CHAPTER- 2

TREATMENT OF OIL WELL EFFLUENT USING

INORGANIC ELECTROLYTES

INTRODUCTION

In many parts of the world, oil has become the most frequently encountered water pollutant [1]. This has become the most inevitable consequence,because of the dependence of rapidly growing population on oil- based technology [2]. Along with this, the stringent quality requirements of the waste water from oil industries to be discharged to sea or to be used for the environmental purposes are also increased. The objectionable nature of the oil pollution has been recognized and the problem has been under continuous study.

The oily wastewater is generated from the activities of oil-well drilling, oil production, oil refinery, automobile, metal working plants, oil washed from roads together with illegal discharge of engine oil etc [3, 4]. These wastewaters contain dissolved, floating and emulsified oil. The concentration of oil in the effluents vary with the source and ranges from several mg/L to as high as 40,000 mg/L [5- 8]. But the Pollution Control Board regulations do not permit the dischrage of more than 10 mg/L of oil in the wastewater [9]. Therefore the oil must be removed before the wastewater is discharged.

The problem of oil pollution has its short and long term effects [10]. The short term effects are seen immediately and are the ones that have received the most publicity [2]. The long term effects have been seen very slowly and have been currently the subject of much discussion. The reduction in light transmission and dissolved oxygen content are the main short term effects caused by the oil pollution. The photosynthesis of the aquatic plants is generally affected by the poor light transmission caused by the oil pollution. The oil film formed on the surface of the water reduces the oxygen uptake by water. Emulsified oil will take-up mineral particles and thus sink to sea bottom. This oil on the sea bottom persists for long period of time and damage the plants and animals.

Water soluble components of the crude oil are toxic to fresh water animals. But the prediction of the toxic effects is very difficult owing to the complex nature of the wastewater and lack of extensive experimentation. The monohydric aromatic components are highly toxic than the aliphatic components and the degree of toxicity increases with the increase in unsaturation [4]. Water insoluble hydrocarbon fraction of the oil destroy the eggs and larvae of the aquatic fauna that float on the surface of the water [10]. Oil pollution destroys marine and inland fisheries. Minute quantities of oil gives undesirable taste to fishes, thus making them unacceptable for food [11,12]. Some studies in which cattle and sheep were given drinking water, polluted with crude oil, showed adverse effect due to the laxative properties of the oils [11]. The different physico-chemical effects of oil well effluent, its biological properties and its disposal have been discussed by Kenz et al in 1987 [13]. Oil and grease in wastewater also serve as the concentration medium for other soluble highly toxic components such as pesticides. These toxic sometimes reach a concentration many times which is beyond the limitation of Pollution Control Board [1, 2]

Due to the high temperature, pressure and the mechanical action at the drilling site, mainly two types of emulsions are formed, 1) water- in- oil emulsions or regular emulsions and 2) oil- in- water emulsions or reverse emulsions [2, 3]. In case of reverse emulsions the oil is broken up into very small droplets and are dispersed in water. Although these emulsions are thermodynamically unstable, oil- in- water emulsions are kinetically stable and must be treated to speed up the phase separation process. The emulsified oil may be present in different forms depending on the particle size. The stability of this emulsion arises mainly because of the formation of the film at the oil-water interface [14,15]. The choice of the method for the treatment of oil-in-water emulsions depends on the availability and cost of the coagulant, the sludge treatment and the disposal considerations [16,17]. Sam etal has discussed the nature of the emulsions, factors affecting the emulsion stability and the use of different emulsifiers for the oil

removal [18]. The floating oil on the surface of the water can be removed by gravity separation and simple skimming operation [19]. But the emulsified oil need special treatment to break the emulsions so that the oil will become free and can be separated by gravity, coagulation or oil floatation methods [19, 20]. The breaking of this oil-in-water emulsion is a complex task and require laboratory scale investigations.

Organic polyelectrolytes have been used for the breaking of the oil-in-water emulsion [3, 21-26]. But the high cost of this polyelectrolytes restrict its use by small scale industries. American Petroleum Institute (API) has developed a large number of methods for the treatment of emulsified oil and free acids.API gravity separator is generally used for oily wastewater treatment [27, 28]. This technique depends on the difference in the gravity of oil and water. One of the major draw backs of this process is that it cannot separate all emulsified oil [3, 16, 28, 29].

