ELECTROCHEMICAL TREATMENT OF OIL EMULSION

by

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ABSTRACT

In this study, destabilization of oil emulsion was investigated in the laboratory by ferric sulfate coagulation and electrophoresis using the jar test apparatus. The colloids in the oil emulsion were of the hydrophilic type which need both desolvation and neutralization of charges for coagulation. The oil concentration in the emulsion was 500 mg/l and the sample size in each beaker was 1000 ml. These two factors were kept constant throughout the study. Ferric sulphate alone was found effective; the efficiency of removal was about 84 percent when a concentration of 200 mg/l of ferric sulfate was used, in a pH range of 5.0 to 10.5. The use of both alternating and direct currents were investigated in combination with ferric sulphate, and the former was found to have little effect on the overall oil removal efficiency. The beakers and the stirrers, both made of stainless steel, were used as two electrodes. In the treatment using direct current and ferric sulphate the effect of polarity was investigated; the treatment using beakers as negative electrodes produced encouraging results. For example, a combination of 200 mg/l of ferric sulphate with direct current of 100 volts applied for 16 minutes showed a removal efficiency of 98 percent, when the pH level was around 7.5. However, it was found that the stirrers were losing weight by giving away ferric ions during treatment.

Some more experiments were carried out at a pH level around 11.0 using direct current and ferric sulphate. Oil removal in the order of 96 percent was obtained when direct current of 100 volts was applied for 16 minutes in conjunction with 200 mg/l of ferric sulfate. No appreciable loss of weight from the stirrers was found.

The change in the amount of sludge produced from the treatment with ferric sulfate alone and in conjunction with direct current was also investigated. Results showed that for the same percent oil removal, the weight of sludge produced remained approximately the same even with the different types of treatment.

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NOTATION

A.C. - Alternating Current

Amp - Ampere

API - American Petroleum Institute

BOD_5 - Biochemical Oxygen Demand (5 days at 20°C)

COD - Chemical Oxygen Demand

D - Dielectric constant

mμ - Millimicron

rpm - Revolution per minute

v - Volts

V - Electrophoretic mobility (microns/sec)(volt)(cm)

X - Applied field (volts)

ζ - Potential difference between interface and liquid (volts)

η - Viscosity of the medium (gm/cm sec)

μ - Micron

π - 3.142857.......

CHAPTER 1

INTRODUCTION

Rapid growth of civilization over the past decades not only contributed to the highly sophisticated standard of living, but also on the other hand created many problems. Pollution of the environment is one such problem and has become a matter of deep concern in view of its increasing effects on everyday life.

Continued expansion of petroleum production, refining and shipping operations, automobile industries, aircraft plants, machine shops, etc., have increased the threat to the environment by oil pollution. In the Metropolitan Sanitary District of Greater Chicago, it was found even 15 years ago that in the wastewater from industries, one of the worst contaminants was oil (18).

Oil spills in the sea, shore and inland water contribute a major part of oil pollution. This is 'free' or 'floating' oil and various methods like skimming techniques, emulsifications, combustion promoters, sinking or sorptions are used to deal with them (3).

The oil present in the industrial wastewaters is mainly emulsified oil. The conventional treatment plants unless equipped with advanced techniques, would not be able to handle such oily wastewaters. Among all the techniques tried to separate oil from oil emulsion, chemical coagulation was found to be the most successful one (3).

Chemical coagulation using ferric sulfate alone or with some other solvents is reported to be effective in destabilization of soluble cutting oil emulsions. However, very little work has been done on treatment of soluble oil emulsions by the electrochemical process.

In this study, the use of both alternating and direct currents in conjunction with ferric sulfate were investigated. The prime object of introducing electric current during coagulation was to reduce coagulant demand and furthermore to minimize sludge production.

CHAPTER 2

LITERATURE SURVEY AND PURPOSE OF THE STUDY

2.1 Types of Oil and Sources

Soluble cutting oil emulsion is an oil-in-water emulsion. In general, there are two types of emulsions, an oil-in-water emulsion and water-in-oil emulsion.

An oil-in-water emulsion consists of oil dispersed in water. This is the most common type of oil emulsion found in most industrial wastes. The water-in-oil emulsion contains water as very small droplets and dispersed in oil. This is relatively of minor concern (43).

Most of the industrial wastes which are oily wastes contain oil-in-water emulsion as the basic contaminant. The petroleum industries and the refineries are mainly responsible for the presence of this soluble cutting oil in the wastewater (3). This type of oil emulsion is very troublesome to destabilize. The other sources are shipping industry, railroad shops, metal processing plants, etc. Even in airports the effluent is reported to contain high concentrations of oil (13). The effluent from these industries always creates water pollution problems, including taste, odour and toxicity. Though very little is known about toxicity, some hydrocarbons have been demonstrated to be quite innocuous (16). The oil-in-water emulsion is present in almost all the effluents from machine shops, automobile assembly plants, roller-bearing plants or transmission plants. These wastewaters contain among other impurities, soaps and alkaline cleaners, acid brightners, free oil, soluble cutting oils, solvents, rusts, inhibitors, paints, metal chips, and grinding fines (25).

It was found by Ries (43) after an extensive literature review, that the cost of oil reclamation is often higher than the price of oil in the market. Presently, a large number of research projects are being carried out on both reclamation and disposal of oily waste. Lagooning is also a common method used for the treatment of oily wastes.

The concentration of oil, in the effluent from different sources, is found to vary in a wide range - from several milligrams per litre (mg/l) to 40,000 mg/l (29). Typical oil concentrations are reported as 442 mg/l at a gear plant (6), 300 mg/l at a roller bearing plant (22) and 2000 mg/l in refinery effluents (7). The effluents from automotive plant and aircraft assembly plant are often found to contain oil ranging from 1000 to 5000 mg/l in concentrations (21).

The reuse of soluble cutting oil is reported in the literature. In most of the cases, the reclaimed soluble oil is allowed to settle, filtered or otherwise treated to remove the metal grindings (40).

2.2 Types of Emulsions and Their Treatment Methods

Emulsion of oil-in-water contains very small globules of oil dispersed in water. The size of these globules are less than 100 mμ (43). These small particles carry a slight negative charge at neutral pH and the repulsive force generated is the main cause for their stability.

Emulsifying agents usually are present to attain the degree of stability which is essential for a stable emulsion (2). Agents which cause or stabilize emulsion can be classified under two headings - ionic or nonionic (3). The ionic emulsifiers have the groups like active carboxyl, sulfonic, amine or hydroxyl groups and soaps which make it chemically active. On the other hand nonionic emulsifying agents are mainly asphaltic resins and, under certain conditions, asphaltenes and waxes.

The most common and widely used emulsifying agents for soluble cutting oil are soaps and sulfonates (43). The soaps used contain fatty acids and the most common fatty acids used are oleic acid, stearic acid and palmitic acids. One of the most accepted emulsifiers for the soluble cutting oil is the mixture of both oleic acid and amines (18).

In 1959, Gilliam (23) reported the use of biological processes for the treatment of refinery wastewater. At the Great Northern Oil Company, three lagoons, a trickling filter and an activated sludge unit were used in series for the treatment of a wastewater containing 10,000 mg/l of oil. The oil removal efficiency of this biological system was very good and the final effluent contained only 3 mg/l of oil. Aerated lagoons, used to treat the wastewater from a steel mill plant, situated on the Missouri River, were reported to remove 89 percent of 200 mg/l of oily waste (49). The chemical oxygen demand (COD) was reduced by 70 percent where the influent COD was 450 mg/l. Cooper (15) reported the treatment of organic industrial wastes by lagooning in California. The wastewater contained many homologues of phenol, partially oxidized water soluble hydrocarbons and sulfur compounds. The average biochemical oxygen demand BOD_5) loading was 53.8 lbs per acre per day and the overall removal was 38.6 percent. A successful lagooning of emulsified oily wastewater, was reported by Griffith (25) but he found that sufficient iron was also present in the wastewater to cause coagulation.

API gravity separator is also used in most of the refineries to separate 'free' or 'floating' oil. Efficiency in removing oil is reported to be as high as 90 percent (7). Dissolved air flotation is also a successful technique in removing oil from this type of wastewater. Rohlich (44) reported that dissolved air flotation process used for a refinery waste emulsion, produced 61 percent oil removal. The oil removal efficiency was increased to 95 percent when alum was added prior to dissolved air flotation (3,44).

Quigley (41) however found that lime alone, or lime plus a trivalent coagulant were very effective in removing emulsified oil.

Oil emulsions that are stabilized by emulsifiers have been more difficult to treat because the colloids present in this type of oil emulsions are of the hydrophilic type. Destabilization of this type of colloids is possible only when the coagulant has the property of desolvation.

Among other techniques, Hart (27) noted that heating emulsions to 160°F, then adding lime and mixing for one hour could destabilize an emulsified waste on a batch basis. After extensive studies, Milne (37) found that coagulation is the most effective means for destabilization of emulsified oil emulsions.

Some laboratory studies were made by Eldridge and Purdy (17) and it was concluded that 1800 to 2400 mg/1 of calcium chloride could salt out most of the stabilized oil. They also described that for 50,000 mg/1 oil concentration, calcium chloride would be added first to destabilize the oil and then would be subjected to ferric sulfate coagulation. For a successful ferric sulfate coagulation, as well as for alum treatment, the alkalinity has to be sufficient (28,18). At St. Thomas, iron salts and calcium chloride are also used by the Ford Motor Company in a preliminary chemical treatment before discharging the oily waste into the lagoons (39). In Canada, the most common chemicals used for coagulation of oil wastewater from automotive plants are reported to be alum, iron salts and lime (38,50).

2.3 The Chemistry of Colloids and Coagulation

The effectiveness of coagulation in a colloidal system mainly depends on the nature and behavior of colloids. A system in which particles of relatively small size (the dispersed phase) are dispersed in a homogeneous medium (the dispersed medium) is called colloidal system and the particles are named colloids (42). The term colloid was one of the earliest contributions by Graham in 1864 (1). He observed some of the characteristics of colloids such as low diffusivity, absence of crystallinity, and of ordinary electrochemical reactions.

The basic properties of colloids can be classified as follows:

a) very large surface area per unit mass,
b) very small settling velocity,
c) all colloids are electrically charged - mainly negative,
d) they have affinity for dispersion medium.

The sizes of the colloidal particles are very small and range from 1 to 100 mμ. They are not visible even with the aid of a high power microscope (45).

Perrin first introduced the terms 'hydrophobic' and 'hydrophilic' in 1905 to differentiate the types of colloids (1). The general terms lyophilic and lyophobic, identify the systems where the dispersed phase has a high affinity for the dispersion medium and low affinity for the dispersion medium respectively. In other words they are called solvent-loving and solvent-hating type of colloids. Hydrophilic colloids possess a shell of water surrounding the particle, resulted from the presence of certain polar groups such as -OH, -COOH and $-NH_2$. This type of colloids move as a unit with the bound water layer, and most of the organic colloids are of this type. But hydrophobic colloids do not have water layer and most of the colloids are inorganic. In general, the hydrophilic colloids are much more stable than hydrophobic colloids (30).

There is another type of classification in colloids known as sols or gels (51). A colloid system of liquid character is known as sols and a system of solid character is known as gels. For example, colloidal clay suspension is a sol and gelatin is a gel.

Lyophobic sols or hydrophobic sols have no interaction between the dispersed phase and continuous phase. These types of colloids were studied thoroughly by different scientists and the reason for their stability was found to be the mutual repulsion of like electrostatic charges (32).

Lyophilic sols have the ability to bind the solvent to the dispersed phase. This affinity for the surrounding solvent is called solvation (35). They have an outermost shell and are more troublesome to coagulate.

The stability of a colloidal system depends upon the net resultant of the repulsive and attractive forces acting on the colloidal particles.

The attraction force is named as van der Waal's force which is caused by the interaction of particle dipoles. For a hydrophobic colloidal system the repulsive force is due to zeta potential but for a hydrophilic colloidal system the repulsive force is not only due to zeta potential but also depends upon the elastic barrier resulted from bound water (42).

The zeta potential is defined as the potential at the shear plane (45). This plane of shear is very important. This plane forms a boundary between the portion of surrounding solution that moves with the particle and the portion which can move independently of the particle. For a hydrophobic colloid, the plane of shear is located very close to the boundary separating the fixed layer from the diffuse layer, but for hydrophilic colloids the plane of shear coincides with the exterior boundary of the bound water (42). The potential at the plane of shear or zeta potential is responsible for the electro-kinetic behavior exhibited by colloidal particles.

Therefore a hydrophobic colloidal system is subjected to two opposing forces. The repulsive force due to the zeta potential and van der Waal's interparticle attractive force. If the van der Waal's attractive force is less than the repulsive force, the particles cannot coalesce.

The zeta potential can be reduced by adjusting the pH to the isoelectric point. But the most common method is to neutralize the negative charges through coagulation. In order to achieve coagulation, the zeta potential has to be decreased to such an extent that the van der Waal's force is more predominant. The procedure of coagulation is to neutralize or decrease the charges, so that the particles coalesce among themselves followed by flocculation and sedimentation. According to Lamer (33), coagulation is particle destabilization by a reduction of repulsive potential of similar electrical double layers surrounding the two particles. He again stated that flocculation denotes destabilization by a chemical bridging mechanism that enmeshes the particles in three dimensional network. Black (10) pointed out that whenever the zeta potential is less than the attractive forces, the phenomenon of coagulation is possible. Repulsive forces can be reduced either by addition of coagulants, electrolytes or by altering the pH so that the isoelectric point is reached. Adjustments of pH level were found important by Barker (5) and a favorable pH range for ferric sulfate coagulation was reported between 8.2 and 8.5. Etzel (18) evaluated ferric sulfate coagulation of four test oil emulsion and reported a new procedure to reach isoelectric point.

The coagulation of hydrophobic colloid is achieved only by reducing the repulsive force, but for hydrophilic colloid it is necessary to break the hydration shell and then neutralize or reduce the charges on the colloid. For this reason the coagulation of hydrophilic colloid is more difficult. The coagulant which is going to achieve coagulation in a hydrophilic colloidal system, must possess the property of desolvation. Coagulation of hydrophilic colloidal system needs a drastic treatment or massive high dosage of coagulants; the dosages can be even twenty times higher than the amount used in conventional water treatment (45).

2.4 Treatment of Wastewater with Electric Current

Since the colloidal particles are charged particles in most of the cases, the effect of current through colloidal systems has been studied. The first investigation was made by Helmholtz in 1879 (1). He produced the mathematical theory of electro-kinetic phenomena which are associated with tangential motion at an interface between a fluid and some other phase. The phenomena are as follows:

1) Electrophoresis (movement of particles with respect to a liquid by an applied field).
2) Electro-osmosis (movement of liquid with respect to a fixed solid by an applied field).
3) Streaming potential (the potential difference set up by the movement of a liquid relative to the solid by the application of mechanical force).
4) Sedimentation potential (the potential difference set up in a liquid by the movement of suspended particles through it in response to an applied force).

Helmholtz assumed that at an interface a separation of charge occurred, giving an electrical double layer; then he gave the basic equation for the velocity of electrophoresis, shown below:

$$V = \frac{Dx\zeta}{4\pi\eta}$$

where V is the electrophoretic mobility (microns/sec) (volt) (cm), x is the applied field (volts), D and η the dielectric constant and viscosity (gm/cm sec) of the medium, and ζ is the potential difference (volts) interface and liquid, i.e. across the double layer.

