final oil conc. (mg/l)	% Oil removed	Electricity consumed (kWh/l)
6.65 pH				
1	10	25.22	49.55	$33.3X\ 10^{-5}$
2	20	13.89	72.22	$66.7X\ 10^{-5}$
3	30	10.89	78.22	$100.0X\ 10^{-5}$
4	40	7.71	84.57	$133.3X\ 10^{-5}$
5	50	6.46	87.08	$166.7X\ 10^{-5}$
7.28 pH				
1	10	26.19	47.62	$33.3X\ 10^{-5}$
2	20	14.93	70.14	$66.7X\ 10^{-5}$
3	30	12.08	75.83	$100.0X\ 10^{-5}$
4	40	8.84	82.31	$133.3X\ 10^{-5}$
5	50	7.48	85.04	$166.7X\ 10^{-5}$
8.63 pH				
1	10	36.84	26.32	$33.3X\ 10^{-5}$
2	20	20.59	58.82	$66.7X\ 10^{-5}$
3	30	15.24	69.53	$100.0X\ 10^{-5}$
4	40	10.75	78.51	$133.3X\ 10^{-5}$
5	50	9.0	82	$166.7X\ 10^{-5}$
4.72 pH				
1	10	14.38	71.23	$33.3X\ 10^{-5}$
2	20	6.19	87.62	$66.7X\ 10^{-5}$
3	30	4.87	90.25	$100.0X\ 10^{-5}$
4	40	4.27	91.46	$133.3X\ 10^{-5}$
5	50	3.65	92.69	$166.7X\ 10^{-5}$

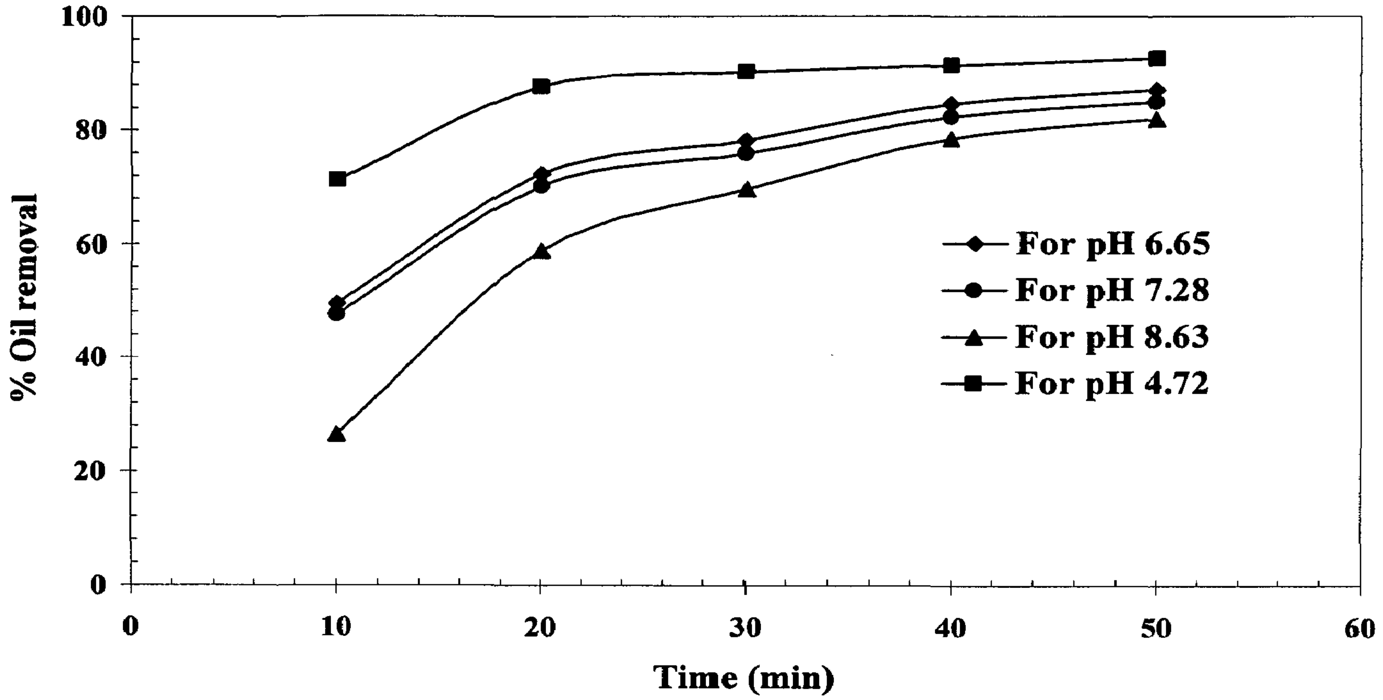


Fig. 5.7. Effect of pH on amount of oil removed for 50 mg/l of concentration of oil.

5.4 EFFECT OF OIL CONCENTRATION

The result in Fig.5.8, Fig.5.9 and Fig.5.10 shows that increasing concentrations 50 to 100 mg/l enhances 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 review indicated that smaller oil drops can not be removed from waste emulsions by electroflotation unless their size is increased **[Markkhasin]**. This leads to an enhancement in collision probability between oil drop and gas bubble.