In 1975 Ghosh put forward a new process for oily wastewater treatment. According to this, two metals in contact with each other and submerged in a conducting aqueous medium, form an electrochemical cell. This develop an electrical charge by which negatively charged oil droplets move to anodic areas and deposit in the anodic surface [30].

There are several advanced techniques for oily wastewater treatment [31] for example ultrafiltration, dissolved air flotation, filtration, coalescers and centrifugation. Many of these techniques are not applicable for the treatment of large volume of water [3]. Air floatation treatment and its application to oil removal is discussed in detail by Bennett [32]. Depending on how the air is introduced, this method can be carried out in two ways, dissolved air floatation and induced air floatation [32]. A removal of 89 and 93% of oil was reported by dissolved air and induced air floatation respectively [33]. But incase of oil field brine treatment only 26% of removal efficiency was obtained using dissolved air floatation method [34]. The main drawback of this method is the

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foaming problem which make the process unsuccessful. The study showed that improved oil separation is possible with electrolytic [19, 35, 36] and electrocoagulation methods [37, 38, 39].

Oil has the ability to disrupt the biological treatment process as it forms a thin film which cover the medium in the percolating filter and the flocs of the activated sludge plants. Moreover biological process cannot be used for the oily wastewater containing large amount of total dissolved salts (for e.g. oil well effluent) since only few micro-organisms can tolerate the high salinity changes [40,41].

All the above mentioned modern treatment techniques are highly expensive and a small scale industry cannot afford such high cost techniques for the treatment of their effluent. This necessitate the need for finding out a simple and economically viable treatment technique. The most successful and the most economical method to separate oil from oil- in water emulsion is chemical coagulation, using, aluminum and iron salts [3, 16,17,19, 31, 42]. $Al_2(SO_4)_3$ [16] and $FeCl_3$ (9) are the generally used inorganic coagulants for this purpose. This method is highly sensitive to change in pH and alkalinity [9]. Large volume of sludge is produced when these coagulants are used for demulsification, which then create sludge disposal problem.There is not much information available done on the oil removal from oil well effluent using combination of inorganic electrolytes. So the present work discusses the demulsification rate of this combined demulsifier and is compared with that of Na_2SO_4, $FeSO_4$ and $FeCl_3$ when they were used individually.

STUDY AREA

The Mehasana Division of Oil and Natural Gas Corporation Ltd.(O.N.G.C.) operates 800 oil wells in the Mehsana region and produces nearly three million tonnes of crude oil and large quantities of associated gas every year. The crude produced from these well heads is an intimate mixture of oil, gas and brine The constituents of the

mixture are separated and processed in O.N.G.C. installations located at South Kadi, North Jotana and South Sobhasan. In these plants, good separation of gas and oil is achieved, however, the final effluent water stream carries salts at 7000 to 13,000 mg/L, and traces of oil that are unacceptable to the state Pollution Control Board authorities.

The output of effluent water from these plants is 5000 M^3 everyday and is likely to go up in near future. It is desired to reduce the traces of oil in the water and utilize it to increase the productivity of agricultural and environmental systems of the Mehsana region. The effluent characteristics: Pretreated Characteristics of effluent is that it contains oil and grease in the vicinity of 200 mg/L and the total dissolved solids around 13,000 mg/L.This effluent has the temperature 80°C and the pH in the range of 7.8 to 8.0.

EXPERIMENTAL PROCEDURE

The effluent samples were supplied by the Mehsana Project, O.N.G.C. The stock solution was shaken well before samples were taken for experiments. The inorganic electrolytes used were of A R grade from Qualigens. Triple distilled water was used for TOC and COD analysis. One litreof the samplewas taken in glass stoppered bottles. Different pH values between 4 to 8 with the difference of 1 unit were adjusted by adding H_2SO_4 and NaOH. To these solutions, different concentrations of Na_2SO_4, $FeSO_4$ and $FeCl_3$ were added and shaken vigorously for 15 minutes, at the temperature 80°C.The sample was kept for 5- 6 hrs. to maximize the demulsification [9]. The floated oil was then removed by filtration.