During the late 1800 and early 1900, there was considerable research work done on electrolytic methods. The method was first patented by Webster (36) in 1889 in the context of the treatment of municipal wastewater. Over the years, considerable developments in the process occurred and this was shown by a great number of patents in the U.S.A. and the U.K. Most of the studies with current were based on the fact that during treatment, the electrodes would produce trivalent or divalent metal ions for coagulation. The use of aluminium and iron or iron alloy electrodes were reported in literature (36). Electrolytic treatment for domestic sewage plants were built both in England and in the U.S.A. as early as 1911, and were followed by several others till the late twenties. The type of current used in these plants was a direct current. All these plants were praised at first for their supposedly high quality effluent and lack of odour. In course of time, by the mid-thirties, most of the plants were shutdown mainly because of the high cost of operation. Since then, the cost of electrical power has gone down and the availability increased appreciably. Improved quality of coagulants and polyelectrolytes made the investigations more feasible to be carried out in recent years on the effect of current on coagulation (20). However, the use of current to help coagulation, raises the point whether a chemical coagulant alone can do the same job at a lower cost or not; but the investigations apparently are very interesting and challenging because of the chance in reducing the sludge production which has a very high cost of disposal. An investigation using direct current and lead dioxide electrodes, on secondary effluent from a municipal activated sludge plant, was carried out and was found to remove 80 and 90 percent of the chemical oxygen demand (COD) and chlorides respectively; the pH level was around 8.0, the level of voltage was 10 and 30 volts, the time of application of the current was varied from 15 minutes to 300 minutes (36). Kanai (31) reported that at an industrial wastewater treatment plant in Tokyo, the fluoride electrolysis procedure was successfully employed. He also reported that the COD was reduced from 248 mg/l to 24 mg/l. The type of current used was a direct current and the level of voltage was around 10 volts. The use of the electric current in the treatment of emulsified wastewater is not reported in the literature; however, Shinoda (46) mentioned the use of the electric current while using an ion exchange resin membrane as a means of demulsification, but unfortunately no further details were reported. Only one reference was available, using alternating currents in conjunction with aluminium electrodes to remove phosphates from domestic sewage (14). This was a laboratory study when two levels of alternating current were used (6 and 12 amps) and the resulting current densities were 0.00265 and 0.00530 amps per cm^2 respectively. The phosphate removal efficiency was reported to be 80 percent. There were some laboratory studies performed by Landreth (34) in which iron-electrodes were used during electrochemical treatment and he reported that when the level of pH was very high (12.0), the electrodes failed to produce iron ions for coagulation. Again no further details were available regarding the parameters used in the treatment.

A review of the literature shows that electric current was not used as a coagulant-aid and it was decided to investigate the use of the electric current in this research as an aid to ferric sulfate coagulation.

2.5 Purpose of the Study

A review of the literature shows that coagulation is an effective technique in destabilizing oil emulsion. Ferric sulfate coagulation is reported to be effective for hydrophilic type of colloids because it has the capacity of both desolvation and charge neutralization. The oil-in-water emulsion used in this study contained hydrophilic type of colloids. Therefore, the electric current was introduced in conjunction with and without ferric sulfate with an idea that the current may help in desolvation of colloids and thus the overall oil removal efficiency would be increased.

The objectives of this study were:

1. to examine the effect of current (voltage and duration of current) both alternating and direct, on oil removal without the addition of any coagulant,
2. to evaluate the influence of current, both alternating and direct, on oil removal when ferric sulfate is used as a coagulant, under varying conditions of voltage, duration of current and amount of coagulant,
3. to compare the effectiveness of oil removal by various measures mentioned in (1) and (2) above with coagulation using ferric sulfate alone, and
4. to determine sludge production under the various conditions so that it can be minimized.

CHAPTER 3

MATERIALS USED IN THE STUDY AND EXPERIMENTAL PROCEDURES

3.1 Materials Used in The Study

3.1.1 Oil Emulsion

The oil emulsion was prepared in the laboratory by mixing paraffin oil, made by Fisher Scientific Company, with an emulsifying agent called triethanololeate. This emulsifying agent was prepared by adding oleic acid to triethanolamine in a predetermined weight ratio. The oil emulsion, prepared by paraffin oil and triethanololeate, represent a popular type of cutting oil actually used in the metal working industry and the weight ratio used was based on the test oil used by Etzel (18).

Paraffin Oil (Fisher Scientific Company) 42.5% by weight
Oleic acid (J.T. Baker Chemical Company) 37.6% by weight
Triethanolamine (J.T. Baker Chemical Company) 19.5% by weight.

The procedure in making this test oil emulsion was to weigh 21.25 grams of paraffin oil in a beaker and then 18.80 grams of oleic acid was added. This mixture was stirred continuously by a magnetic stirrer for 2 to 3 minutes producing a clear mixture, followed by the addition of 9.95 grams of triethanolamine. The resulting mixture was stirred with a great speed to produce a clear mixture with entrapped air bubbles inside the solution. This oil emulsion of 50 grams was diluted with deionized water to 2 litres. The mixture formed in contact with the water was a white, sticky mass which needed a number of rinsings before it went into solution completely. This oil emulsion was used, as a 25,000 mg/l concentrated stock solution which was milky-white in colour after blending in Waring blender for 5 minutes. This foamy and milky-white emulsion was found to be stable for approximately 3 weeks and the working stock solution was prepared by diluting this to 1000 mg/l of soluble oil with Ottawa tap water. Since this diluted stock was found to be unstable after 48 hours, it had to be prepared every other day.

This oil emulsion was completely emulsified because of the high dosages of emulsifying agents. Emulsifier was used in a range of 57.5% by weight and is high enough to make a complete oil emulsion (43). Oleic acid and triethanolamine were added on the basis of 1:1 molar ratio; so that there was not any excess of acid or amine.

Very often in the actual waste, the concentration of soluble oil is found to be around 500 mg/l (43). Therefore, the concentration of oil for actual studies was reduced to 500 mg/l in all the experiments, by dilution with Ottawa tap water.

3.1.2 Coagulants

The only coagulant, used in this study, was ferric sulfate ($Fe_2(SO_4)_3,9H_2O$) made by J.T. Baker Chemical Company.

Ten grams of ferric sulfate were taken in a beaker and diluted to a litre. This solution was stirred vigorously with the help of a magnetic stirrer till it produced a clear deep yellow solution. This was the concentrated stock solution of 10,000 mg/l. The daily working stock was made by diluting 100 ml of concentrated stock to a litre reducing the concentration of ferric sulfate to 1000 mg/l.

3.1.3 Currents

The use of both alternating and direct current was investigated in this study. Alternating current (A.C.) was drawn from the supply (110 v) through a variac with a range from 0 to 110 volts. A direct current power source with a voltage range '0 v - 150 v' and current strength '0 - 6 amps', was installed and direct current was drawn from it.

3.1.4 Sludge Testing Equipment

porcelain funnels of 126 mm internal diameter made by Fisher Scientific Company were used. The filter papers, made by Whatman, with pore size of 5μ, were of 125 mm diameter to fit properly in the funnel. These funnels were connected to a suction pump through the filtering apparatus to ensure quick filtration. The sludge collected on the filter paper after complete filtration was dried in a Isotemp Oven, made by Fisher Scientific Company, at 103°C for 1 hour and weighed.

3.2 Experimental Procedures

3.2.1 Spectrophotometric Measurements

Spectrophotometry is a very common and popular method used to determine the concentration of a particular substance in a sample by measuring the absorbance or transmittance at a predetermined optimum wave length.

The instrument used in this study was a Spectronic 20 made by Bausch and Lomb, having wave length range from 340 mμ to 960 mμ. All the experiments were made at a fixed wave length of 440 mμ which was found to be the optimum absorbance wave length (Chapter 4, 4.1.1). The instrument was set to 100 percent transmission for distilled water in a fixed cell to avoid any unnecessary errors in the results, prior to measuring transmittance of the oil emulsion.

3.2.2 Jar Test

One of the most simple and adequate methods of determining the coagulant dosages to stabilize a colloidal system is through the jar test. Jar test apparatus, as the name implies, generally consists of six beakers and the same number of stirrers. A Phipps and Bird instrument was used in this study. Six stainless steel beakers, each of 1200 milliliters capacity, were used in contrast to glass beakers generally used in Jar tests. Stainless steel beakers and the stirrers formed the two electrodes when current was passed through the medium, conducted for fixing up coagulant dosages in water or wastewater treatment. During stirring, the speed of rotation of all the stirrers was identical. The speed of stirring was controlled by a variable speed drive and the range was from 0 to 100 rpm.

A very common procedure which was followed throughout the study is described below:

1. All samples were stirred for 1 minute at 100 rpm.
2. Chemicals were added as required while stirring all samples at 100 rpm.
3. After the last addition of chemicals stirring was continued for 1 minute at 100 rpm to ensure a good mixing.
4. After 1 minutes of stirring the speed was brought down to 30 rpm and let mix for 15 minutes.
5. Stirring was stopped after 15 minutes and the beakers were taken out. The settling period was two hours.
6. When the settling time was over the clarified water was siphoned into a small beaker and the percent transmission was obtained.
7. The pH was obtained within a short period.

8. The sample was filtered and the dry weight of the sludge was taken.

The total volume of sample in each beaker was 1000 ml. Since the dosages of the coagulant were different in every beaker, the dilutions were made in such a way that the final volumes were always 1000 ml in each beaker. This was very important in order to avoid the dilution effect on percent transmission. The dilution water used was Ottawa tap water. The beakers and the stirrers were always cleaned before and after each test to avoid any error.

3.2.3 pH Adjustments

pH of the samples was measured immediately after the treatments. The pH meter used was a Model 801/Digital pH meter fabricated by Orion Research Incorporated and it was standardized with a pH 7.0 buffer solution every day.

Both sodium hydroxide and hydrochloric acid were used according to the requirements for pH adjustment and were of strength 0.1 N . The normality was standardized once a week.

3.2.4 Sludge Filtration

Whatman filters of 5.0μ pore size were used in the filtering apparatus, connected with a suction pump to ensure quick filtration. The main object was to get the total dry weight of sludge produced after treatment. The filter papers were first dried at 105°C in a Fisher made Isotemp Oven and the weights were recorded. After filtration, the filter papers were dried again at 105°C for 1 hour and the weights were again recorded. The difference gives the dry weight of sludge produced.

CHAPTER 4

EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Preliminary Studies

Preliminary studies were directed to examine the various methods to be used for destabilization of oil emulsions through electrochemical treatment, so that detailed studies could be carried out on the more promising alternatives. Preliminary studies were also made to establish the optimum wave length for estimating the percent transmittance of the oil emulsion and to relate percent transmission with percent oil removal after treatment. Details of preliminary studies are discussed below.

4.1.1 Optimum Wave Length for Percent Transmission

Since percent transmission through Spectronic 20 was the method to determine the oil concentration, it was necessary to calibrate the curve of percent transmission against various wave lengths. This was done to find out the wave length at which the oil emulsion produced maximum absorbance or minimum percent transmission and this wave length is often termed as optimum wave length for the particular substance used.

An arbitrary oil concentration was chosen and the percent transmissions were recorded (Table 1) at different

TABLE 1

Percent Transmissions of Oil Emulsion at Various Wavelenghts

Wavelength (mµ)	Percent Transmission
420	
430	35.0
435	34.5
440	34.0
445	34.4
450	35.1
460	36.2
470	37.0
480	38.2
490	42.0
500	44.2
510	46.0
520	48.1
530	51.5
540	53.4
550	55.5
560	58.8
570	60.0
580	62.7
590	63.8
600	65.4

wavelengths ranging from 420 to 600 mμ. These results were plotted in Figure 1 which show a smooth curve with a maximum depression at a wave length of 440 mμ. This value was the optimum wave length for the test oil emulsion and was used throughout the study. The following study was carried out to establish the relationship between percent transmission and the percent oil removal using various oil concentrations. Percent transmissions, for different oil concentrations were taken at the optimum wave length (440 mμ), and are illustrated in Figure 2. This graph (Figure 2) is drawn in a semi-logarithmic paper keeping percent transmission on the log scale and the plot is found to be a straight line. From Figure 2, it is possible to find out the oil concentration of any unknown sample if the percent transmission is determined at the optimum wave length of 440 mμ. The oil samples used throughout this study had an initial oil concentration of 500 mg/l before undergoing treatment. Using this value (500 mg/l) as the original oil concentration and the oil concentration after treatment from Table 2, it was possible, to develop a graph (Figure 3) which gives the percent oil removal for different percent transmissions, based on Table 3.

4.1.2 Effect of pH on Oil Emulsion

Using the jar test procedure, samples having 500 mg/l of oil concentration adjusted to various pH values, were stirred and allowed to settle; pH values of the samples were adjusted using sodium hydroxide and hydrochloric acid

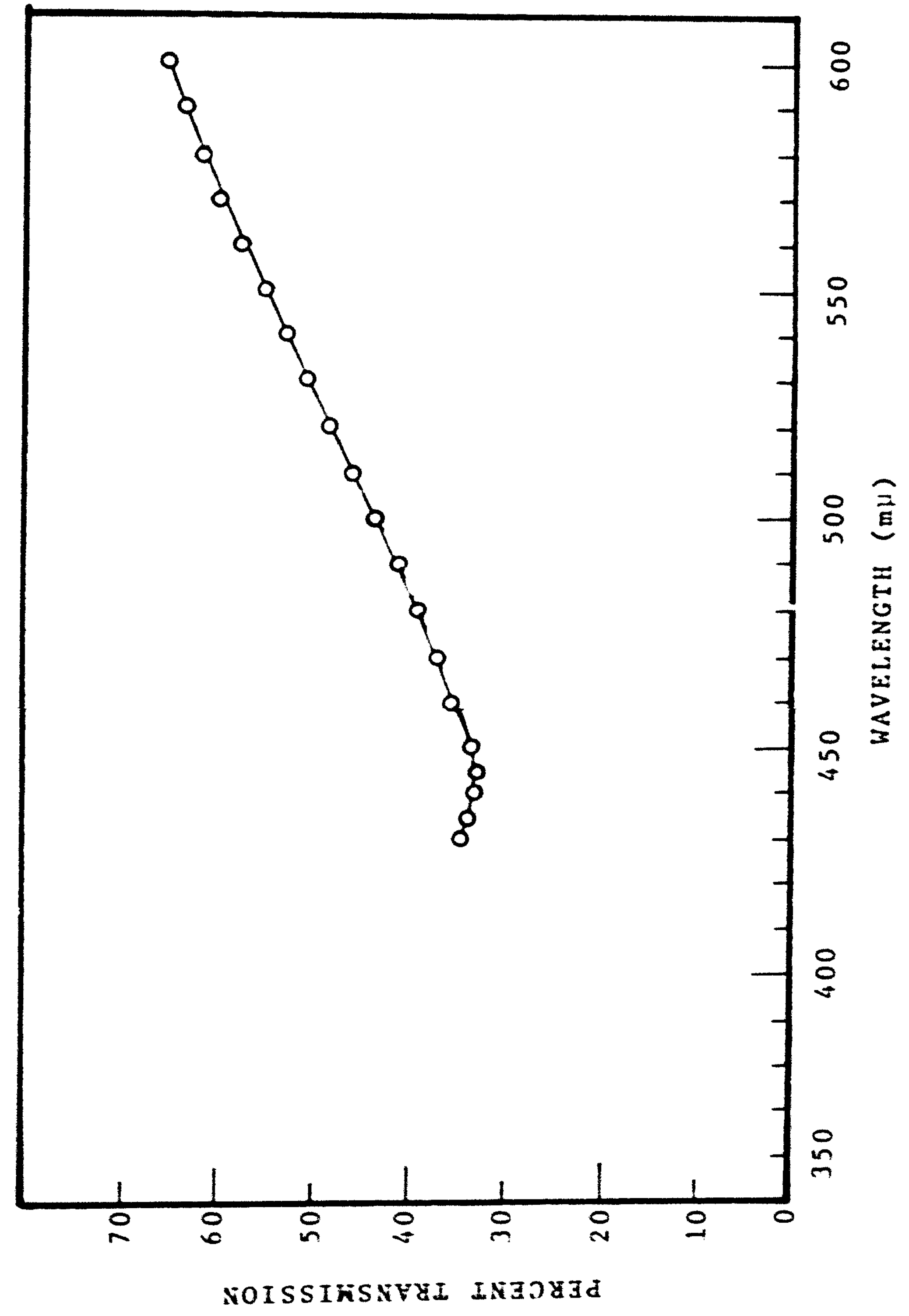

Figure 1 Spectrum Analysis of Oil Emulsion

TABLE 2

Percent Transmissions of Various Oil Concentrations at Optimum Wavelength of 440 mμ

Oil Concentration (mg/l)	Percent Transmission
0	100.0
10	94.0
50	78.0
100	62.0
200	37.3
300	23.9
400	14.0
500	9.0