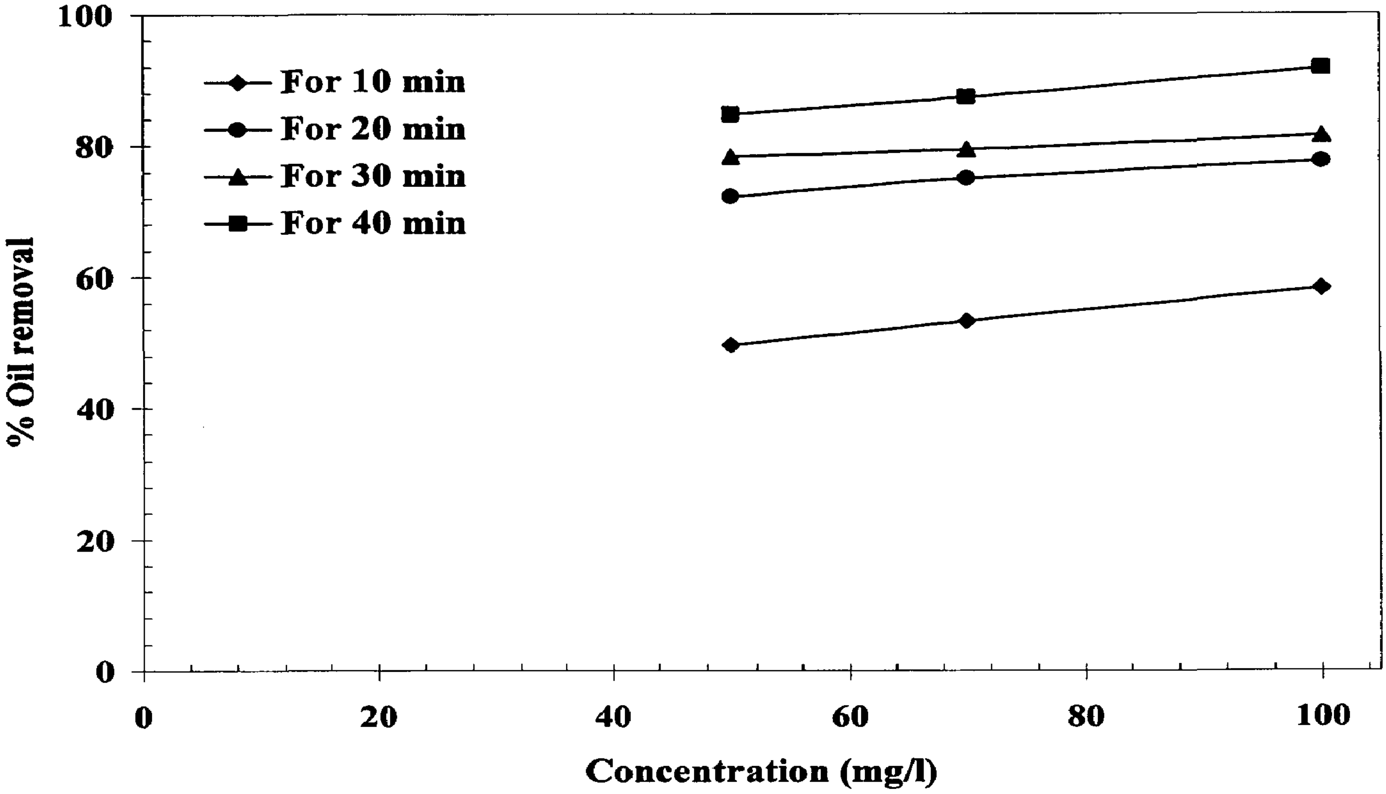


Fig.5.8. Effect of concentration on amount of oil removed at 2.5 V

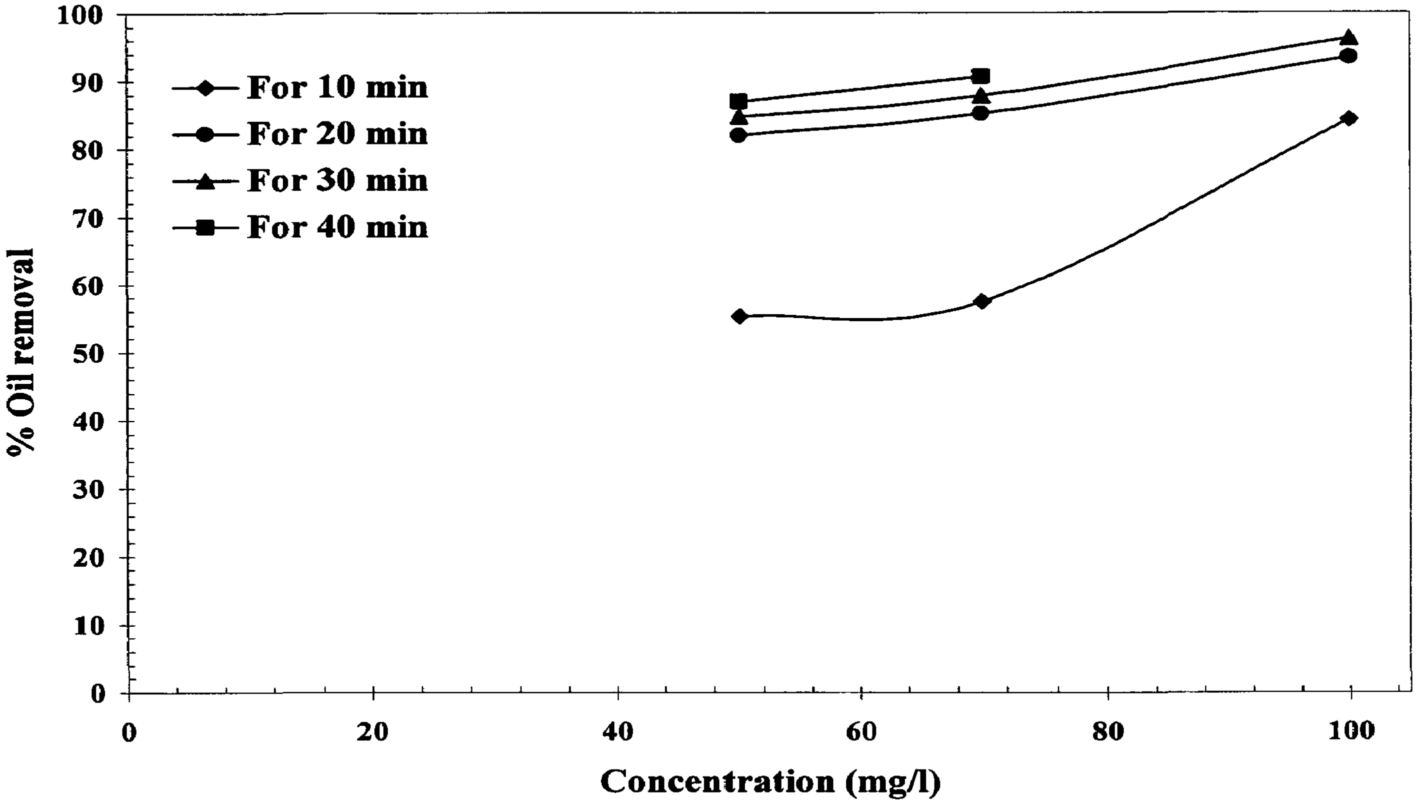


Fig. 5.9. Effect of concentration on amount of oil removed at 5.0 V

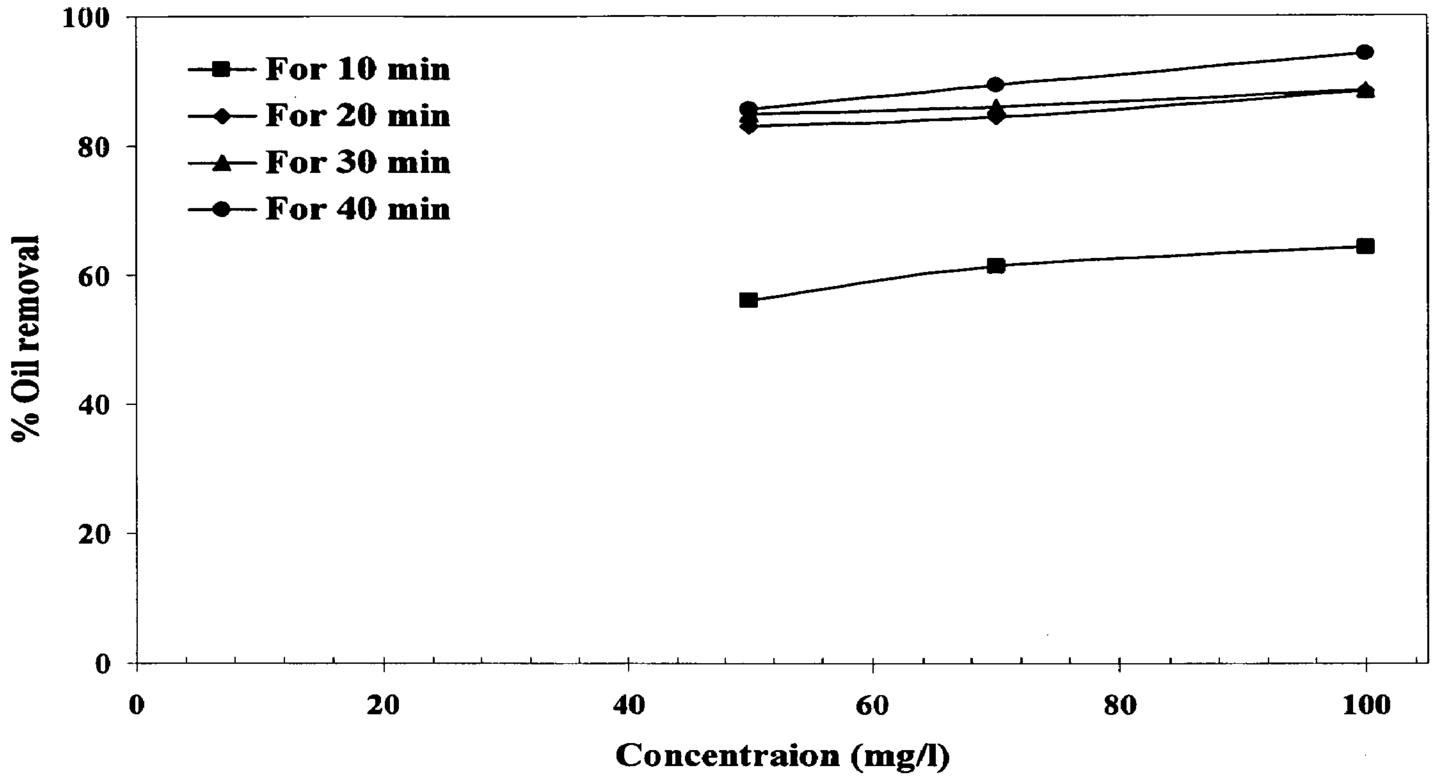


Fig. 5.10. Effect of concentration on amount of oil removed at 7.5 V

5.5 EFFECT OF FLOTATION TIME