The residualoil remaining in the water was analyzed gravimetrically using Mettler balance and Spectrophotometrically using Shimadzu-240 UV-Vis spectrophotometer. For the spectrophotometric analysis the residual oil was extracted by cyclohexane and the absorbance was measured at 228 nm.A standard graph has

been plotted (absorbance versus known amount of oil). For the unknown, the absorbence at the peak maxima was noted and the concentration (A) at that absorbence was calculated from the standard graph. The oil remaining in mg/L was obtained by the equation,

$$\frac{A \times 1000}{ml.\ sample}$$

The total organic carbon (TOC) value is significant as it indicates the amount of dissolved organic substances in water and can be applied to study the oily waste water from the industries. The determination of oxidisable organic compound is also possible by COD method Also attempts were made in the present work to corrilate the COD and TOC. The COD of the sample is measured by refluxing the sample with sulphuric acid dichromate mixture and the amount of dichromate remaining at the end of the refluxing period being determined by the titration with ferrous ammonium sulphate.

In this method 50 ml. of the sample was taken and 25 ml. of 0.1 N potassium dichromate was added. Sulfuric acid mixture (concentrated sulfuric acid+silver sulphate) and mercuric chloride were added and this mixture was then refluxed for two hours.. The solution is then cooled, diluted and titrated with ferrous ammonium sulphate using ferroin indicator.

The total carbon content is determined by the combustion of a sample in a high temperature (950°C) furnace where the CO_2 is produced. It is then converted into methane by heating it at 450°C in the presence of nickel catalyst.The methane is measured by FID detector as in GC. The Instrument is calibrated for the ranges 0 to 50 and 0 to 100 milligrams per litre of carbon.

TABLE - 1

The Influence of Sodium Sulfate Concentration on Removal of Residual Oil from Oil-in- Water Emulsion

pH	Concentration of Na_2SO_4 mg/L			
	250	500	750	1000
4	50	36	28	19
5	57	46	31	29
6	64	55	48	40
7	69	59	50	46
8	85	66	57	54

Oil Content Determined Gravimetrically as mg of Oil Remaining in 1 Litre of effluent

TABLE - 2

The Influence of Sodium Sulfate Concentration on Removal of Residual Oil from Oil- in- Water Emulsion

pH	Concentration of Na_2SO_4 mg/L			
	250	500	750	1000
4	50	35	25	20
5	55	50	30	30
6	60	55	45	40
7	70	60	50	45
8	85	70	60	55

Oil Content Determined Spectrophotometrically as mg/L of oil remaining in one litre of effluent.

TABLE - 3

The Efficiency of Ferrous Sulfate in Removing Residual Oil from Oil- in-Water Emulsions

pH	Concentration of $FeSO_4$ mg/L			
	250	500	750	1000
4	64	44	30	21
5	60	38	20	15
6	70	50	38	24
7	75	56	45	40
8	80	63	54	44

* Residual Oil Determined Gravimetrically as mg/L of effluent.

TABLE - 4

Spectrophotometric Results.

pH	Concentration of $FeSO_4$ mg/L			
	250	500	750	1000
4	70	45	30	25
5	60	40	20	20
6	70	45	40	25
7	75	55	45	45
8	80	60	55	50

* Residual Oil Determined Spectrophotometrically as mg/L of Effluent.