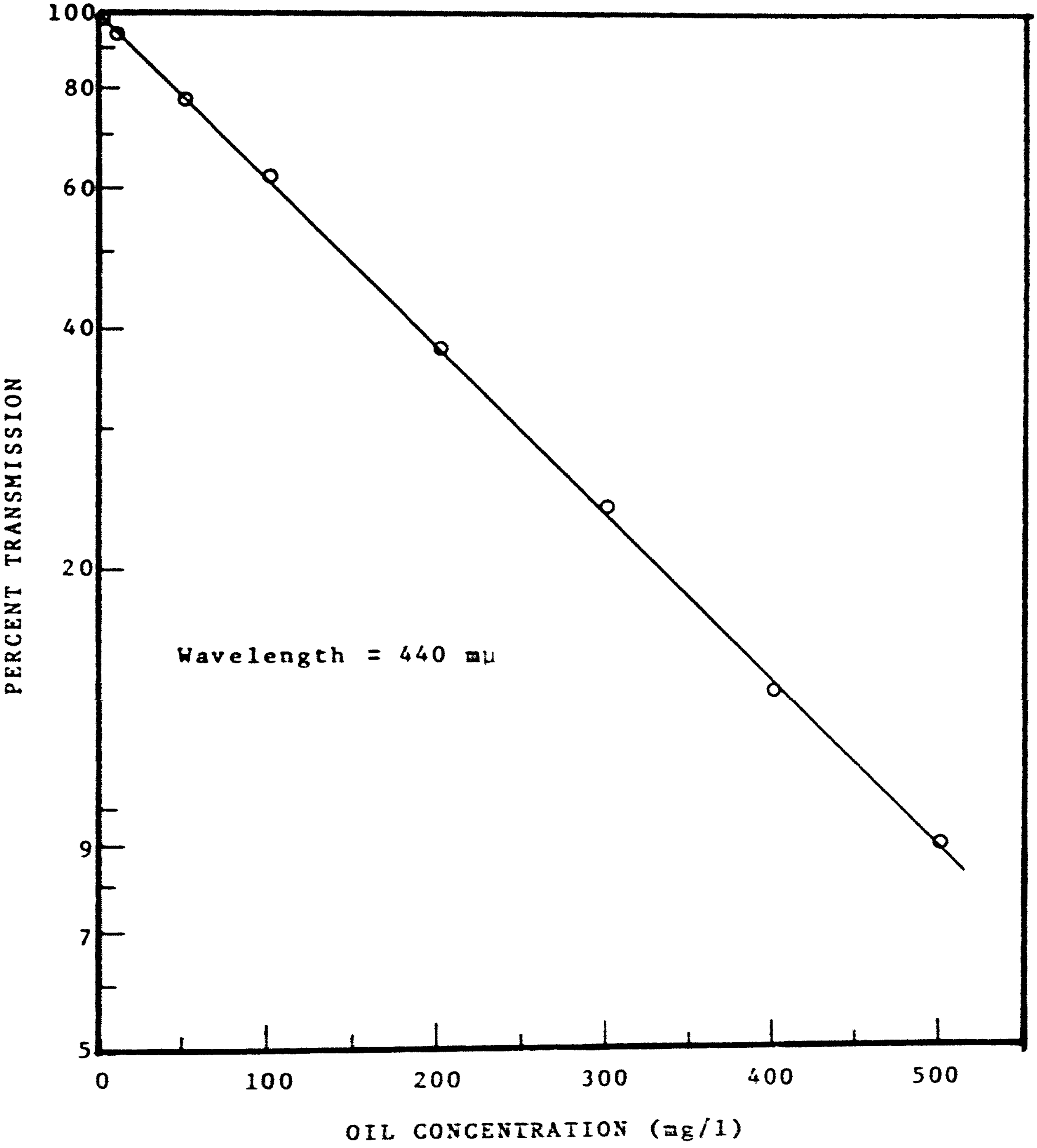

Figure 2 Typical Curve of Various Oil Concentrations with Percent Transmission at Wavelength of 440 mμ

TABLE 3

Percent Oil Removal at Different Levels of Percent Transmission

Percent Transmission	Oil Concentration Percent (mg/l)	Percent Oil Removal
9.0	500	0.0
14.0	405	19.0
24.0	295	41.0
38.0	200	60.0
50.0	140	72.0
69.0	75	85.0
78.0	50	90.0
94.0	10	98.0
100.0	0	100.0

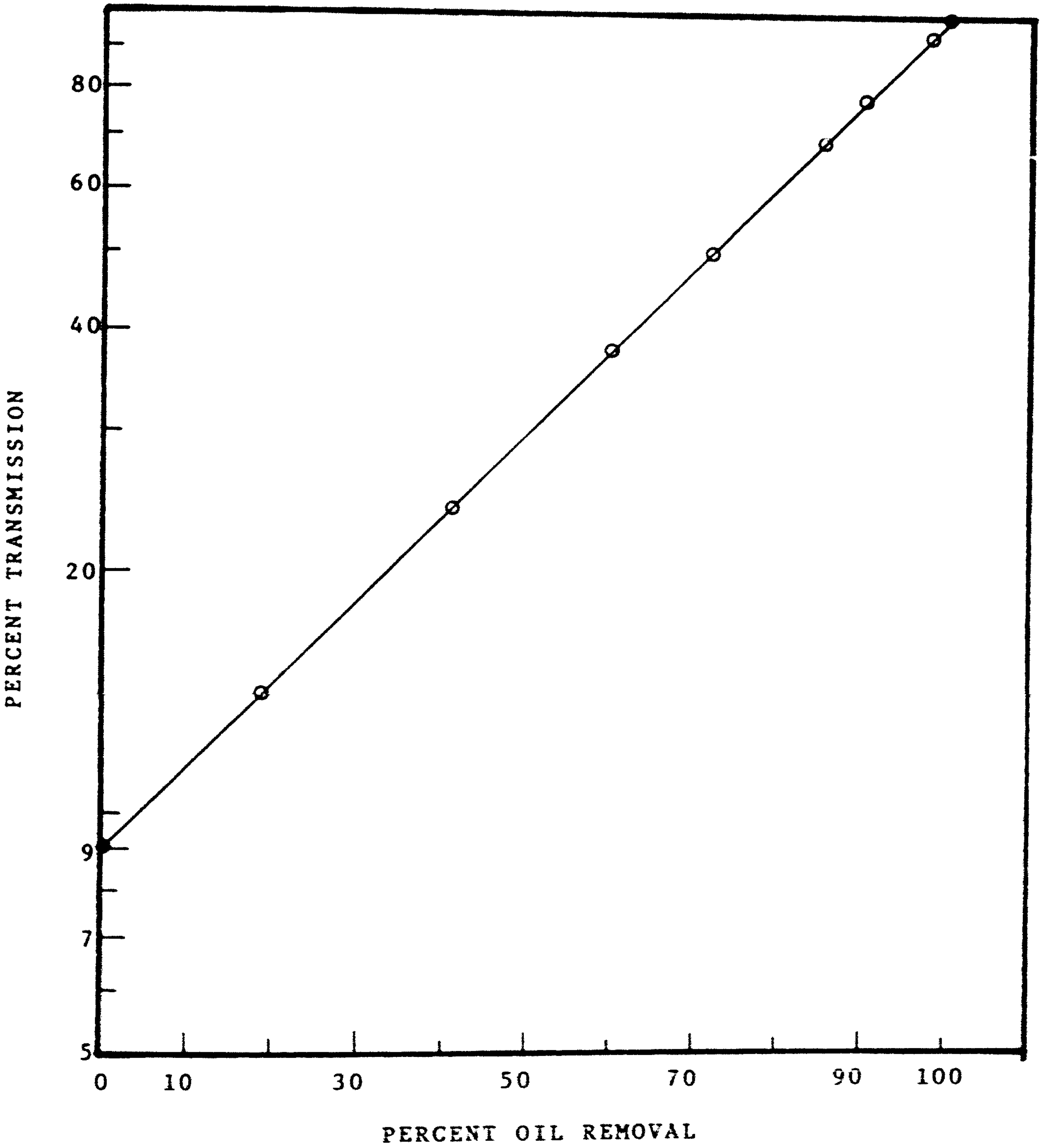

Figure 3 Reference Curve for Percent Oil Removal at Various Percent Transmission

both being of 0.1 N strength. The pH values of the samples were varied from 3.5 to as high as 11.9. The data and the corresponding plot are shown in Table 4 and Figure 4 respectively. Very little changes were noticed in the samples after the treatment when pH values were below 11.3. The curve (Figure 4) is almost horizontal up to pH 11.3 indicating insignificant change in percent oil removal; but beyond a pH of 11.3, the effect on oil removal was significant. Therefore, a pH level higher than 11.3 is effective in removing oil from the emulsion.

4.1.3 Destabilization of Oil Emulsion by Ferric Sulfate at Different pH Levels

This part of the preliminary studies was carried out to investigate the effectiveness of ferric sulfate in destabilizing the oil emulsion at various pH levels. The dosages of ferric sulfate were chosen at three levels, 50, 100 and 200 mg/l, respectively; the levels of pH, for each level of ferric sulfate, were varied from 2.1 to 10.0 approximately. The results are given in Table 5. By using 50 mg/l of ferric sulfate, no appreciable change was noticed in the oil emulsion (Figure 5); but both 100 mg/l and 200 mg/l of ferric sulfate dosages produced better oil removal from the test oil emulsion. By using a dosage of 100 mg/l, 48 percent of oil removal was possible when the pH was above 6.8. In a pH range from 4.0 to 6.5, a dosage of 200 mg/l

TABLE 4

Effect of pH on Oil Emulsion

Oil Concentration = 500 mg/l

0.1 N NaOH (ml)	0.1 N HCl (ml)	pH	Percent Transmission	Percent Oil Removal
0.0	35.0	3.48	12.0	12.0
0.0	25.0	3.81	14.5	20.0
0.0	23.0	5.01	11.8	11.5
0.0	20.0	5.79	12.5	13.5
0.0	0.0	7.22	12.1	12.0
1.5	0.0	8.01	11.0	9.0
5.0	0.0	8.98	12.5	13.5
25.0	0.0	10.07	12.0	12.0
55.0	0.0	11.38	24.0	41.0
57.0	0.0	11.55	47.5	69.5
58.0	0.0	11.80	56.9	77.0
60.0	0.0	11.85	64.0	82.0
62.0	0.0	11.90	62.8	81.0

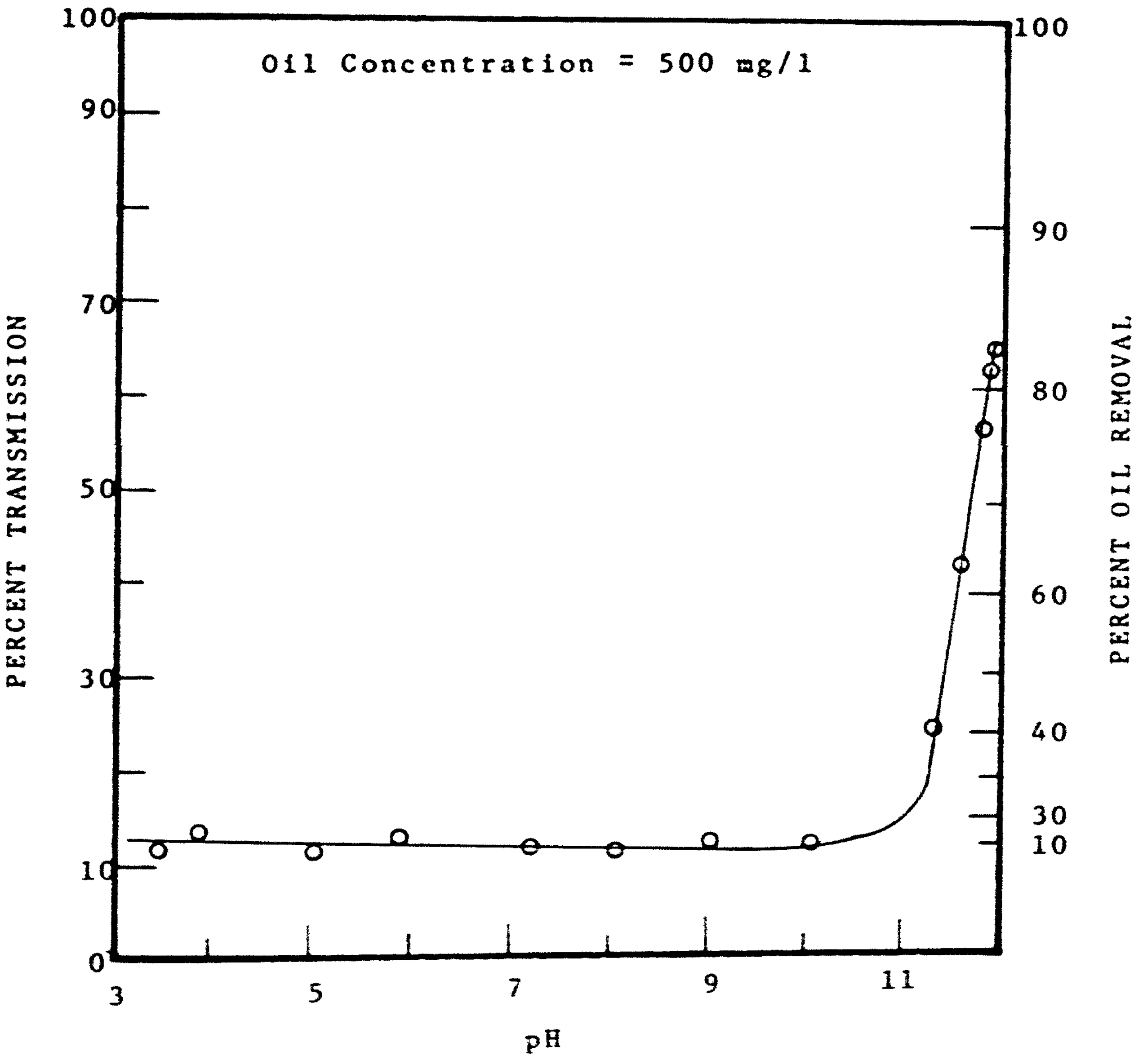

Figure 4 Effect of pH on Oil Emulsion

TABLE 5

Destabilization of Oil Emulsion Using Ferric Sulfate Alone at Different pH Levels

Oil Concentration = 500 mg/1

0.1 N HCl (ml)	0.1 N NaOH (ml)	Ferric Sulfate (mg/1)	Percent Transmission	pH	Percent Oil Removal
50.0	0.0	50	8.2	2.25	
25.0	0.0	50	10.0	4.33	4.0
20.0	0.0	50	10.5	5.41	6.1
0.0	0.0	50	11.0	6.68	8.1
0.0	8.0	50	12.3	8.50	13.0
0.0	20.0	50	13.0	9.72	15.0
0.0	25.0	50	16.5	9.80	25.0
0.0	50.0	50	33.2	11.12	55.0
45.0	0.0	100	12.1	2.11	9.0
20.0	0.0	100	21.0	4.58	35.0
5.0	0.0	100	24.5	5.79	42.0
0.0	0.0	100	28.5	6.81	48.0
0.0	9.0	100	28.8	8.20	48.5
0.0	20.0	100	28.5	9.50	48.0
0.0	30.0	100	33.8	9.89	55.0
0.0	50.0	100	40.0	10.75	62.2
30.0	0.0	200	5.0	2.28	
15.0	0.0	200	33.1	4.21	55.0
5.0	0.0	200	51.5	5.50	73.0
0.0	0.0	200	60.0	6.39	79.0
0.0	10.0	200	65.5	6.98	83.0
0.0	15.0	200	67.0	7.90	84.0
0.0	20.0	200	67.5	8.00	84.5
0.0	40.0	200	68.0	9.99	85.0