Fig.5.11 to Fig.5.19 shows the variation in oil concentration with flotation time. For example at initial concentration equal to 50 mg/l. For flotation time of 30 and 50 minutes at 5.0 volt, the oil concentrations are 7.64 and 5.34 mg/l, respectively. The oil removal values are 84.72% and 89.32% for 30 and 50 minutes, respectively.

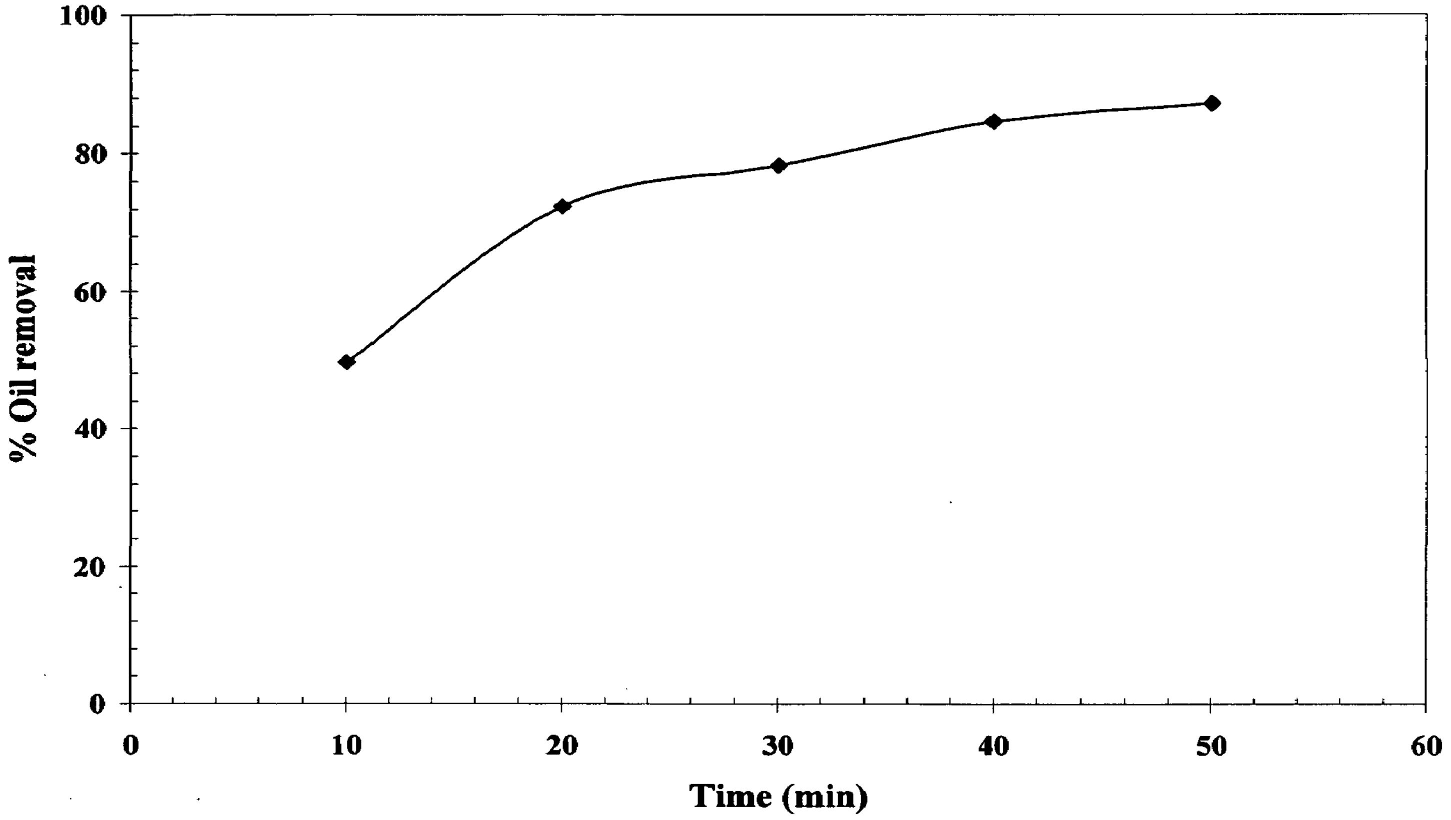


Fig.5.11. Effect of flotation time on amount of oil removed at 2.5 V for 50 mg/l of oil concentration.