TABLE - 5

The Efficiency of Ferric Chloride in Removing Residual Oil from oil- in- Water emulsions

PH	Concentration of FeCl₃ mg/L			
	250	500	750	1000
4	60	40	21	17
5	62	35	19	15
6	73	52	37	26
7	80	62	56	43
8	86	70	60	51

Residual Oil determined Gravimetrically as mg/L of effluent

TABLE - 6. The Efficiency of Ferric Chloride in Removing Residual Oil from oil- in-,water emulsions.

pH	Concentration of FeCl₃ mg/L			
	250	500	750	1000
4	70	40	25	20
5	60	35	20	20
6	75	45	35	25
7	80	60	55	45
8	80	70	60	55

*   Residual oil determined Spectrophotometrically as mg/L of effluent

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TABLE - 7

The efficiency of Combinations of ferrous and Sodium Sulfates in Removing Residual oil from Oil- in- Water emulsions.

pH	$FeSO_4/Na_2SO_4$ 250/250 mg/L each	$FeSO_4/Na_2SO_4$ 500/500 mg/L each
4	15	16
5	13	12
6	40	31
7	43	37
8	45	42

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Fig.1. Effect of pH on liberation of oil from oil-water emulsion at different Na_2SO_4 concentration
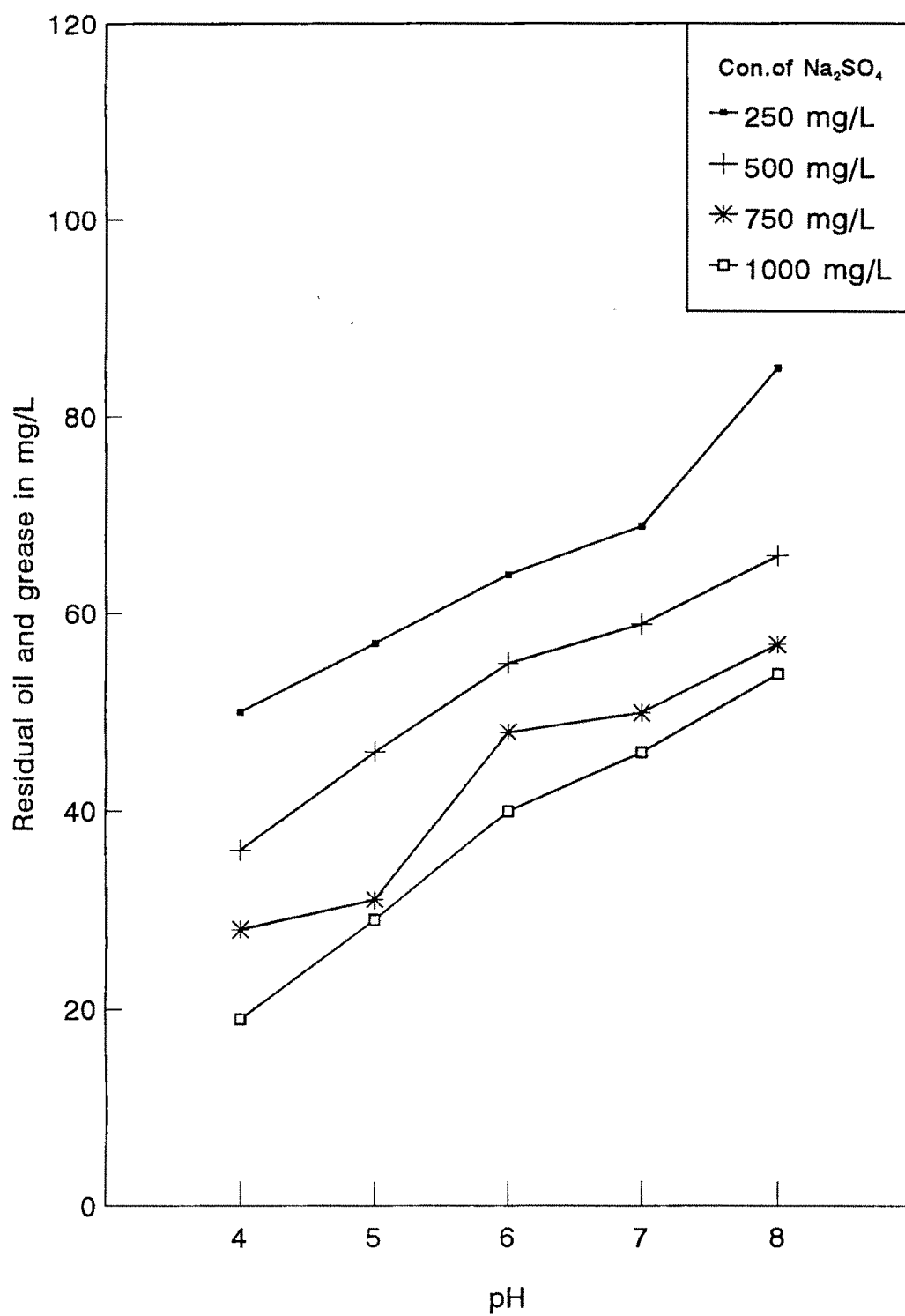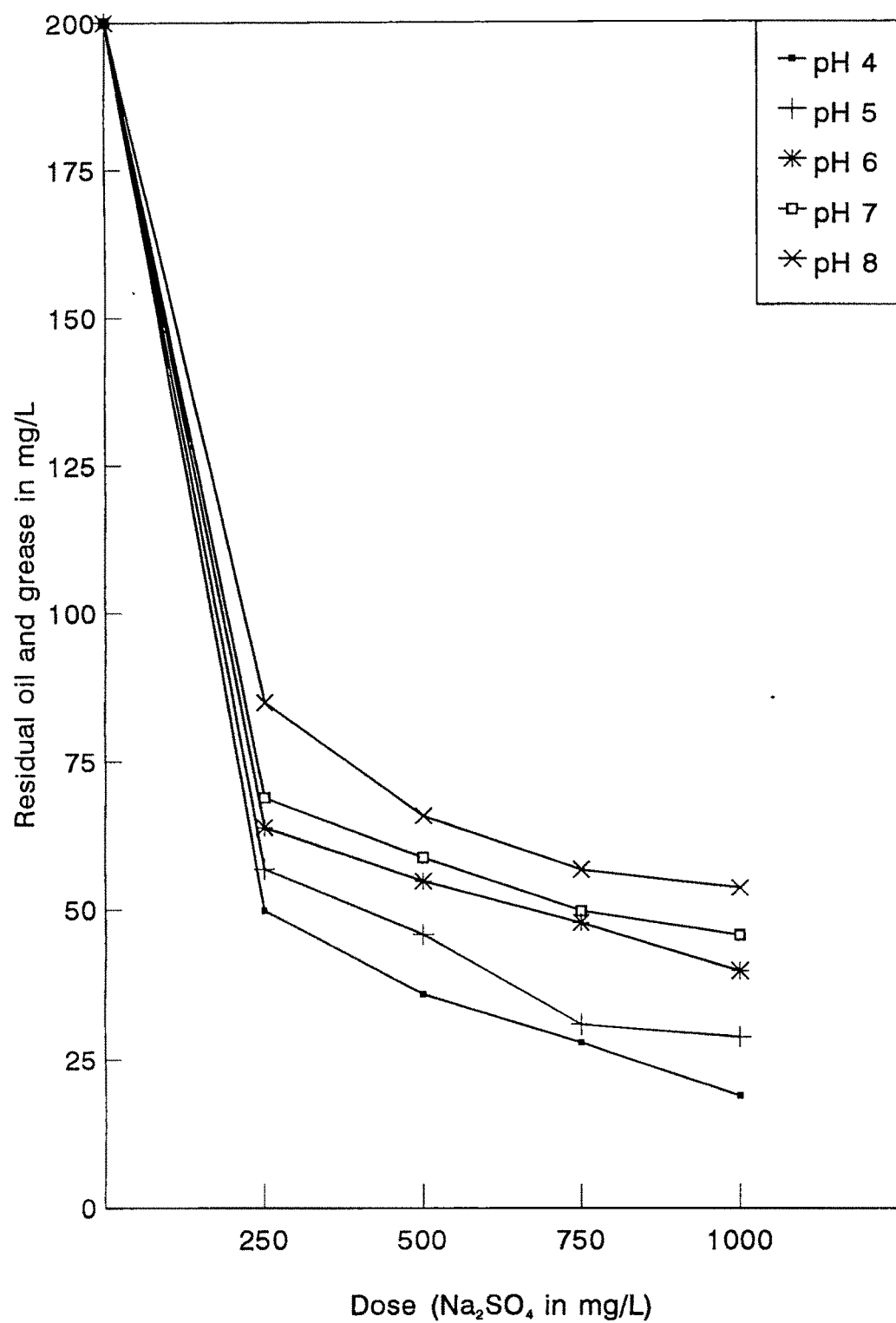
Fig.2. Effect of concentration of Na_2SO_4 on oil liberation at different pH