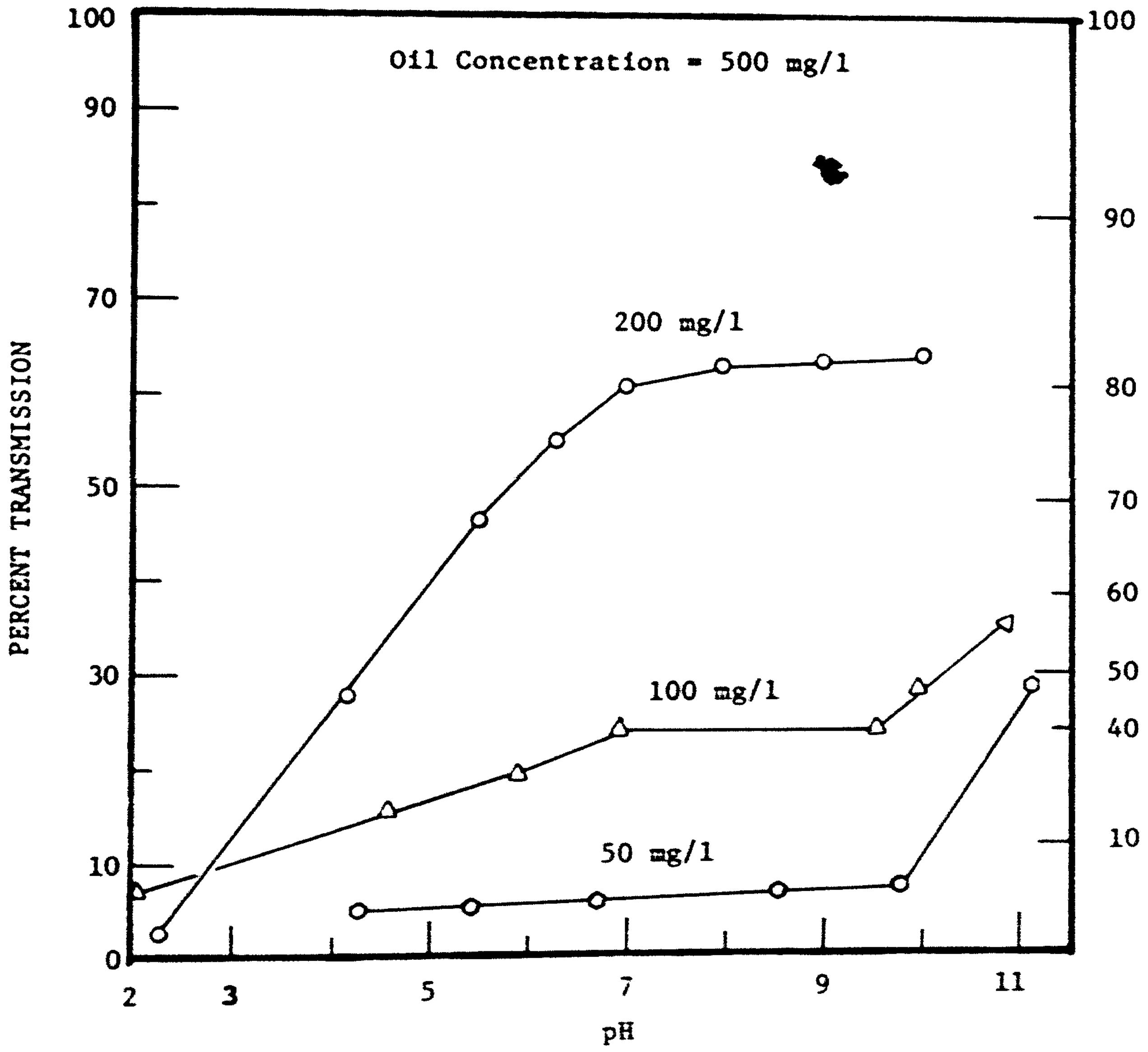

Figure 5 Destabilization of Oil Emulsion Using Ferric Sulfate Alone at Different pH levels.

showed a constant increase in oil removal up to 83 percent and was almost steady thereafter. To destabilize the oil emulsion in a pH range from 6.0 to 9.0, a dosage of 50 mg/l of ferric sulfate was found insufficient. But with a higher dosage (e.g. 100 mg/l) of ferric sulfate it was possible to destabilize the oil emulsion to the extent of 50 percent.

4.1.4 Destabilization of Oil Emulsion by Alternating Current and Ferric Sulfate

From the last investigation, it was found that only ferric sulfate dosage of 200 mg/l removed 84 percent of oil from the oil emulsion. This dosage was fairly high. In this part of the study, alternating current and ferric sulfate were used so that the current would help in desolvation of the colloids with the resultant decrease in the dosage of ferric sulfate. Stainless steel beakers and stirrers were used as the two electrodes and the sizes of the test samples were 1000 ml. Four levels of ferric sulfate dosages, i.e., 50, 100 and 200 mg/l and two levels of voltage, i.e., 30 and 100 were selected. The pH levels were fixed around 7.5. The current was applied during flashmix only, i.e., 1 minute. The data are given in Table 6, and Figure 6 shows the plot of coagulant dosages against percent transmission and percent of oil removal respectively. The oil emulsion before treatment had a percent transmission equal to 12 percent (Figure 6). The

TABLE 6

Destabilization of Oil Emulsion Using Alternating Current and Ferric Sulfate - Time of Application of Current=1 minute (Flashmix)

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Volts	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	12	7.2	8.1
0.0	5.0	0	50	8	7.9	
0.0	10.0	0	100	46	7.1	68.0
0.0	20.0	0	200	67	7.7	84.0
0.0	0.0	30	0	12	7.4	8.1
0.0	5.0	30	50	7	7.3	
0.0	10.0	30	100	44	7.5	66.0
0.0	20.0	30	200	68	7.7	84.5
0.0	0.0	100	0	13	7.7	15.0
0.0	5.0	100	50	9	7.6	0.0
0.0	10.0	100	100	47	7.2	69.0
0.0	20.0	100	200	66	7.8	83.0

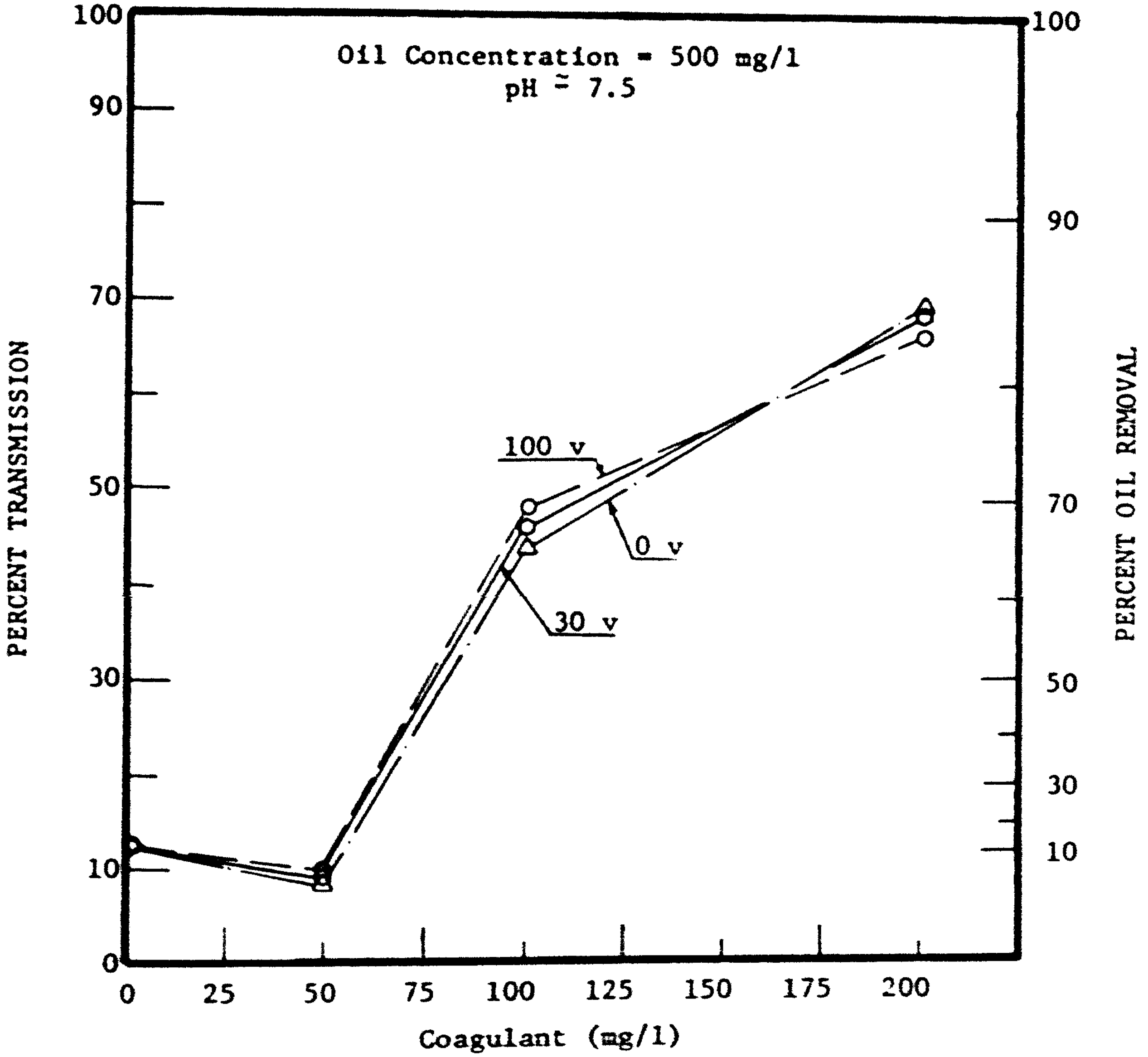

Figure 6 Destabilization of Oil Emulsion Using Alternating Current and Ferric Sulfate - Time of Application of Current = 1 minute (Flashmix).

efficiency of oil removal was higher with the increase in coagulant dosages. The treatment with current and higher dosages of ferric sulfate, e.g., 100 and 200 mg/l, show (Figure 6) a steady increase in percent oil removal. A ferric sulfate dosage of 50 mg/l was unable to produce any oil removal and caused a yellow colour to give lower percent transmission which was found throughout the study.

Figure 6 provides the curves in which the effect of alternating current was found to be insignificant. The treatment using ferric sulfate alone (200 mg/l) was capable in removing 84 percent of oil whereas an addition of alternating current (100 v) produced 83 percent of oil removal with 200 mg/l of ferric sulfate. This clearly indicated that the influence of alternating current was not prominent when the time of application of current was during flashmix only.

In a subsequent test, the time of application of current was increased to 16 minutes, equivalent to the time required for both flashmix and flocculation. Results are presented in Table 7. The coagulant dosages (0, 50, 100 and 200 mg/l) and the levels of alternating current (0, 30 and 100 v) were the same; the levels of pH were around 7.5. Figure 7 is the plot of the results and a ferric sulfate dosage of 200 mg/l with alternating current of 100 volts removed only 2 percent oil more than the treatment using ferric sulfate (200 mg/l) alone. Alternating current of 30 volts was less efficient than the treatment using only ferric sulfate. Results from the study indicate that

TABLE 7

Destabilization of Oil Emulsion Using Alternating Current and Ferric Sulfate -

Time of Application of Current = 16 minutes
(Flashmix and Flocculation)

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Voltage (volts)	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	12	7.1	12.0
0.0	5.0	0	50	10	7.2	4.0
0.0	10.0	0	100	48	7.9	70.0
0.0	20.0	0	200	71	8.1	86.0
0.0	0.0	30	0	12	8.0	12.0
0.0	5.0	30	50	7	7.7	
0.0	10.0	30	100	44	7.2	66.0
0.0	20.0	30	200	62	7.5	80.5
0.0	0.0	100	0	12	7.8	12.0
0.0	5.0	100	50	8	7.3	
0.0	10.0	100	100	49	7.9	7.1
0.0	20.0	100	200	73	7.6	87.5

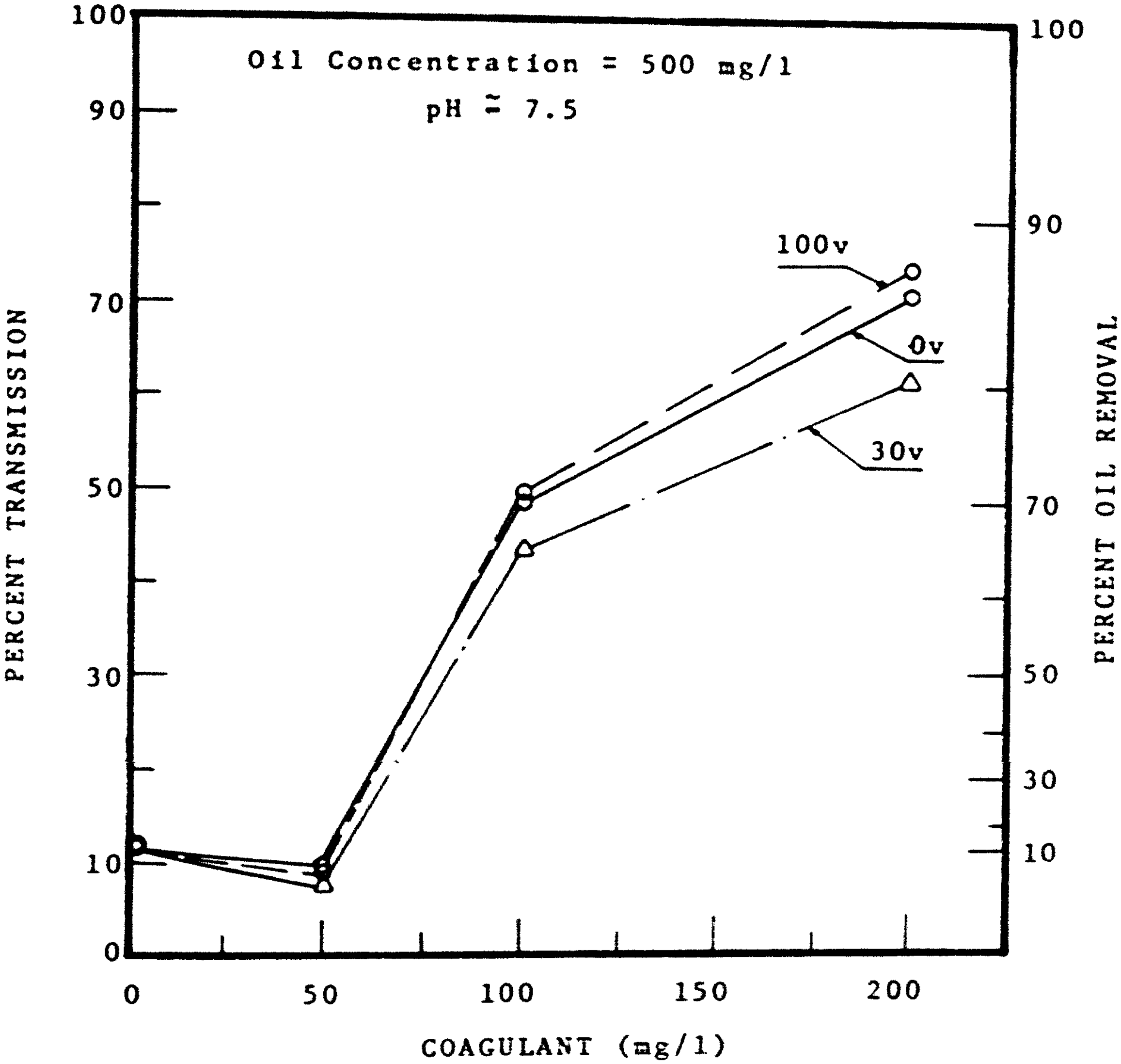

Figure 7 Destabilization of Oil Emulsion Using Alternating Current and Ferric Sulfate - Time of Application of Current = 16 minutes (Flashmix and Flocculation)

neither the duration of application nor the current (A.C.) itself had any significant effect on the removal of oil.

4.1.5 Destabilization of Oil Emulsion by Direct Current and Ferric Sulfate

In this part of the study, direct current was applied at different levels (0, 30 and 100 v). The ferric sulfate dosages were as before: 0, 50, 100 and 200 mg/l. While using D.C., the polarities were also taken into account. Data are given in Table 8, using the beakers as positive electrodes; the pH was adjusted to 7.5 and the time of application of current was only during flashmix (1 minute).