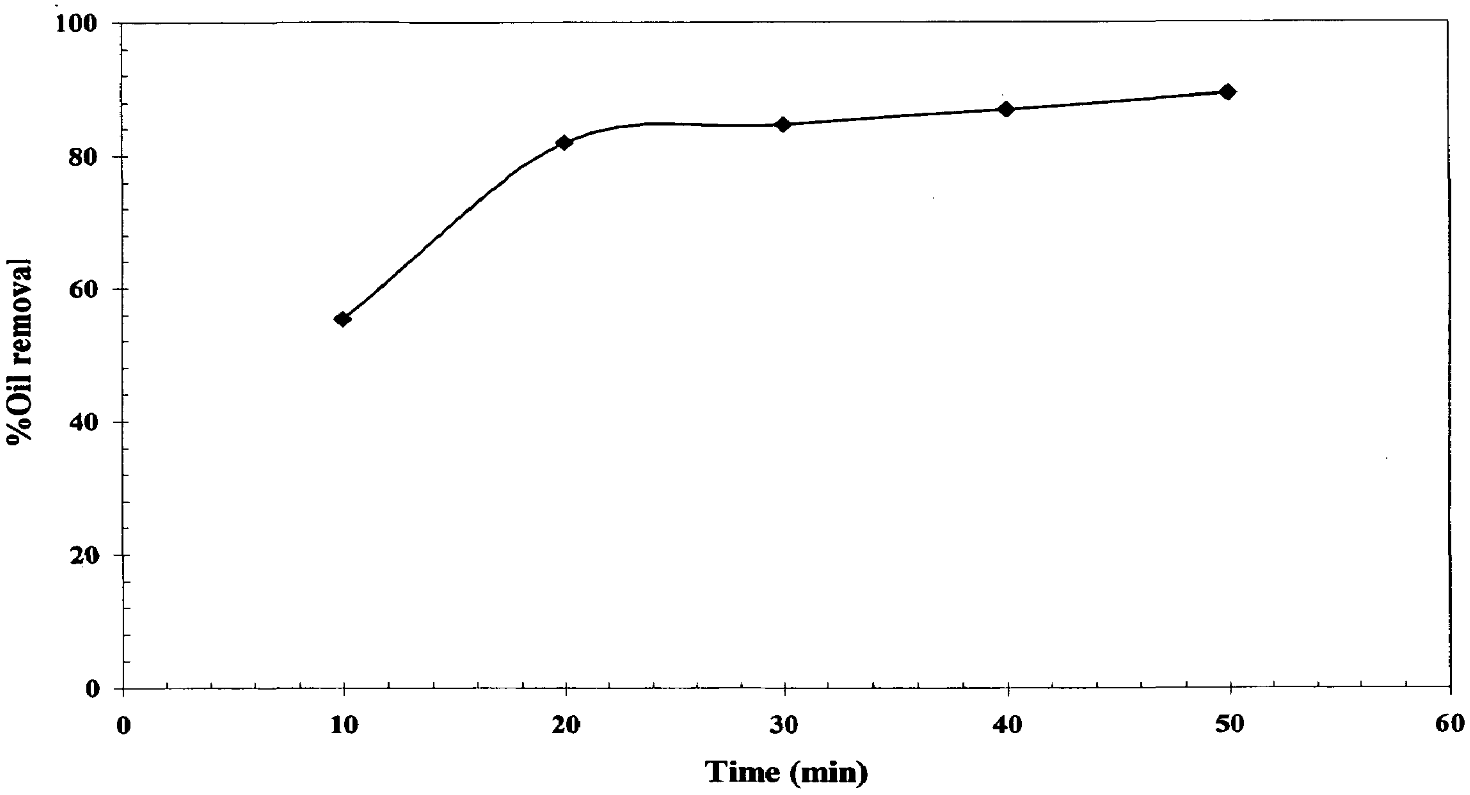


Fig. 5.12. Effect of flotation time on amount of oil removed at 5.0 V for 50mg/l of oil concentration.