Fig.3. Effect of concentration of $FeSO_4$ on oil liberation at different pH
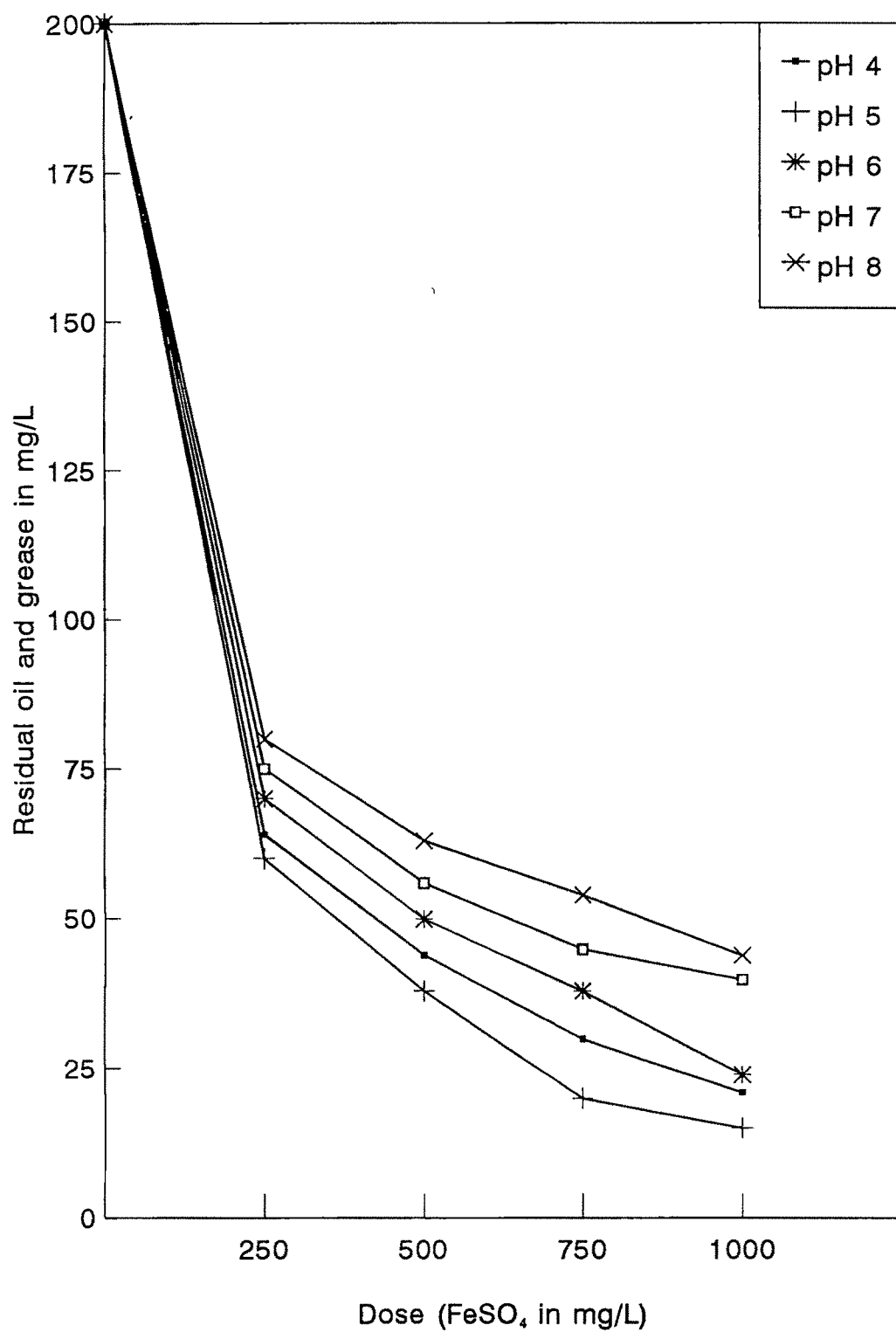