Figure 8 shows that all the combinations of treatment gave almost the same amount of percent oil removal and direct current was proved to have little effect on the oil removal. In a following study, coagulant dosages and the levels of voltage of direct current were the same but the polarities of the electrodes were reversed. Beakers were used as the negative electrode. The time of application of current was again 1 minute, i.e., during flashmix only. Results are tabulated in Table 9. In spite of the different combinations of direct current and coagulant dosages, the oil removal efficiencies were almost the same (Figure 9). Hence, it was decided to increase the duration of direct current to 16 minutes which is equivalent to the time of flashmix and flocculation. Ferric sulfate dosages were used in four

TABLE 8

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate -

Time of Application of Current = 1 minute
(Flashmix) and Beakers as Positive Electrodes

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Voltage (volts)	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	14	7.3	18.5
0.0	5.0	0	50	7	7.3	
0.0	10.0	0	100	49	7.7	71.0
0.0	20.0	0	200	70	7.2	85.5
0.0	0.0	30	0	12	7.5	12.0
0.0	5.0	30	50	9	7.8	0.0
0.0	10.0	30	100	46	8.0	66.0
0.0	20.0	30	200	68	7.2	84.0
0.0	0.0	100	0	12	7.9	12.0
0.0	5.0	100	50	10	7.7	4.0
0.0	10.0	100	100	46	7.5	68.0
0.0	20.0	100	200	72	7.6	87.0

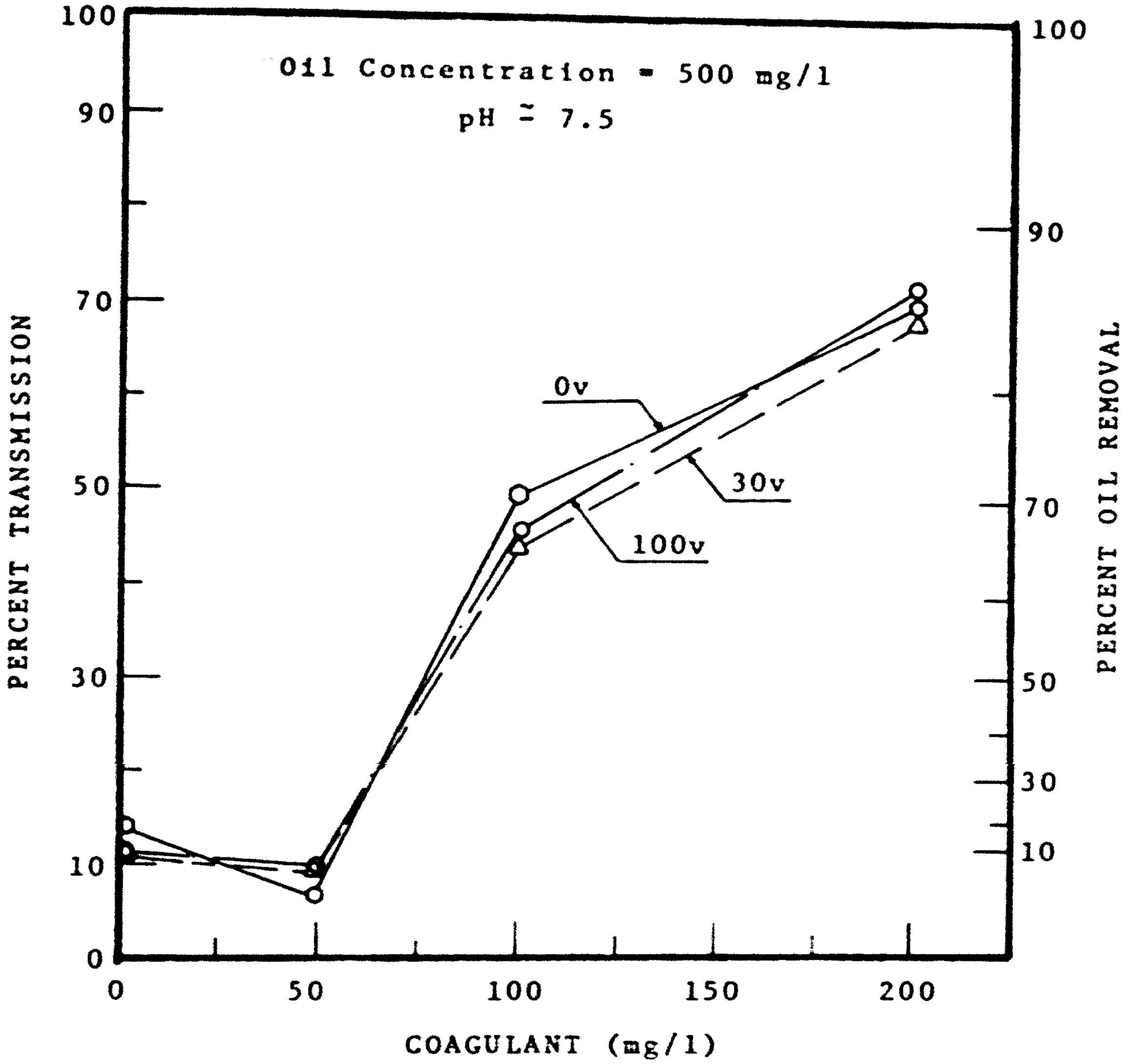

Figure 8 Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate - Time of Application of Current = 1 minute (Flashmix) and Beakers as Postive Electrodes

TABLE 9

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate -

Time of Application of Current = 1 minute
(Flashmix) and Beakers as Negative Electrodes

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Voltage (volts)	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	13	7.5	15.0
0.0	5.0	0	50	7	7.6	
0.0	10.0	0	100	51	7.3	72.5
0.0	20.0	0	200	69	7.9	85.0
0.0	0.0	30	0	12	7.2	12.0
0.0	5.0	30	50	8	7.5	
0.0	10.0	30	100	48	7.3	70.0
0.0	20.0	30	200	70	7.8	85.5
0.0	0.0	100	0	12	7.8	12.0
0.0	5.0	100	50	6	8.0	
0.0	10.0	100	100	50	7.6	71.5
0.0	20.0	100	200	71	7.2	86.0

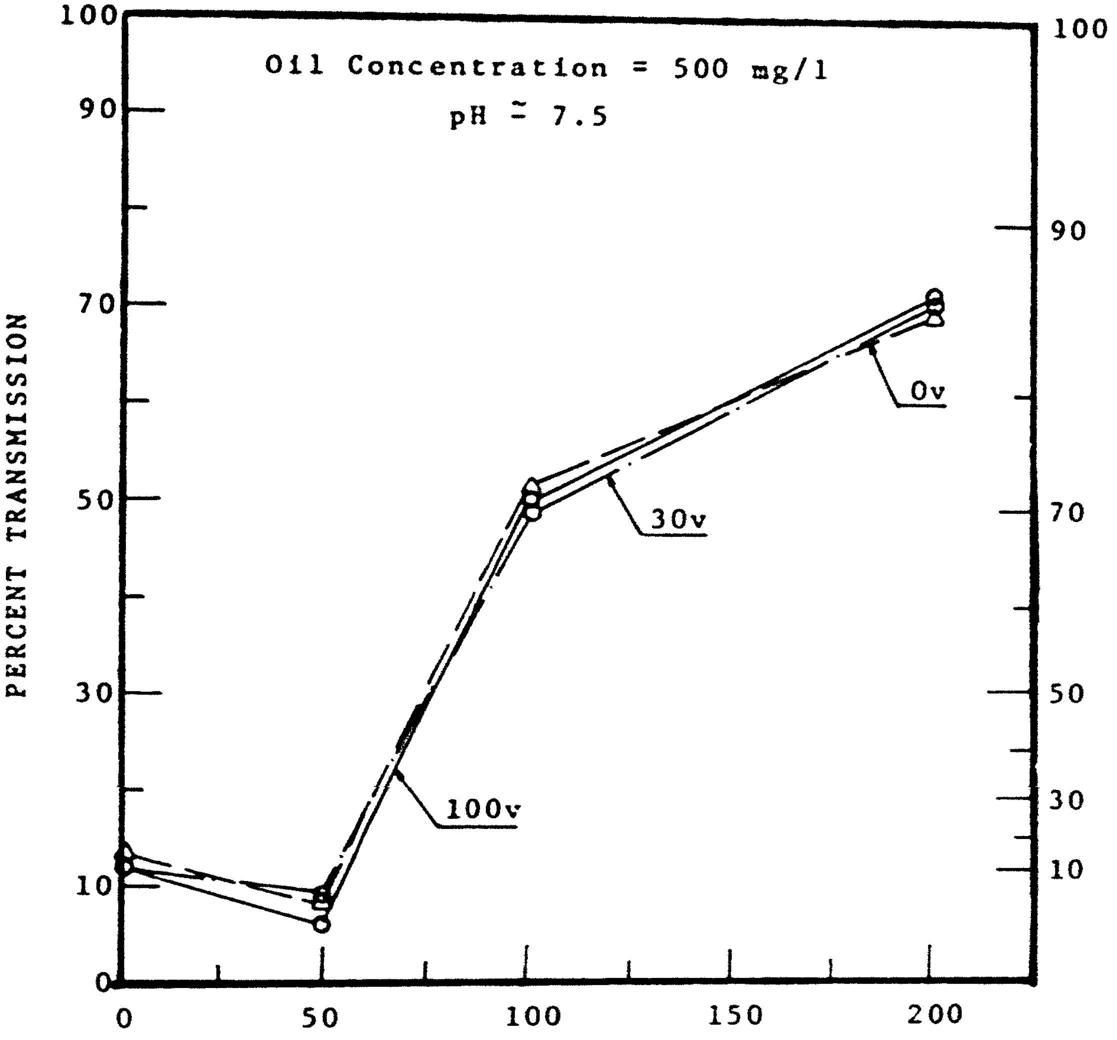

Figure 9 Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate - Time of Application of Current = 1 minute (Flashmix) and Beakers as Negative Electrodes

levels, i.e., 0, 50, 100 and 200 mg/l and the value of direct current voltages were chosen in three levels, i.e., 0, 30 and 100 v. The pH was adjusted to 7.5. In the first set of experiments, the polarities of the beakers were positive and the data are presented in Table 10. Again very little increase in oil removal efficiency was noticed by using direct current for 16 minutes with different ferric sulfate dosages (Figure 10). In a subsequent study, the polarities of the electrodes were reversed. Beakers were used as negative electrodes. Coagulant dosages and direct current voltage levels were used in the same order of magnitudes; the time of application of current and the pH levels were 16 minutes and 7.5 respectively.

Table 11 reveals the experimental results and the curves are plotted in Figure 11. It can be seen that the use of direct current (100 v) in conjunction with coagulant gives an increase in efficiency over the treatment using only ferric sulfate. Ferric sulfate dosage of 200 mg/l, when used with the addition of direct current of 100 volts, applied for 16 minutes, was capable of removing oil from oil emulsion to an extent of 98 percent (Figure 11). Treatment using 30 volts of direct current produced about 5 percent increase in oil removal efficiency when 200 mg/l of ferric sulfate was used. To visualize the influence of direct current, a summary plot (Figure 12) is drawn and only direct current of 100 volts with 200 mg/l of ferric sulfate showed a significant in-

TABLE 10

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate -

Time of Application of Current = 16 minutes
(Flashmix and Flocculation) and Beakers as
Positive Electrodes

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Voltage (volts)	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	11	7.9	8.0
0.0	5.0	0	50	7	7.7	
0.0	10.0	0	100	51	7.1	72.5
0.0	20.0	0	200	71	7.9	86.0
0.0	0.0	30	0	12	7.2	12.0
0.0	5.0	30	50	9	7.5	0.0
0.0	10.0	30	100	50	7.7	71.5
0.0	20.0	30	200	69	7.6	85.0
0.0	0.0	100	0	12	7.6	12.0
0.0	5.0	100	50	5	7.3	
0.0	10.0	100	100	57	7.5	77.0
0.0	20.0	100	200	75	7.8	88.5

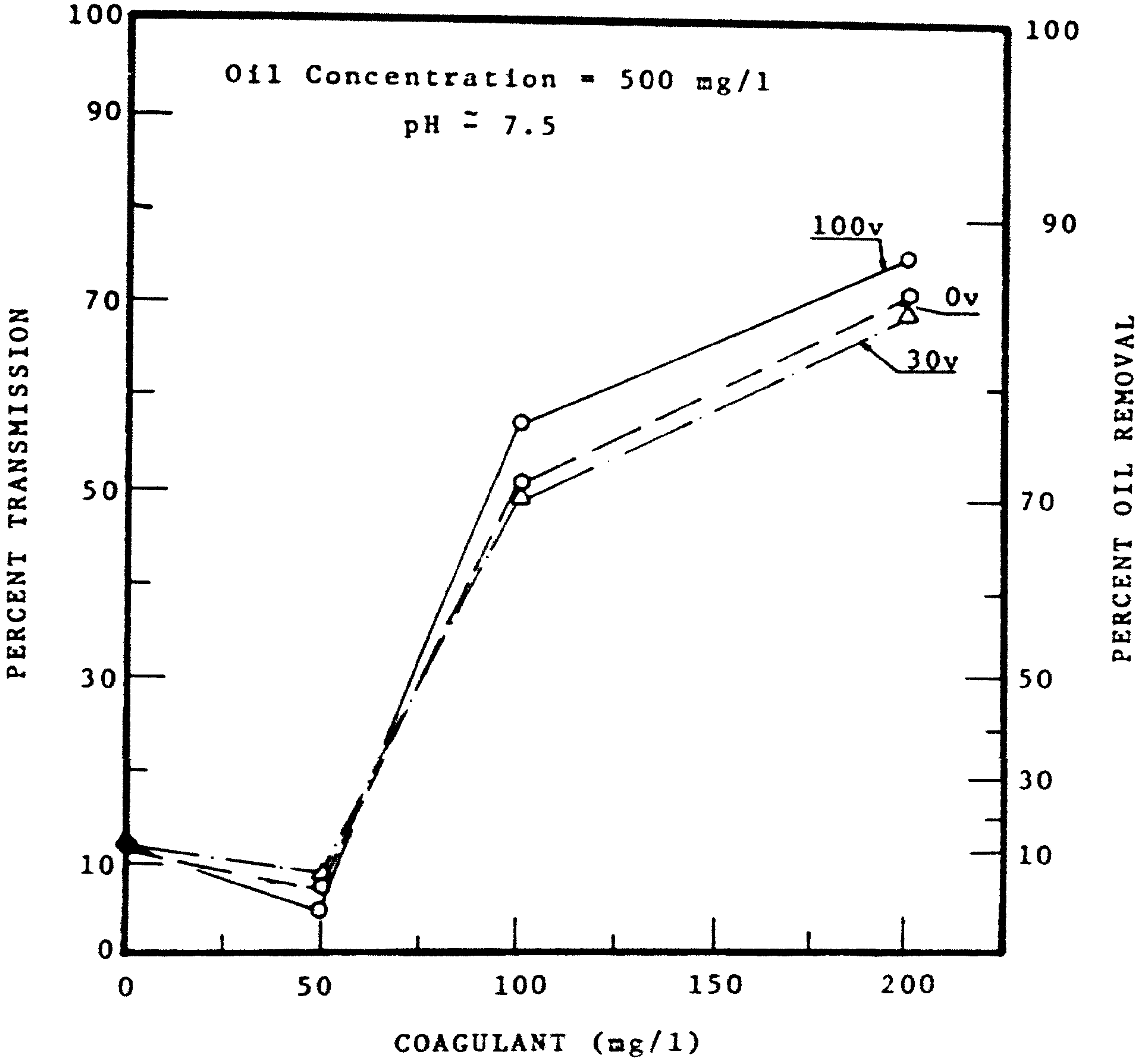

Figure 10 Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate - Time of Application of Current = 16 minutes (Flashmix and Flocculation) and Beakers as Postive Electrodes

TABLE 11

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate -

Time of Application of Current = 16 minutes
(Flashmix and Flocculation) and Beakers as
Negative Electrodes

Oil Concentration = 500 mg/l

0.1 N HCl (ml)	0.1 N NaOH (ml)	Voltage (volts)	Coagulant Dosages (mg/l)	Percent Transmission	pH	Percent Oil Removal
0.0	0.0	0	0	12	7.3	12.0
0.0	5.0	0	50	8	7.3	
0.0	10.0	0	100	48	7.7	70.0
0.0	20.0	0	200	69	7.9	85.0
0.0	0.0	30	0	11	7.5	8.0
0.0	5.0	30	50	5	7.6	
0.0	10.0	30	100	55	7.8	75.5
0.0	20.0	30	200	74	7.4	88.0
0.0	0.0	100	0	14	7.9	18.5
0.0	5.0	100	50	7	7.5	
0.0	10.0	100	100	70	8.0	85.5
0.0	20.0	100	200	96	7.2	99.0

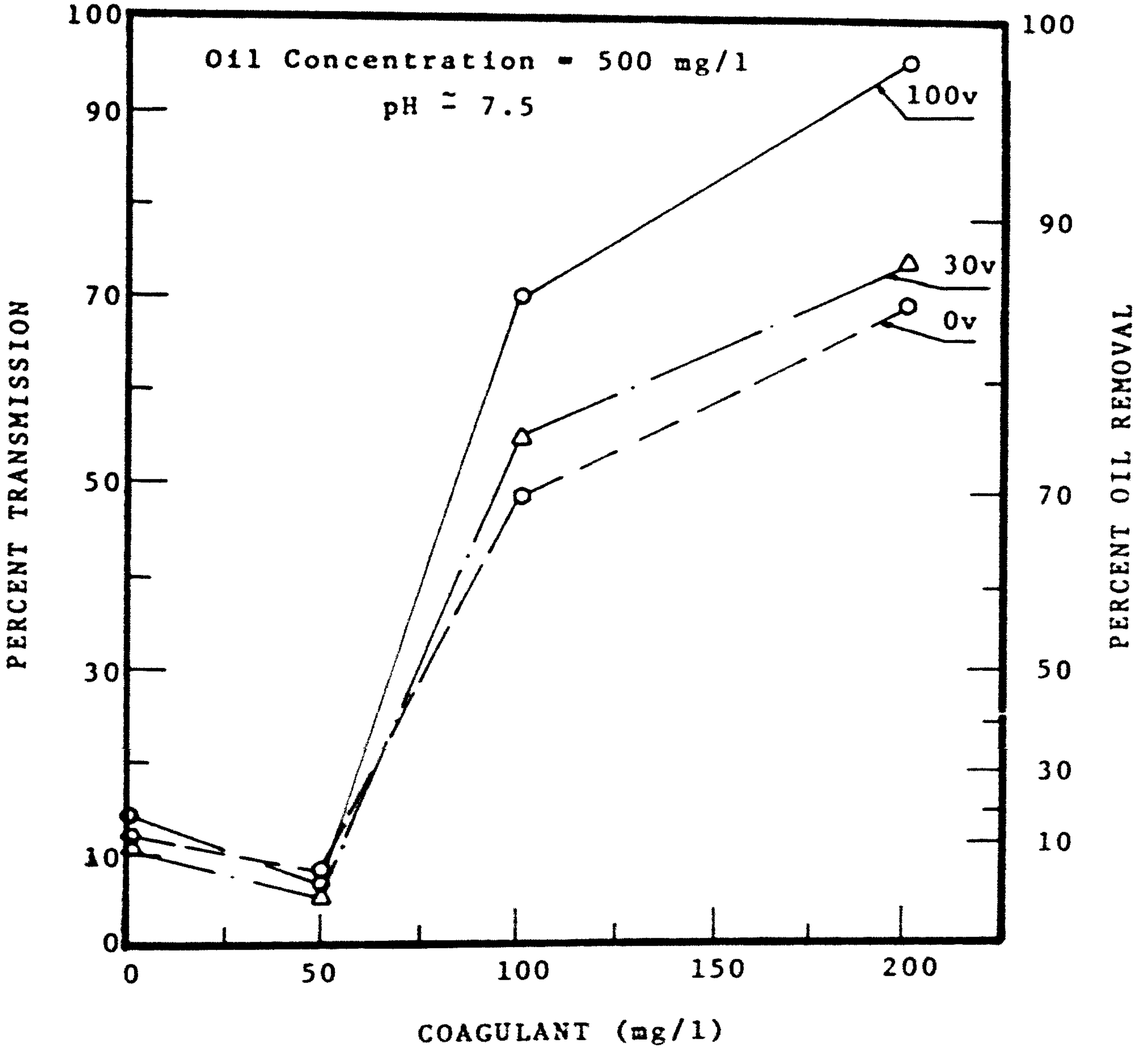

Figure 11 Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate - Time of Application of Current = 16 minutes (Flashmix and Flocculation) and Beakers as Negative Electrodes.