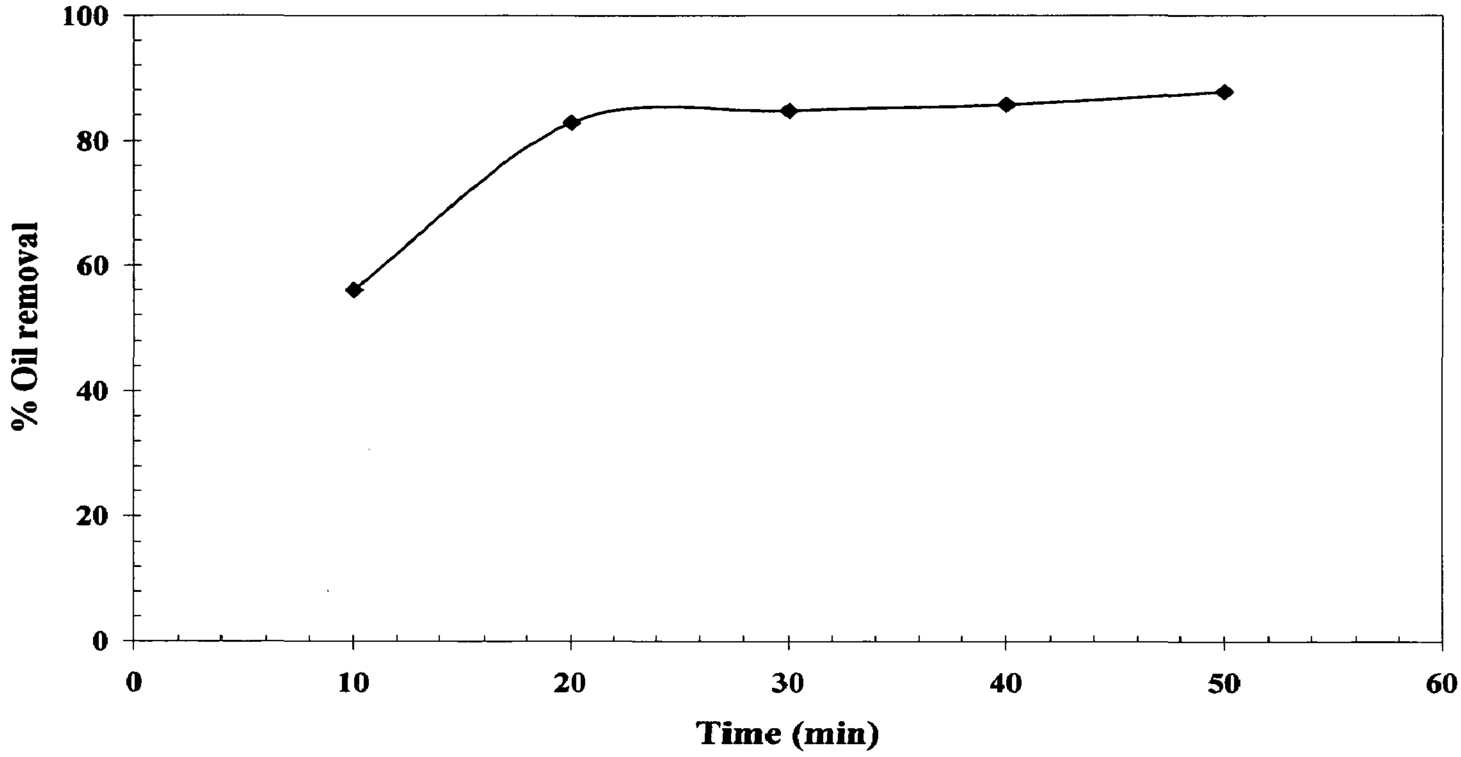


Fig-5.13. Effect of flotation time on amount of oil removed at 7.5 V for 50 mg/l of oil concentration.

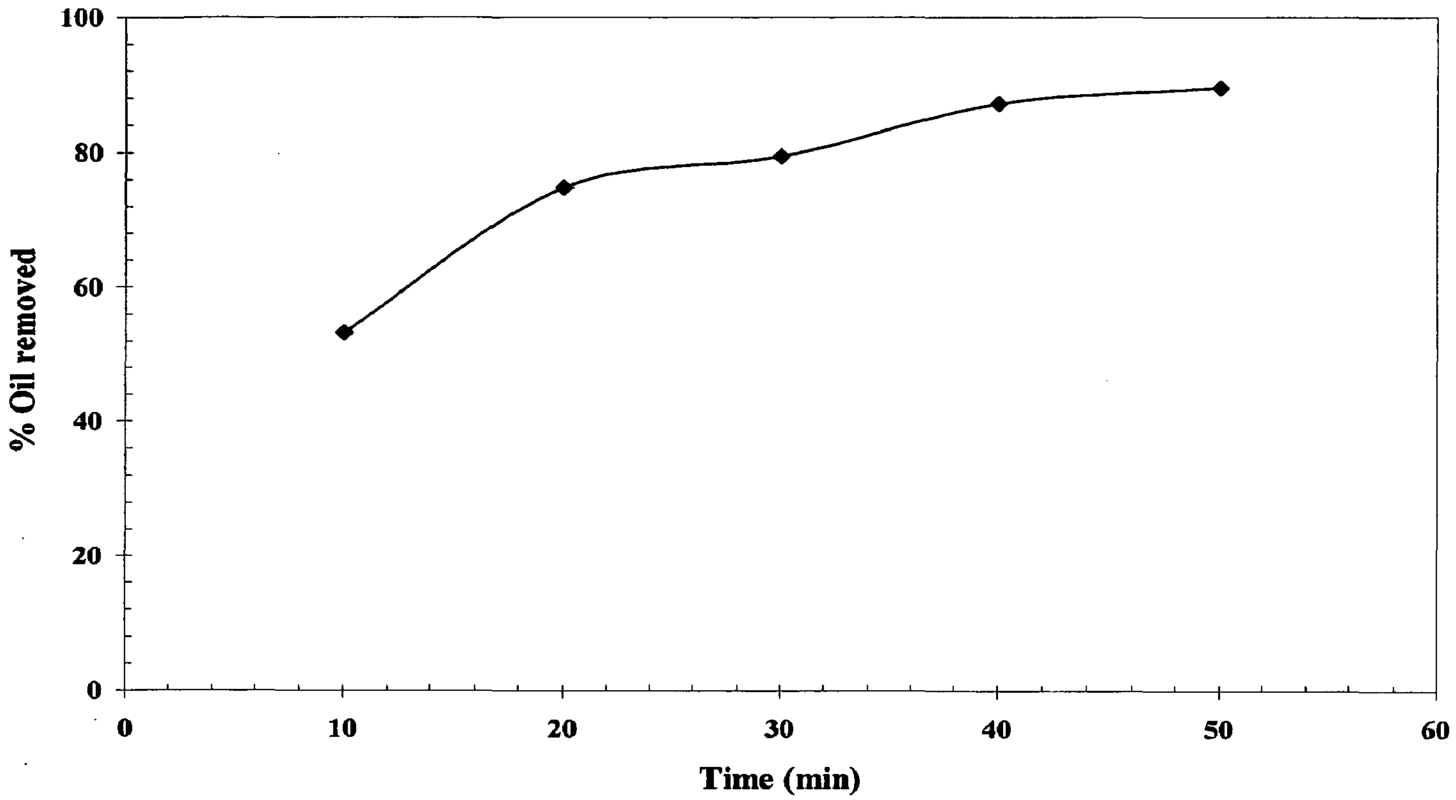


Fig. 5.14. Effect of flotation time on amount of oil removed at 2.5 V for 70 mg/l of oil concentration.