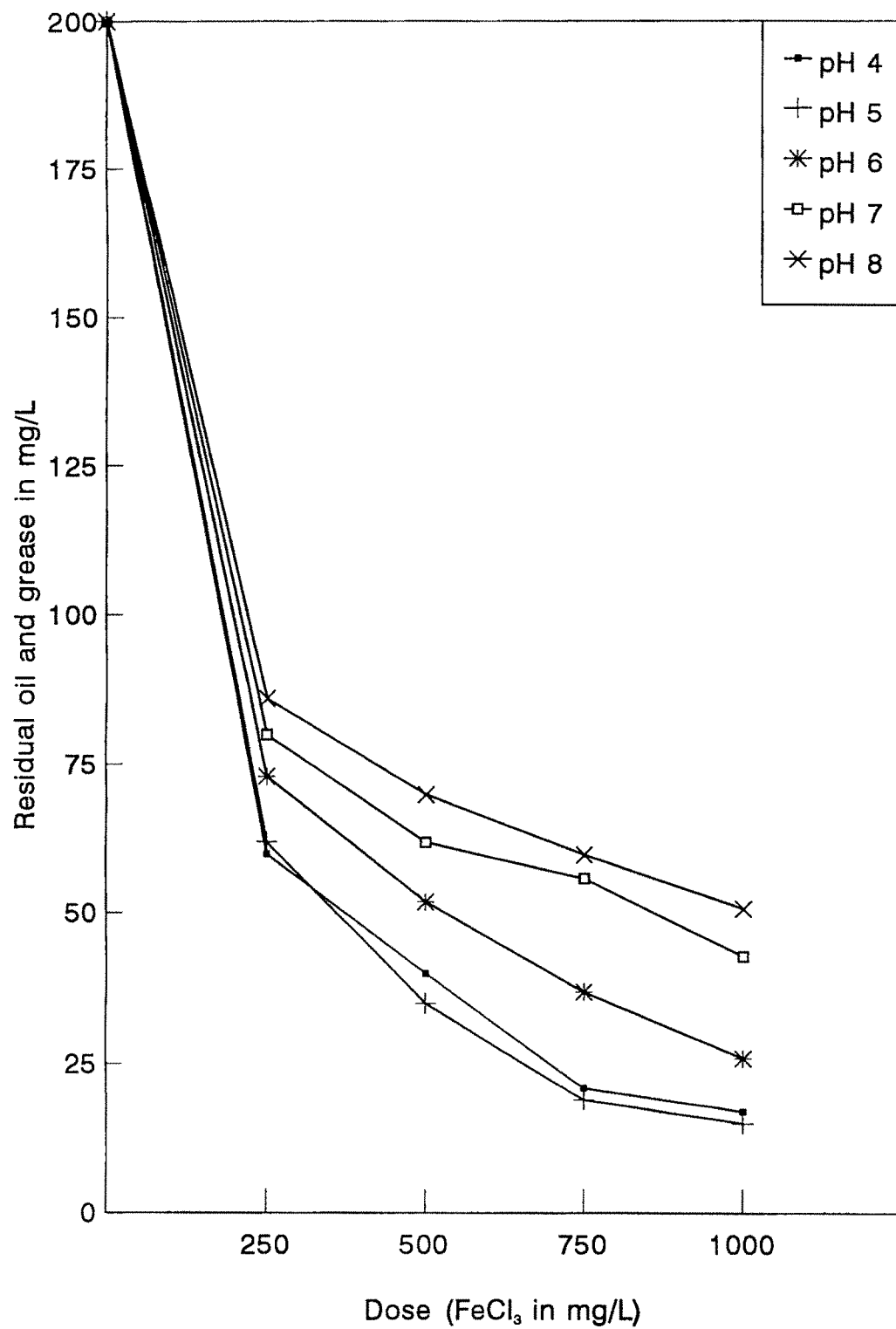Fig.4. Effect of concentration of FeCl₃ on oil liberation at different pH