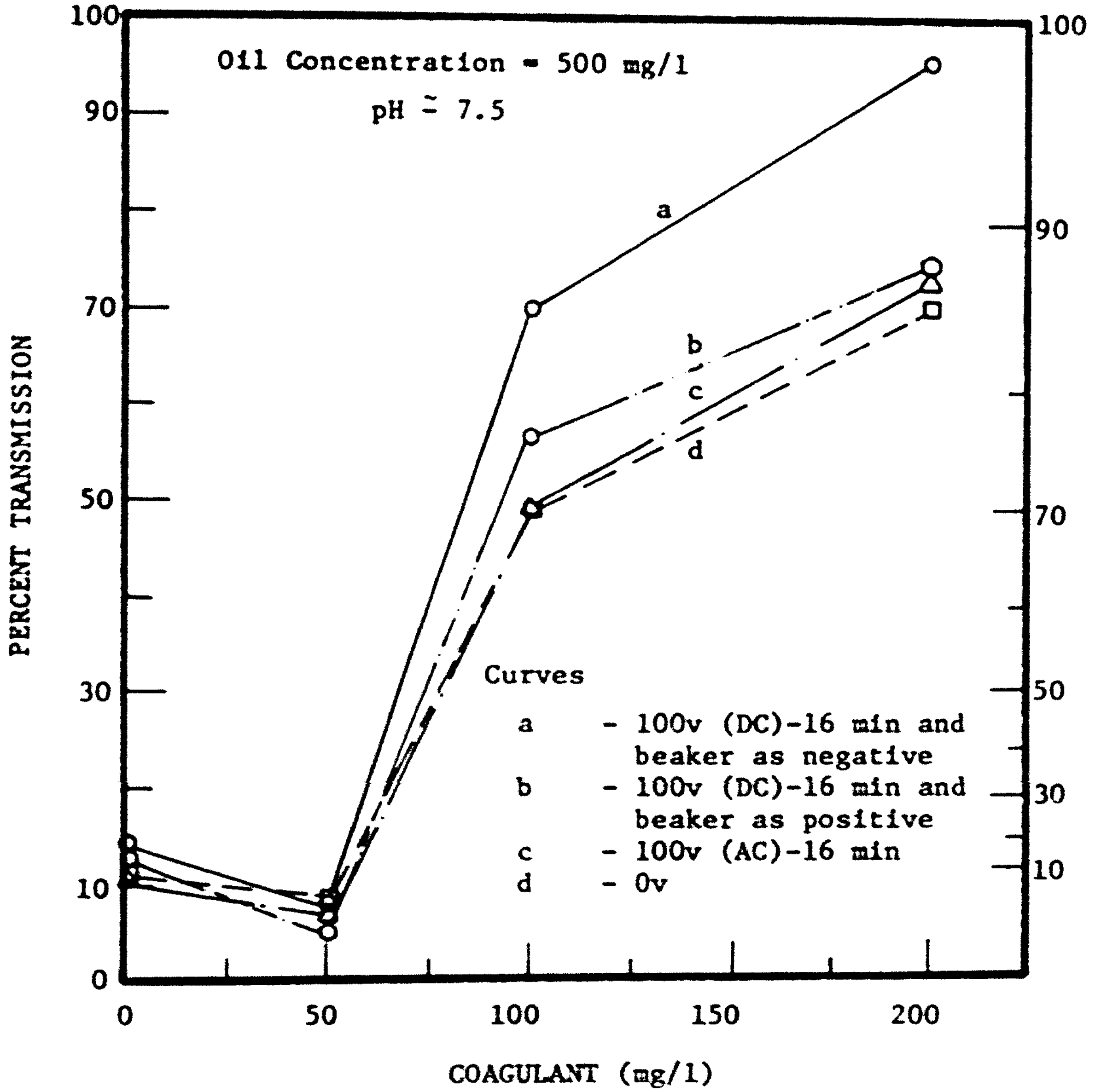

Figure 12 Typical Destabilization Curves Using Ferric Sulfate and Either With Direct or Alternating Currents

fluence on oil removal under the following conditions:

1. the polarities of the beakers were negative electrodes,
2. pH was around 7.5,
3. time of application of current was 16 minutes (both flashmix and flocculation).

4.1.6 Summary of Preliminary Studies

The optimum wave length was found to be 440 mμ for the oil emulsion. It was also found that percent transmission would be a satisfactory means of estimating the oil removal, and the plot between percent transmission and percent oil removal was found to be a straight line when percent transmission was plotted in log scale and percent oil removal in regular scale. By changing the pH levels of the test oil emulsion, it was observed that the test oil emulsion is fairly stable in the pH levels range of 3.5 to 11.0.

A ferric sulfate dosage of 200 mg/l alone was able to destabilize oil to an extent of 84 percent within the pH range of 6.0 to 10.0. The dosages of ferric sulfate in the range from 50 to 100 mg/l, failed to produce appreciable removal efficiency unless the pH was raised as high as 10.0.

Alternating current alone was found to have little effect on the overall removal and even with the addition of coagulant, no appreciable improvement was noticed. The use of direct current in conjunction with ferric sulfate, was found to be effective in destabilizing the oil emulsion when the polarities of the beakers were negative and the time of application of current was longer (e.g. 16 minutes) than 1 minute.

Therefore, detailed studies were directed to investigate the destabilizing capacity of ferric sulfate in conjunction with direct current using the beakers as the negative electrodes and are described in the subsequent paragraphs.

4.2 Detailed Studies Using Direct Current and Ferric Sulfate

The previous investigations showed clearly that direct current helped in destabilization of oil emulsion. The polarities of the electrodes and duration of application of current were found to be two important factors which influenced the overall oil removal. This part of the study was designed according to a factorial design procedure in which four levels of coagulant (0, 50, 100 and 200 mg/l) and voltages (0, 25, 50 and 100 v) were used. The time of application of direct current was selected in six levels (0, 1, 2, 4, 8 and 16 minutes); pH was adjusted around 7.5 and beakers were used as negative electrodes. Among these 96 possible combinations from factorial design, 20 more runs were replicated and these 116 runs were made at random to avoid any effect of time, room temperature and unknown factors on the stock solution.

In the preliminary studies the physical characteristics of the electrodes were checked by visual observation only. Both the stirrers and the beakers were found to be unaffected during the electrochemical treatment process. However, during this final part of the study, the weight of the electrodes were taken before and after the treatment.

Results are tabulated in Table 12. Figure 13 shows a steady increase in percent oil removal with increase in coagulant dosages, voltages and time of application of current. Maximum oil removal efficiency was obtained by using 100 volts applied for 16 minutes and was closely followed by the treatment with 100 volts for 8 minutes. For both cases the coagulant dosage was 200 mg/l. Ferric sulfate dosage of 50 mg/l, again failed to produce oil removal higher than 10 percent with any combination of voltages and time of application of current (Figure 13). Since the time of application of current was found to have some influence on the oil removal, a comparison set of curves is shown in Figure 14. All the curves were drawn with percent oil removal against time of application of current. Treatment using ferric sulfate dosage of 200 mg/l in conjunction with 100 volts of direct current (curve "a" in Figure 14), was found to be very much influenced by the time of application of current from 0 to 8 minutes. Duration of current, higher than eight minutes created almost horizontal curves signifying very little influence on the oil removal irrespective of the type of treatment.

TABLE 12

Destabilization of Oil Emulsion Using Ferric Sulfate and Direct Current

Oil Concentration = 500 mg/l

No.of Runs	0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Applications (minutes)	Coagulant Dosages (mg/l)	Loss in Weight of Stirrers or Beakers [Stirrers 'S'] [Beakers 'B'] (gm)	pH	Percent Transmission	Percent Oil Removal
1	0.0	0	0	0	0.0	7.4	11	8
2	5.0	0	0	50	0.0	7.0	7	
3	10.0	0	0	100	0.0	7.1	44	66
4	20.0	0	0	200	0.0	7.9	65	83
5	0.0	0	1	0	0.0	7.6	9	0
6	5.0	0	1	50	0.0	8.0	8	
7	10.0	0	1	100	0.0	7.6	41	63
8	20.0	0	1	200	0.0	7.5	69	85
9	0.0	0	2	0	0.0	8.1	10	4
10	5.0	0	2	50	0.0	7.3	9	0
11	10.0	0	2	100	0.0	7.9	44	66
12	20.0	0	2	200	0.0	7.6	64	82
13	0.0	0	4	0	0.0	7.2	12	12
14	5.0	0	4	50	0.0	7.7	11	8
15	10.0	0	4	100	0.0	7.5	45	67
16	20.0	0	4	200	0.0	7.4	71	86
17	0.0	0	8	0	0.0	7.9	13	15
18	5.0	0	8	50	0.0	7.3	7	
19	10.0	0	8	100	0.0	7.8	47	69
20	20.0	0	8	200	0.0	7.8	70	85

Table 12 continued

No.of Runs	0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Applications (minutes)	Coagulant Dosages (mg/l)	Loss in Weight of Stirrers or Beakers [Stirrers 'S'] [Beakers 'B'] (gm)	pH	Percent Transmission	Percent Oil Removal
21	0.0	0	16	0	0.0	7.6	9	0
22	5.0	0	16	50	0.0	7.7	8	
23	10.0	0	16	100	0.0	7.5	39	61
24	20.0	0	16	200	0.0	7.5	68	
25	0.0	25	0	0	0.0	7.6	10	4
26	5.0	25	0	50	0.0	7.2	9	0
27	10.0	25	0	100	0.0	7.4	41	63
28	20.0	25	0	200	0.0	7.1	72	87
29	0.0	25	1	0	0.0	7.9	11	8
30	5.0	25	1	50	0.0	7.3	7	
31	10.0	25	1	100	0.0	7.2	38	60
32	20.0	25	1	200	0.0	7.4	65	82
33	0.0	25	2	0	0.0007(S)	8.6	11	8
34	5.0	25	2	50	0.001(S)	7.7	7	
35	10.0	25	2	100	0.0	8.5	42	64
36	20.0	25	2	200	0.001(S)	7.6	74	88
37	0.0	25	4	0	0.0	7.7	14	18
38	5.0	25	4	50	0.0	7.4	10	4
39	10.0	25	4	100	0.001(S)	7.5	49	71
40	20.0	25	4	200	0.001(S)	7.2	72	87
41	0.0	25	8	0	0.001(S)	7.9	12	12
42	5.0	25	8	50	0.001(S)	7.8	9	0
43	10.0	25	8	100	0.002(S)	8.0	46	68
44	20.0	25	8	200	0.002(S)	7.1	68	83
45	0.0	25	16	0	0.001(S)	7.7	12	12

Table 12 continued

No.of Runs	0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Applications (minutes)	Coagulant Dosages (mg/l)	Loss in Weight of Stirrers or Beakers [Stirrers 'S'] [Beakers 'B'] (gm)	pH	Percent Transmission	Percent Oil Removal
46	5.0	25	16	50	0.002(S)	7.6	14	18
47	10.0	25	16	100	0.0	7.4	50	71
48	20.0	25	16	200	0.001(S)	7.5	71	86
49	0.0	50	0	0	0.0	7.3	12	12
50	5.0	50	0	50	0.0	7.7	9	0
51	10.0	50	0	100	0.0	7.6	44	66
52	20.0	50	0	200	0.0	7.5	68	84
53	0.0	50	1	0	0.0	7.4	11	8
54	5.0	50	1	50	0.0	7.9	7	
55	10.0	50	1	100	0.0	7.7	41	63
56	20.0	50	1	200	0.001(S)	7.5	71	86
57	0.0	50	2	0	0.0	7.6	9	0
58	5.0	50	2	50	0.001(S)	7.5	10	4
59	10.0	50	2	100	0.002(S)	7.3	48	70
60	20.0	50	2	200	0.002(S)	7.7	75	89
61	0.0	50	4	0	0.001 (S)	7.9	12	12
62	5.0	50	4	50	0.002 (S)	7.7	9	0
63	10.0	50	4	100	0.002 (S)	7.2	56	76
64	20.0	50	4	200	0.003 (S)	7.1	74	88
65	0.0	50	8	0	0.002 (S)	7.6	9	0
66	5.0	50	8	50	0.001 (S)	7.5	9	0
67	10.0	50	8	100	0.001 (S)	7.8	54	75
68	20.0	50	8	200	0.006 (S)	7.5	77	90
69	0.0	50	16	0	0.003 (S)	7.8	19	31
70	5.0	50	16	50	0.002 (S)	7.6	12	12

Table 12 continued

No.of Runs	0.1 N NaOH (ml)	Volt-age (volts)	Duration of Current Applications (minutes)	Coagulant Dosages (mg/1)	Loss in Weight of Stirrers or Beakers [Stirrers 'S'] [Beakers 'B'] (gm)	pH	Percent Trans-mission	Percent Oil Removal
71	10.0	50	16	100	0.002(S)	7.6	58	78
72	20.0	50	16	200	0.008(S)	7.3	84	93
73	0.0	100	0	0	0.0	7.1	11	8
74	5.0	100	0	50	0.0	7.9	10	4
75	10.0	100	0	100	0.0	7.2	43	65
76	20.0	100	0	200	0.0	7.7	68	84
77	0.0	100	1	0	0.0	7.9	9	0
78	5.0	100	1	50	0.001(S)	8.0	12	12
79	10.0	100	1	100	0.0	7.2	42	64
80	20.0	100	1	200	0.0	7.7	72	87
81	0.0	100	2	0	0.001(S)	7.8	11	8
82	5.0	100	2	50	0.001(S)	7.8	11	8
83	10.0	100	2	100	0.002(S)	7.4	49	71
84	20.0	100	2	200	0.001(S)	7.5	74	88
85	0.0	100	4	0	0.002(S)	7.5	13	15
86	5.0	100	4	50	0.002(S)	7.9	12	12
87	10.0	100	4	100	0.005(S)	7.6	56	76
88	20.0	100	4	200	0.004(S)	7.4	75	89
89	0.0	100	8	0	0.001(S)	7.3	4	
90	5.0	100	8	50	0.0	7.7	3	
91	10.0	100	8	100	0.004(S)	7.5	64	82
92	20.0	100	8	200	0.006(S)	7.4	94	98
93	0.0	100	16	0	0.002(S)	7.6	14	18
94	5.0	100	16	50	0.003(S)	7.7	11	8
95	10.0	100	16	100	0.002(S)	7.4	65	82