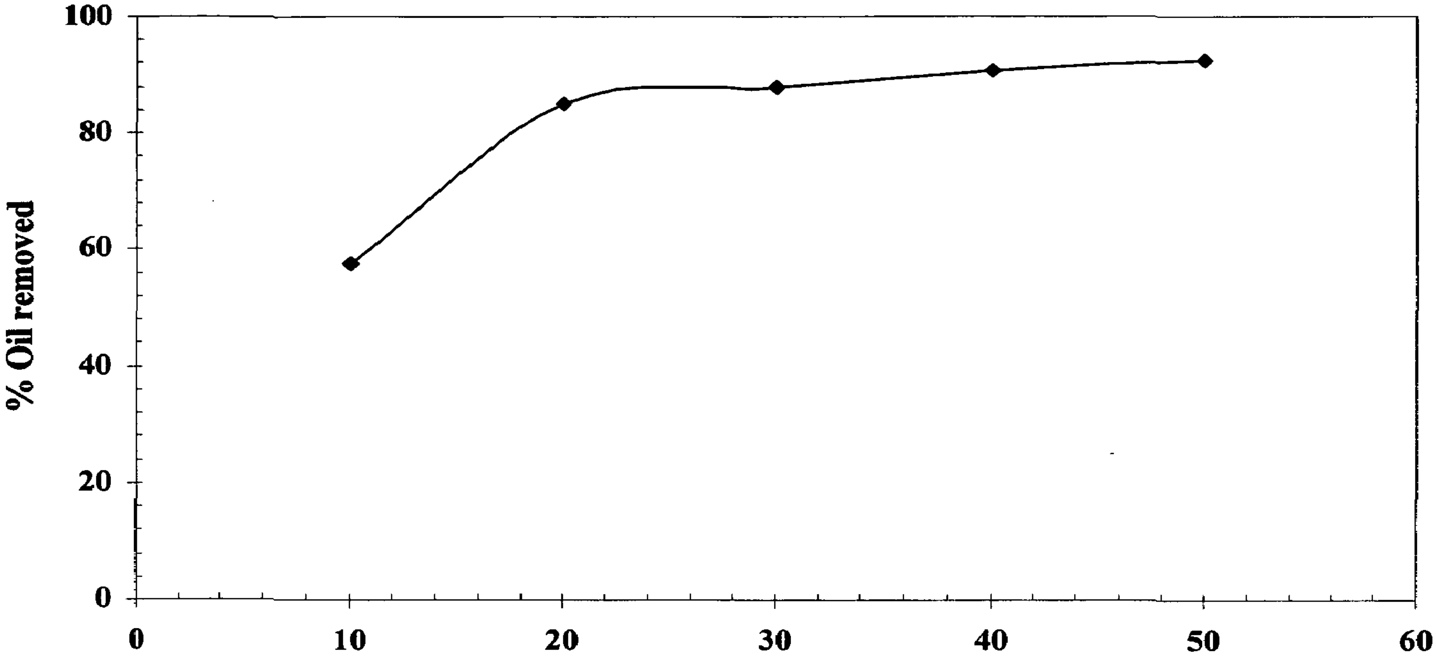


Fig. 5.15. **Effect of flotation time on amount of oil removed at 5.0 V for 70 mg/l of oil concentration.**

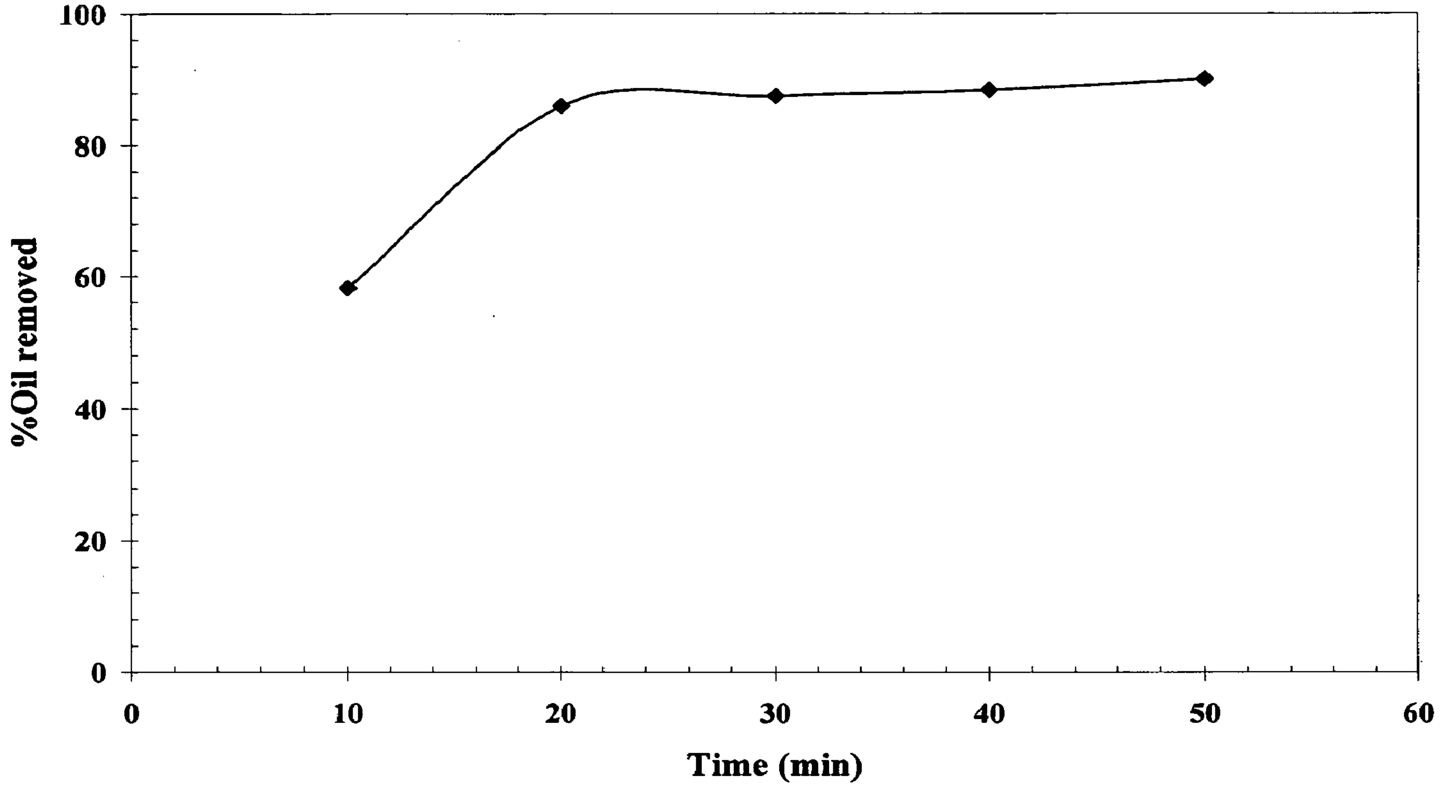


Fig. 5.16. Effect of flotation time on amount of oil removed at 7.5 V for 70 mg/l of oil concentration.

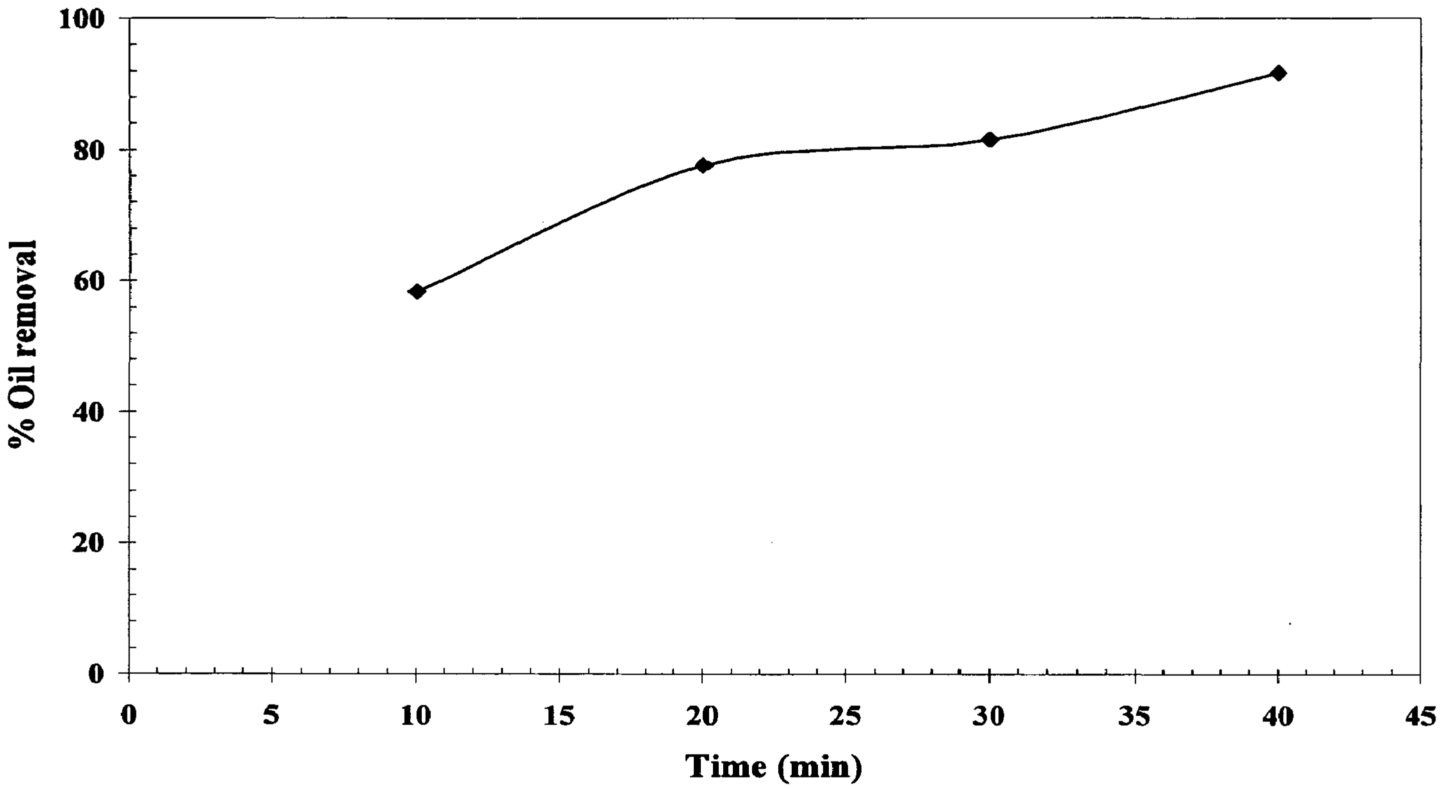


Fig.-5.17. Effect of flotation time on amount of oil removed at 2.5 V for 100 mg/l of oil concentration.

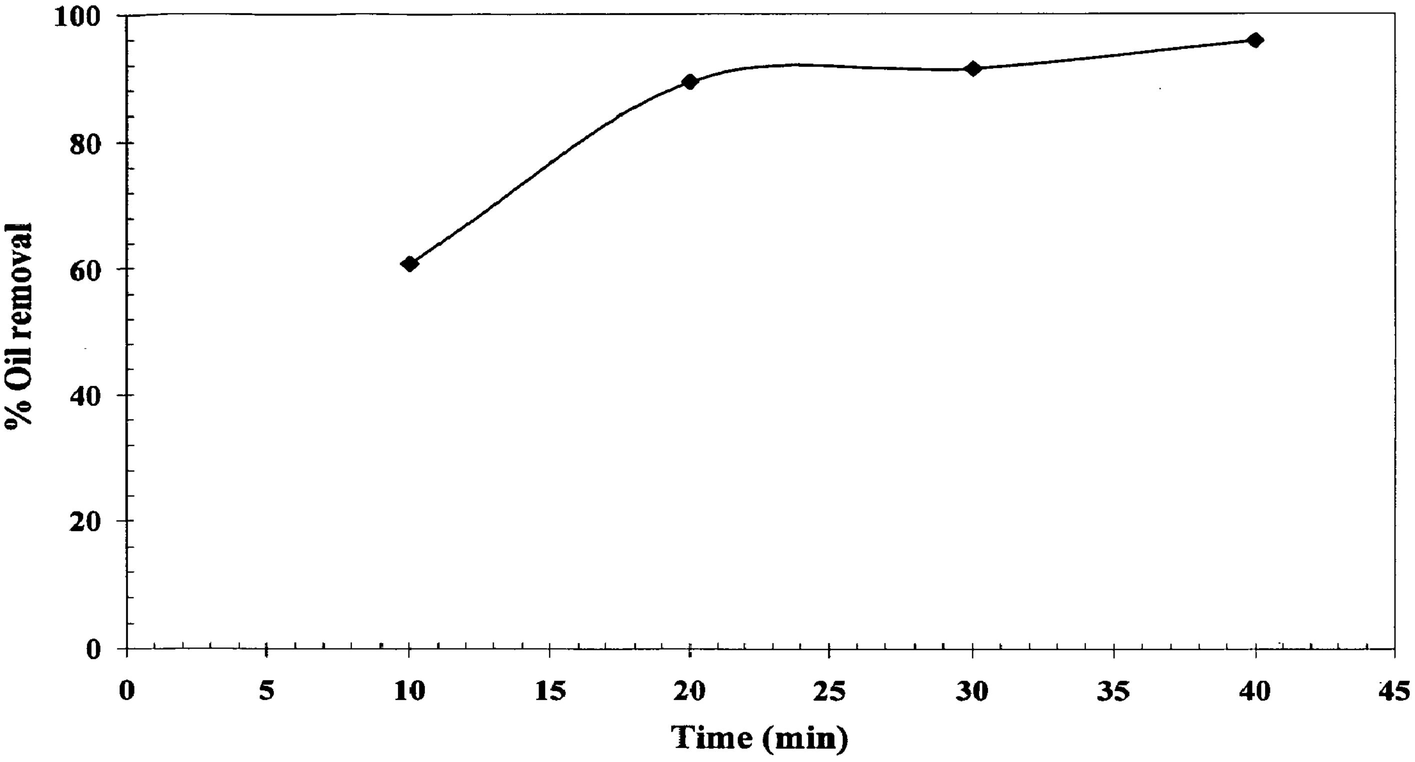


Fig. 5.18. Effect of flotation time on amount of oil removed at 5.0 V for 100 mg/l of oil concentration.