Table 12 concluded

No.of Runs	0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Applications (minutes)	Coagulant Dosages (mg/l)	Loss in Weight of Stirrers or Beakers [Stirrers 'S'] [Beakers 'B'] (gm)	pH	Percent Transmission	Percent Oil Removal
96	20.0	100	16	200	0.007(S)	7.5	98	99
97	5.0	25	8	50	0.001(S)	7.8	11	8
98	0.0	100	0	0	0.0	7.3	12	12
99	5.0	25	1	50	0.0	7.6	7	
100	20.0	100	2	200	0.002(S)	7.2	75	89
101	0.0	50	2	0	0.0	7.9	9	0
102	10.0	0	0	100	0.0	7.6	40	62
103	0.0	100	16	0	0.003(S)	7.5	15	21
104	20.0	50	16	200	0.005(S)	7.2	89	96
105	0.0	50	0	0	0.0	7.4	9	0
106	10.0	25	8	100	0.002(S)	7.4	49	71
107	20.0	25	0	200	0.0	7.7	68	85
108	0.0	50	1	0	0.0	7.6	12	12
109	0.0	100	8	0	0.0	7.9	4	
110	10.0	50	2	100	0.002(S)	7.8	48	70
111	0.0	100	1	0	0.001(S)	7.5	11	8
112	0.0	50	8	0	0.002(S)	7.5	12	12
113	5.0	50	16	50	0.002(S)	7.3	12	12
114	0.0	50	4	0	0.001(S)	7.6	11	8
115	5.0	25	2	50	0.00	7.2	10	4
116	10.0	25	4	100	0.001(S)	7.8	50	72

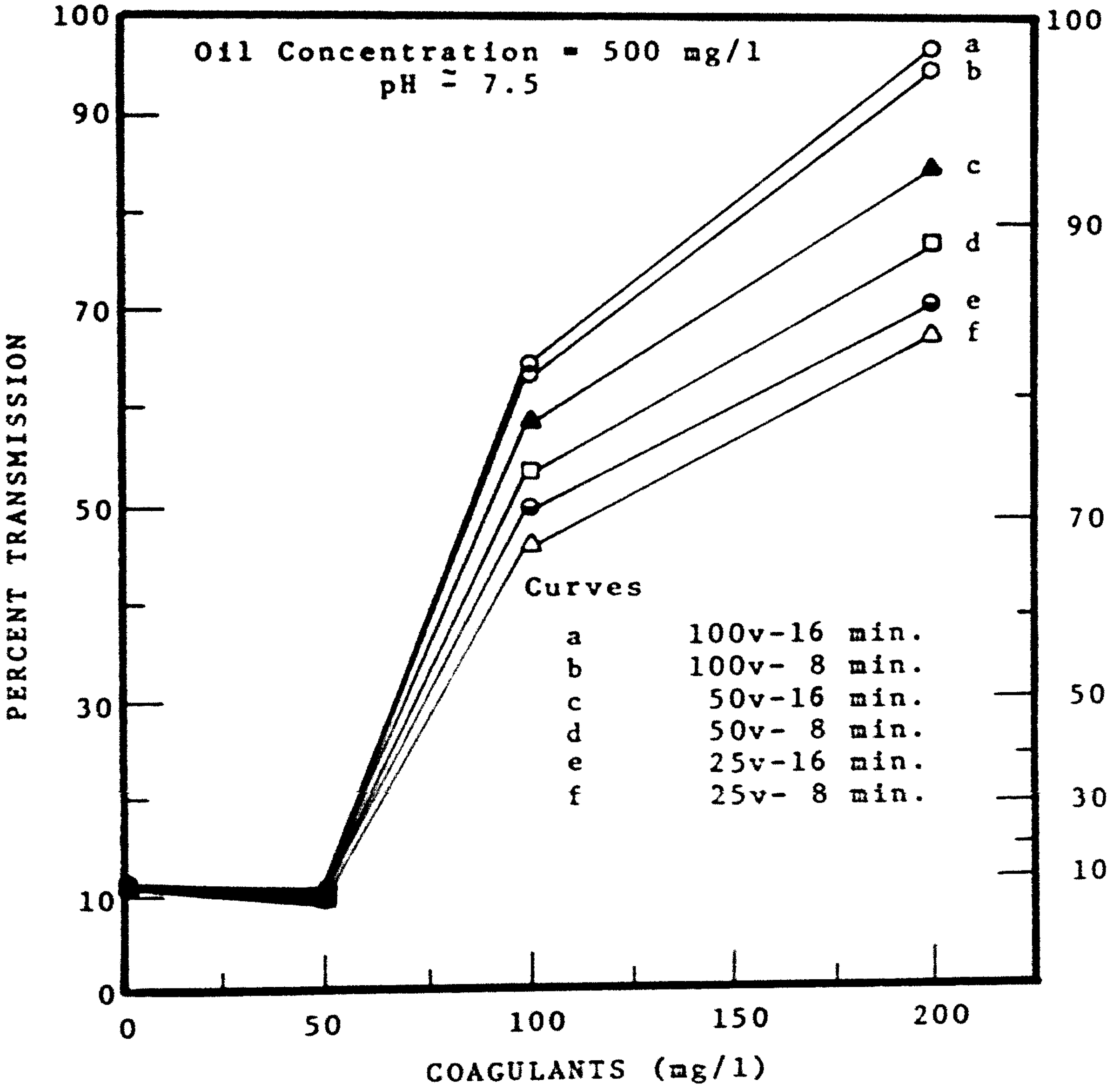

Figure 13 Typical Curves for Comparison Using Best Results with 100, 50 and 25 volts Applied for 16 and 8 minutes, respectively.

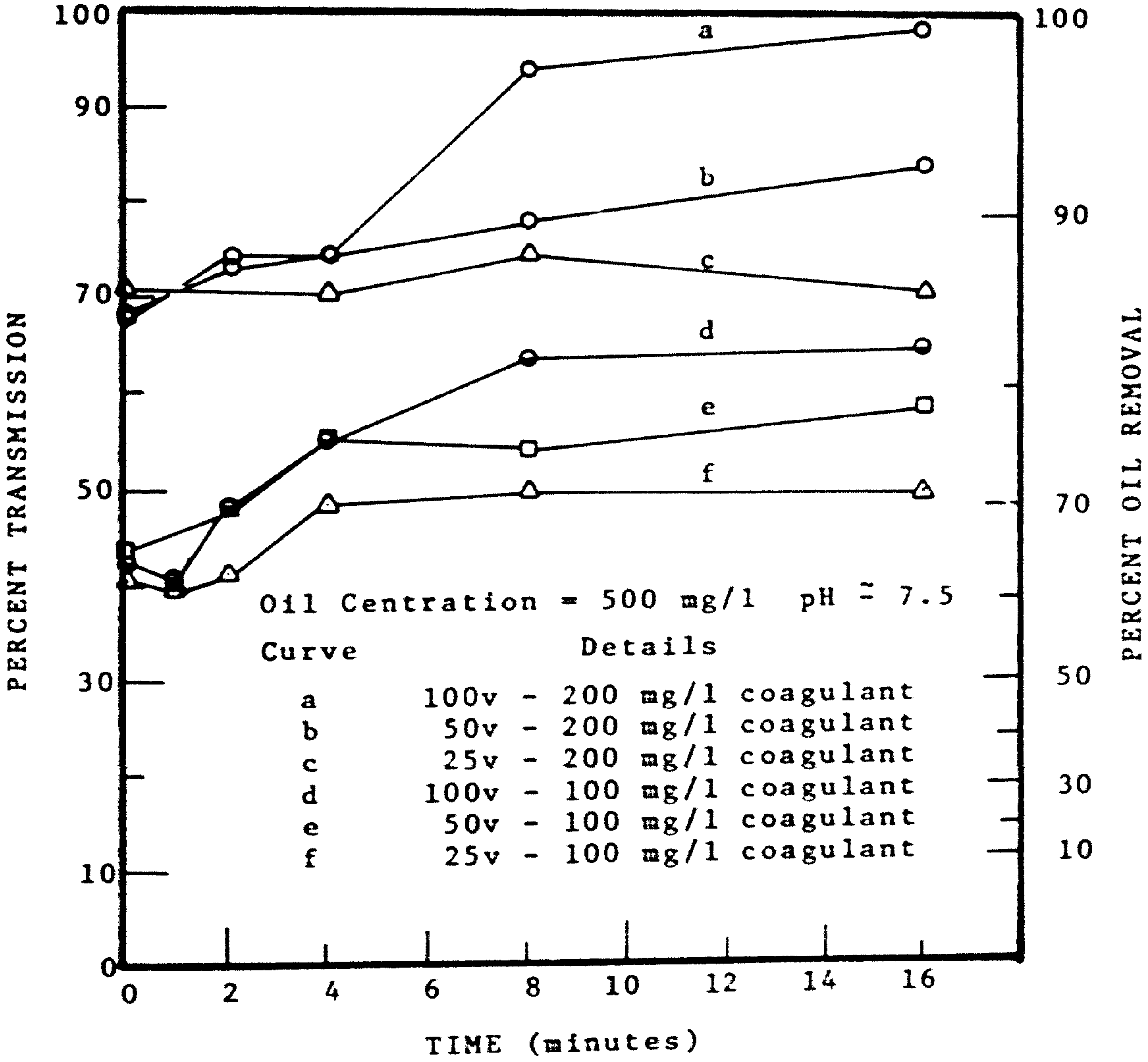

Figure 14 Effects of Time and Coagulants on Overall Oil Removal

As mentioned earlier in this part of the chapter, loss in weight of the electrodes (both stirrers and beakers) during treatment was taken into account and tabulated in Table 12. The stirrers had the positive polarity throughout this study (Table 12) and were always found to lose weight after the treatment. This was probably due to higher current densities around the stirrers because of their relatively smaller surface areas than the beakers. Whenever there was any loss in weight from the stirrers, it was regarded as iron loss in the form of (Fe^{3+}) and eventually increased the original ferric sulfate dosages.

The increase in coagulant dosage resulting from the loss in weight of the stirrer was calculated for the run number 92 (Table 12). In this particular treatment 6 mg of iron, as Fe^{3+}, were leached out and increased the ferric sulfate dosage of 200 mg/l by 15.1 percent.

To examine the weight loss of stirrers at high pH, a set of experiments was carried out using direct current of 100 volts applied for 16 minutes with nine levels of ferric sulfate dosages: 0, 25, 50, 75, 100, 125, 150, 175 and 200 mg/l. The pH level was maintained at 11.0 which was slightly below the critical value (pH = 11.3). The maximum level of voltage (100 volts) and time of application of current (16 minutes) were chosen presuming it would create favourable conditions for dissolution of stirrers. The polarities of the beakers were negative. Curves are drawn in Figure 15

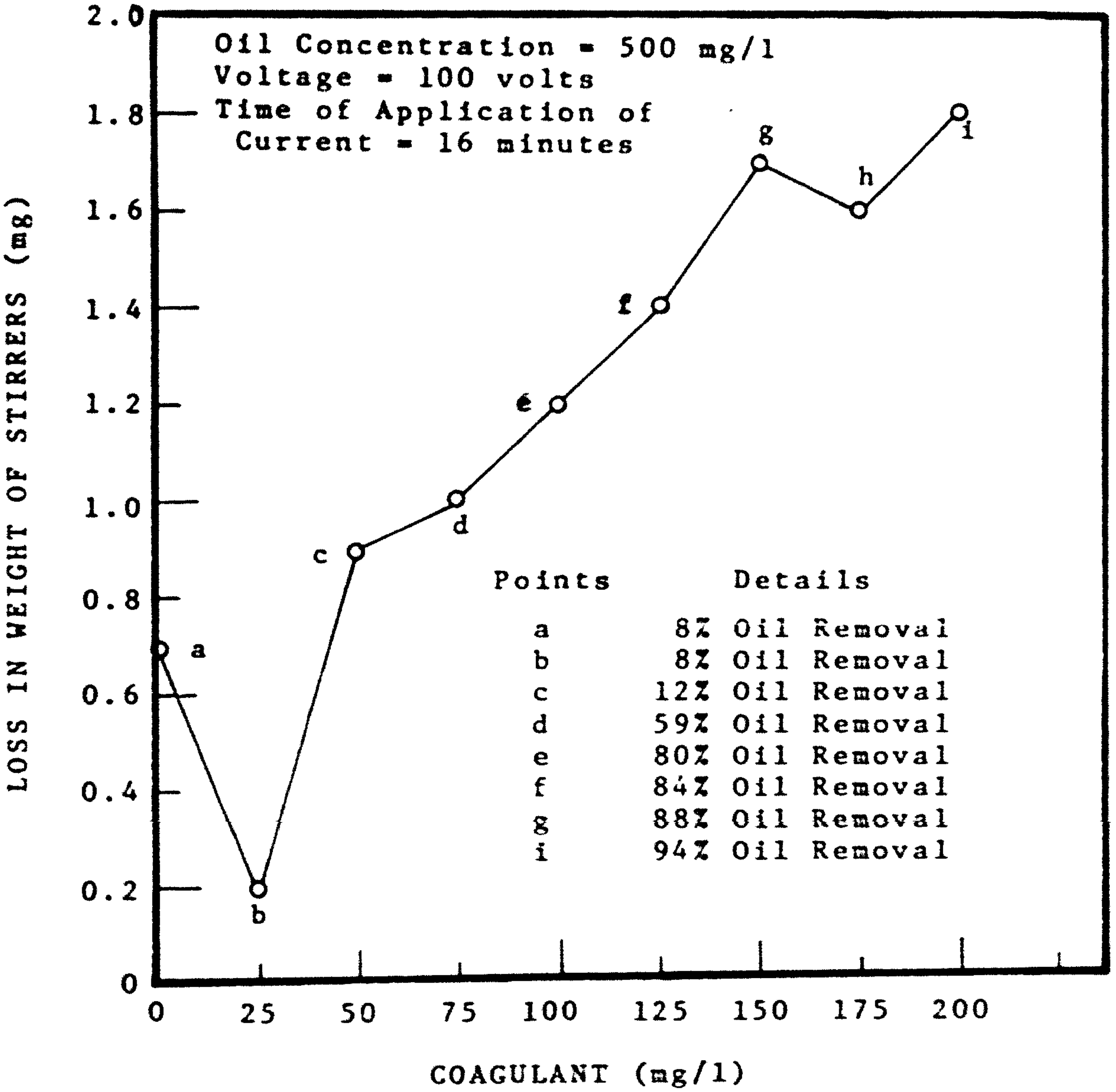

Figure 15 Relationship Between Loss in Weight of Stirrers and Coagulant Dosages at pH ≃ 11.0

which summarizes data from Table 13. Figure 15 is drawn with weight losses of stirrers against coagulant dosages at different values of percent oil removal. Maximum loss in weight of stirrer was 1.8 mg for a ferric sulfate dosage of 200 mg/l. This amount (1.8 mg as Fe^{3+}) increased the ferric sulfate dosage of 200 mg/l by less than 5 percent compared to the previous value of 15.1 percent.