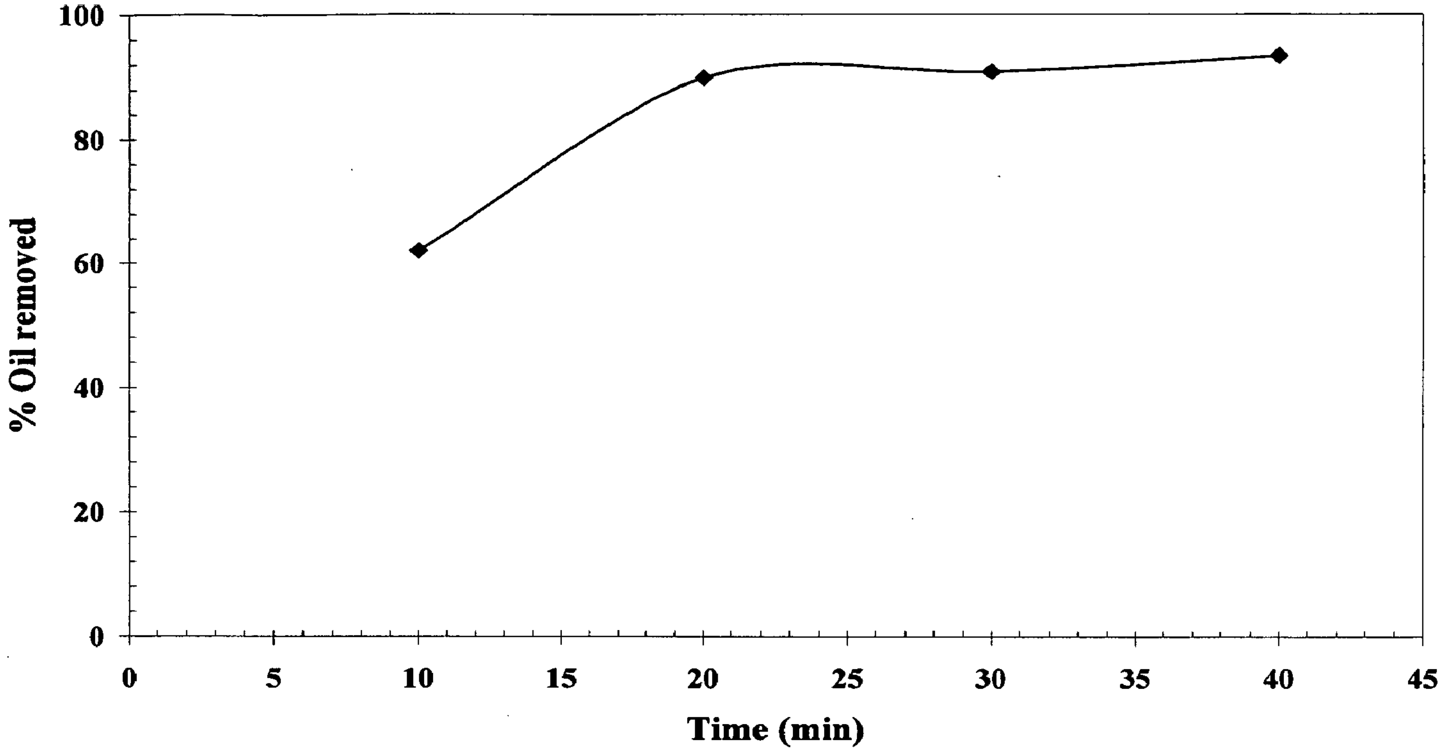


Fig. 5.19. Effect of flotation time on amount of oil removed at 7.5 V for 100 mg/l of oil concentration.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

From the present study, the following conclusions are drawn:

1. Electroflotation is an excellent technique of oil removal from waste water. The byproduct hydrogen gas was generated, though, in small quantities, could be utilized for other purpose.
2. 20 minute treatment of the effluent with 5.0 volt and 0.4 Ampere current is sufficient to bring down oil content within permissible limit of 10mg/l for surface disposal.
3. 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.
4. More than 90% oil could be removed at $pH = 4.72$ in 30 minutes treatment time.
5. Destabilization of the effluent was faster at low salinity (4.0 g/l) of effluent. The electroflotation technique could remove almost all the oil within 10 minutes from the low salinity effluent.
6. The technique is more efficient in case of effluents with higher oil content.

6.2 RECOMMENDATIONS

1. The physics of stability and destabilization of oil-water emulsion shall be studied with the measurement of Zeta potential, electophoretic mobility and UV absorption.
2. FTIR spectroscopy shall be attempted for the supernatant and the oil-water emulsion in order to understand the phenomena of demulsification.
3. Various parameters for the design and operation of continuous method shall be studied.

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APPENDIX A

Determination of Oil in Water

Apparatus

1. Separating Funnel
2. Beaker- 500 ml capacity
3. Conical flask- 50 ml capacity

Reagents

1. CCl_4
2. Anhydrous Sodium Sulphate.

Procedure

1. A beaker of 500 ml capacity is cleaned well. Conical flask of 50 ml is cleaned and dried in oven.
2. 10 ml of sample is taken in beaker.
3. To the sample in beaker 10 ml of CCl_4 solution is added for 3-4 different portion of time.
4. It is then taken in separating funnel. The funnel is shaken for 1 minute. The liquid layers are allowed to separate. The aqueous layer is rejected after it is drawn from the funnel.
5. 2 gm of anhydrous sodium sulphate is placed insides the Whatman filter paper cone and the organic solvent phase is filtered out from the separating funnel through this filter paper into a 50 ml conical flask.
6. Absorbance of organic solvent phase is measured in UV spectrometer at 430 nm.
7. From standard curve of mg/l crude oil Vs absorbance concentration of sample is calculated.