Summary of the previous studies clearly indicates that for electrophoretic effect as an aid in the destabilization of oil emulsion, it is necessary to have the voltage level higher than 50 volts. The duration of current was also very important and the effective level was found to be at least 8 minutes. Coagulant was probably the most significant parameter. Dissolution of iron as Fe^{3+} could be minimized by raising the pH to 11.0. Therefore, some more experiments were made to compare the effect of voltages and duration of current while the loss in weight from the stirrers were kept to a minimum. The data are provided in Table 14 where only two levels of voltages (100 and 50 v) were used in combination with five levels of ferric sulfate dosages (0, 50, 100, 150 and 200 mg/l) and the timesof application of current were 8 and 16 minutes respectively. The level of pH was around 11.0 and the polarities of the beakers were negative. The results are plotted in Figure 16 which shows an increase in oil removal with an increase in all the three parameters such as coagulants, voltage levels, and time of

TABLE 13

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate at pH $\simeq$ 11.0 - Time of Application of Current = 16 minutes (Flashmix and Flocculation)

Beakers as Negative Electrodes

Oil Concentration = 500 mg/l

0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Application (minutes)	Coagulant dosages (mg/l)	pH	Loss in wt. of Stirrers (gm)	Percent Transmission	Percent Oil Removal
45.0	100	16	0	11.1	0.0007	11	8
50.0	100	16	25	11.15	0.002	11	8
52.0	100	16	50	11.2	0.0009	12	12
54.0	100	16	75	10.95	0.001	37	59
55.0	100	16	100	11.0	0.0012	61	80
58.0	100	16	125	11.05	0.0014	68	84
60.0	100	16	150	11.2	0.0017	74	88
62.0	100	16	175	11.1	0.0016	80	91
65.0	100	16	200	11.0	0.0018	86	94

TABLE 14

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate at pH Level ≈ 11.0

Beakers as Negative Electrodes

Oil Concentration = 500 mg/l

0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Application (minutes)	Coagulant dosages (mg/l)	pH	Loss in wt. of Stirrers (gm)	Percent Transmission	Percent Oil Removal
45.0	100	16	0	10.95	0.0002	14	18
50.0	100	16	50	10.9	0.0002	12	12
55.0	100	16	100	11.0	0.009	62	80
60.0	100	16	150	11.15	0.0011	75	88
65.0	100	16	200	11.1	0.0015	88	95
45.0	100	8	0	11.05	0.0002	14	18
50.0	100	8	50	10.9	0.0001	14	18
55.0	100	8	100	11.0	0.0003	56	76
60.0	100	8	150	11.2	0.0006	70	85
65.0	100	8	200	11.0	0.0009	81	92
45.0	50	16	0	11.1	0.00	14	18
50.0	50	16	50	11.05	0.0003	12	12
55.0	50	16	100	11.15	0.0002	57	77
60.0	50	16	150	10.95	0.0006	67	83
65.0	50	16	200	10.9	0.0008	77	90
45.0	50	8	0	11.0	0.00	13	15
50.0	50	8	50	11.15	0.00	13	15
55.0	50	8	100	11.1	0.0001	54	74
60.0	50	8	150	11.2	0.0003	64	82
65.0	50	8	200	11.25	0.0005	75	89

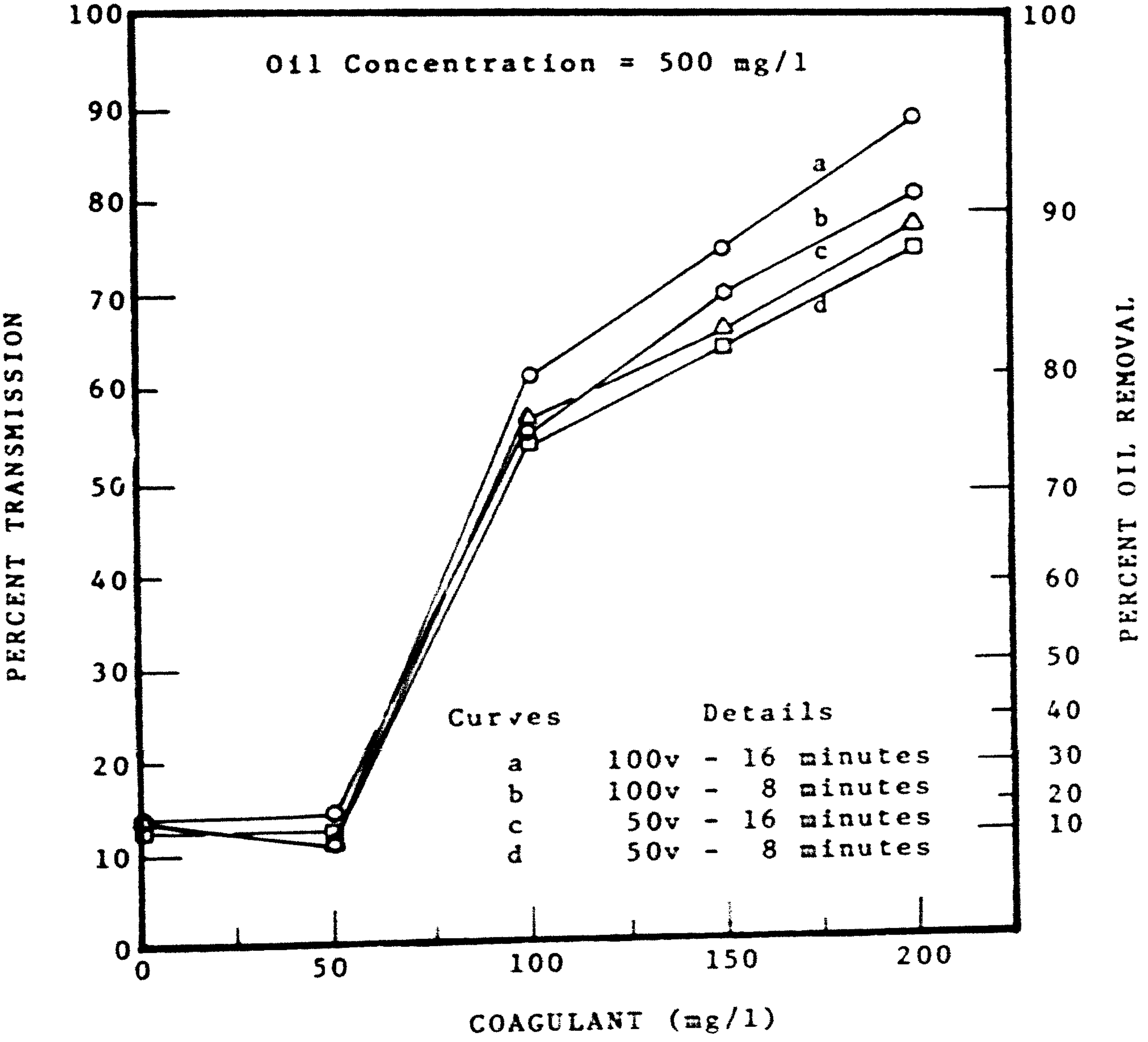

Figure 16 Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate at pH ≅ 11.0

application of current. A ferric sulfate dosage, higher than 50 mg/l showed an uprise pattern of curves with every combination of voltage level and time of application of current. The treatment using 100 volts has a slight edge over 50 volts for a high percent removal, like 80 percent transmission (90% oil removal) and above. For a percent transmission of 75 (89 percent oil removal) the best combination was 50 volts for 8 minutes with 200 mg/l coagulant. Comparing Figures 12 and 16, it could be seen that only one combination of coagulant (200 mg/l) with 100 volts for 16 minutes gave a 10% increase in overall removal over the treatment without current at a coagulant level of 100 mg/l and more. All other combinations of current failed to produce more than 10% increase in treatment efficiency over the treatments where current was not used.

The amount of sludge produced is a very important factor in coagulation studies because the cost of sludge removal is very high. Therefore, some test runs were made to evaluate the amount of sludge produced and these are described in the following paragraph.

4.3 Sludge Production

The objectives of this part of the study were to compare the amount of sludge production, using ferric sulfate in conjunction with direct current, with the treatment where ferric sulfate was used alone. The dosages of ferric sulfate were chosen in five levels, i.e., 0, 50, 100, 150 and 200 mg/l and two levels of voltages, i.e., 50 and 100 volts were used for 16 minutes. The results are presented in Table 15 where the level of pH was around 11.0 and the polarities of the beakers were negative. Figure 17 reveals the curves drawn with weight of sludge produced against coagulant dosages. For the same degree of oil removal, the amount of sludge produced was found to be almost the same which showed that the type of treatment, i.e., whether chemical or electrochemical, did not influence sludge production. For example, ferric sulfate dosage of 200 mg/l removed 82 percent oil (Table 15) and produced 310 mg of sludge while a treatment using 100 volts for 16 minutes with 100 mg/l of ferric sulfate removed the same amount (82 percent) of oil and the sludge amounted to 300 mg. A difference noticed was that the sludge formed after treatment using current was found floating at the top of the solution like a scum layer, while on the otherhand the sludge produced by treatment without current settled to the bottom of the beakers. The reason might be that the formation of gas in the emulsion, during current application, forced the sludge upwards and made it float as a scum layer.

TABLE 15

Destabilization of Oil Emulsion Using Direct Current and Ferric Sulfate at pH ≃ 11.0 -

Quantity of Sludge Produced

Beakers as Negative Electrodes

Oil Concentration = 500 mg/1

0.1 N NaOH (ml)	Voltage (volts)	Duration of Current Application (minutes)	Coagulant Dosages (mg/1)	pH	Percent Transmission	Weight of Sludge Produced (gm)	Percent Oil Removal
45.0	0	0	0	10.8	14	0.00	18
50.0	0	0	50	10.95	11	0.00	8
55.0	0	0	100	11.0	41	0.21	63
60.0	0	0	150	11.0	52	0.27	73
65.0	0	0	200	11.1	64	0.31	82
45.0	100	16	0	11.2	12	0.00	12
50.0	100	16	50	11.1	15	0.00	21
55.0	100	16	100	11.07	64	0.30	82
60.0	100	16	150	10.95	77	0.35	80.
65.0	100	16	200	11.1	90	0.41	96
45.0	50	16	0	11.0	13	0.00	15
50.0	50	16	50	11.05	14	0.00	18
55.0	50	16	100	11.1	53	0.29	74
60.0	50	16	150	11.15	69	0.31	85
65.0	50	16	200	10.98	78	0.38	90

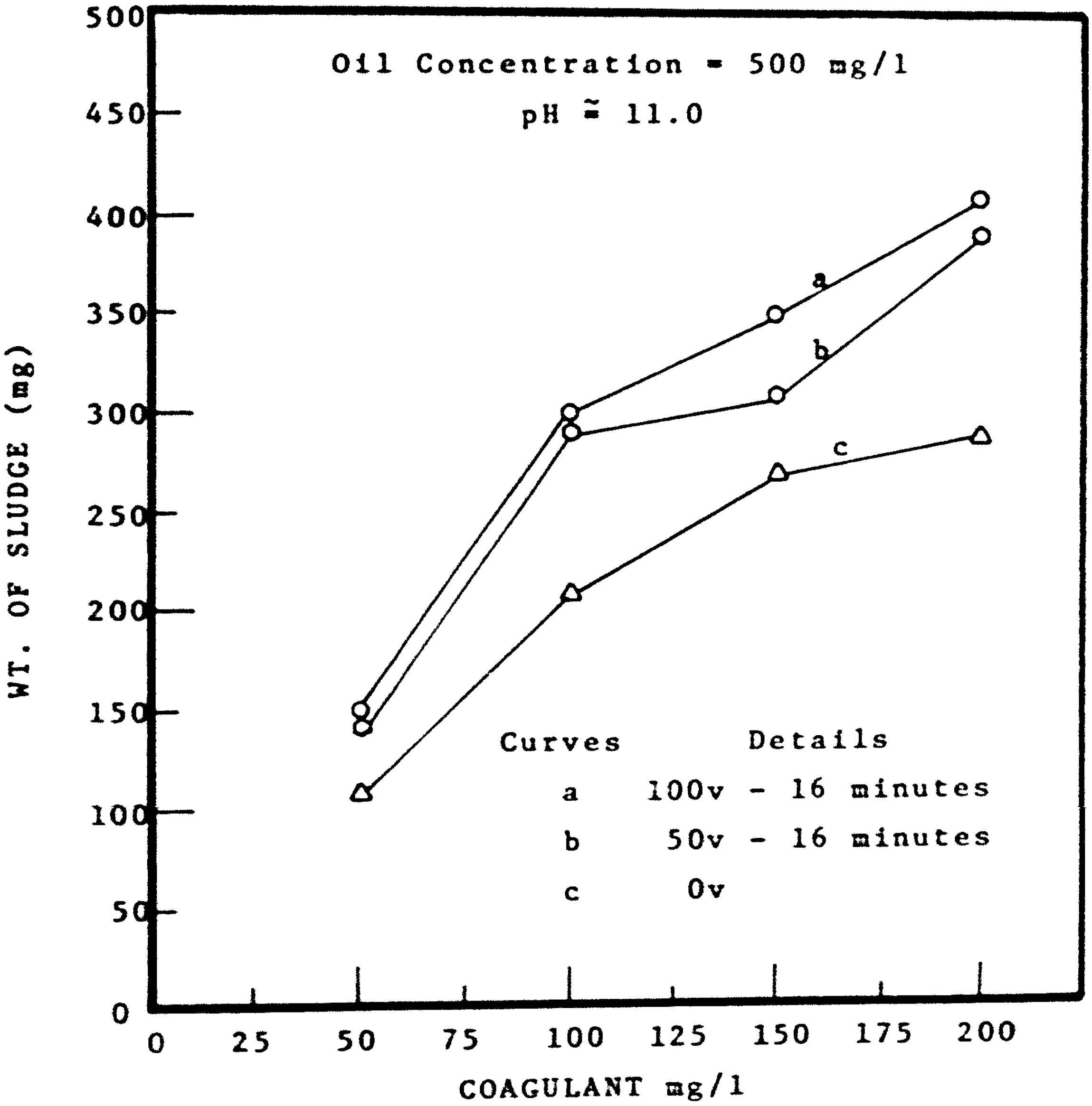

Figure 17 Relationship Between Coagulant Dosages and Weight of Sludge Produced

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary

In this study, destabilization of oil-in-water emulsion was investigated in the laboratory by electrochemical treatment using jar test apparatus. The sample size used in the experiments was 1000 ml. The oil concentration used throughout the study was of 500 mg/l because it was found to be the most common concentration of oil in the industrial wastewater.

The type of colloid in this type of oil emulsion is hydrophilic type which needs both desolvation and charge neutralization. Ferric sulfate was found to possess both the properties and was used as the only coagulant in this study. The prime object of this research was to improve the efficiency of coagulation by introducing current as an aid for desolvation while ferric sulfate acted primarily to neutralize the charge; minimization of sludge production was also another aspect studied. The studies were carried out using both alternating and direct currents, with and without coagulant.

Destabilization of the oil emulsion was possible by using ferric sulfate alone but the dosages required were fairly high, for example, for 68 percent transmission (84% oil removal), the required dosage was 200 mg/l. First alternating current was used with or without any ferric sulfate. The voltage was as high as 100 volts and the longest duration of current was for 16 minutes. But there was no significant change on overall removal. The subsequent studies were carried out with direct current of different voltage levels (0, 25, 50 and 100 v) and the durations of application of current were also varied from 0 minutes to 16 minutes. the pH level was kept around 7.5. The removal efficiency was found to be as high as 96%, but it was noticed that the stirrers were giving away ferric ions during electrolysis. Therefore, the pH level was raised to 11.0 which is high enough to minimize dissolution of the electrodes. The removal efficiency was found to be as high as 96%, using 150 mg/l of ferric sulfate, the current was 100 volts continued for 16 minutes.

The last part of this investigation was devoted in finding out the amount of sludge produced. The amount of sludge produced was the same, for the same degree of treatment, with or without current. It showed that percent transmission or removal was proportional to the weight of sludge produced and independent of the type of treatment.

5.2 Conclusions

1. The destabilization of the test oil emulsion was possible by charge neutralization and desolvation of colloid.

2. The optimum wave length of the oil emulsion was 440 mμ.

3. Spectrophotometry was a satisfactory technique to measure the percent oil removal.

4. Change in pH from 3.5 to 11.0 were not found to have significant influence on the removal of oil from the soluble oil emulsion; but an appreciable increase was found on the oil removal, when the pH level was higher than 11.3.

5. Ferric sulfate alone was found to be capable of charge neutralization and desolvation of hydrophilic colloid.

6. Alternating current alone was found to have little effect on the overall oil removal and even with the addition of ferric sulfate, no appreciable improvement was noticed.

7. Direct current with ferric sulfate was found to be effective in destabilizing the oil emulsion when the beakers were negatively charged. The voltage supplied had to be above 50 volts and the duration of current application at least 8 minutes in order to achieve oil removal efficiency above 70 percent.

8. When direct current was used along with coagulants and a pH around 7.5, ferric ions were leached from the stainless steel stirrers. An increase in pH level, around 11.0, reduced the leaching effect.

9. The change in the amount of sludge produced from the treatment with ferric sulfate alone and in conjunction with

direct current, was also investigated. Results showed that for the same percent oil removal, the weight of sludge produced remained approximately the same even with the different types of treatment.

5.2.1 Suggestions for Further Research

It was shown in this research that destabilization of soluble oil emulsion was possible by ferric sulfate coagulation combined with direct current. Further investigations should be carried out using direct current in conjunction with other coagulants or polyelectrolytes.

The use of electrodes, made of materials more chemically inert than stainless steel, e.g., carbon, should be investigated.

A detailed economic study, scaling up the laboratory results would be of interest. Since the use of direct current is more costly than alternating current, some investigations may be worthwhile using alternating current at a level above 100 volts and with a changed frequency.

It may be worthwhile to conduct further studies to destabilize the oil emulsion, only by raising the level of pH. The economics involved in raising the pH and disposing of the sludge are areas of further interest.

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