Fig.5. Water pollution parameters at varying pH after treatment with 1000 mg/L of Na_2SO_4
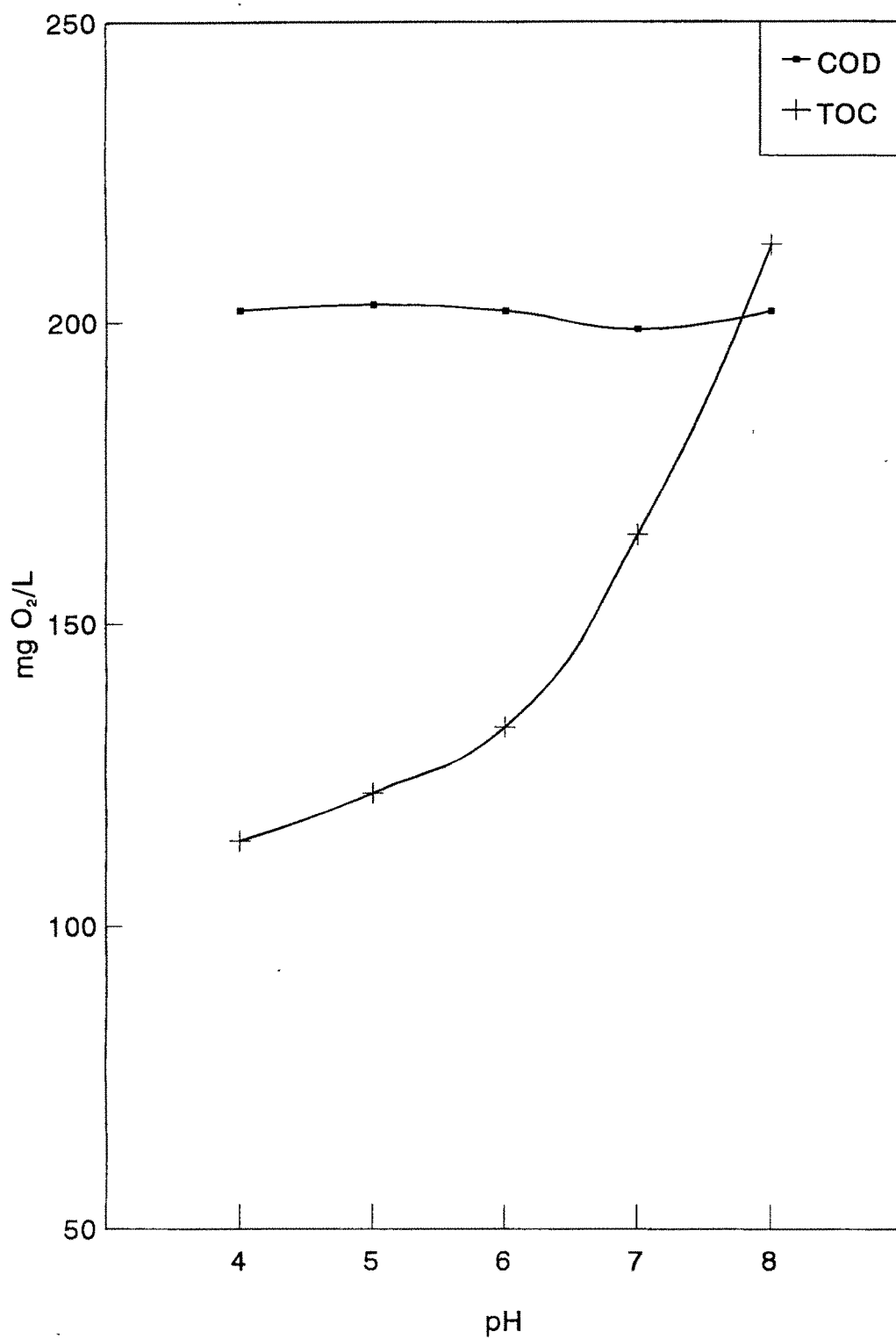
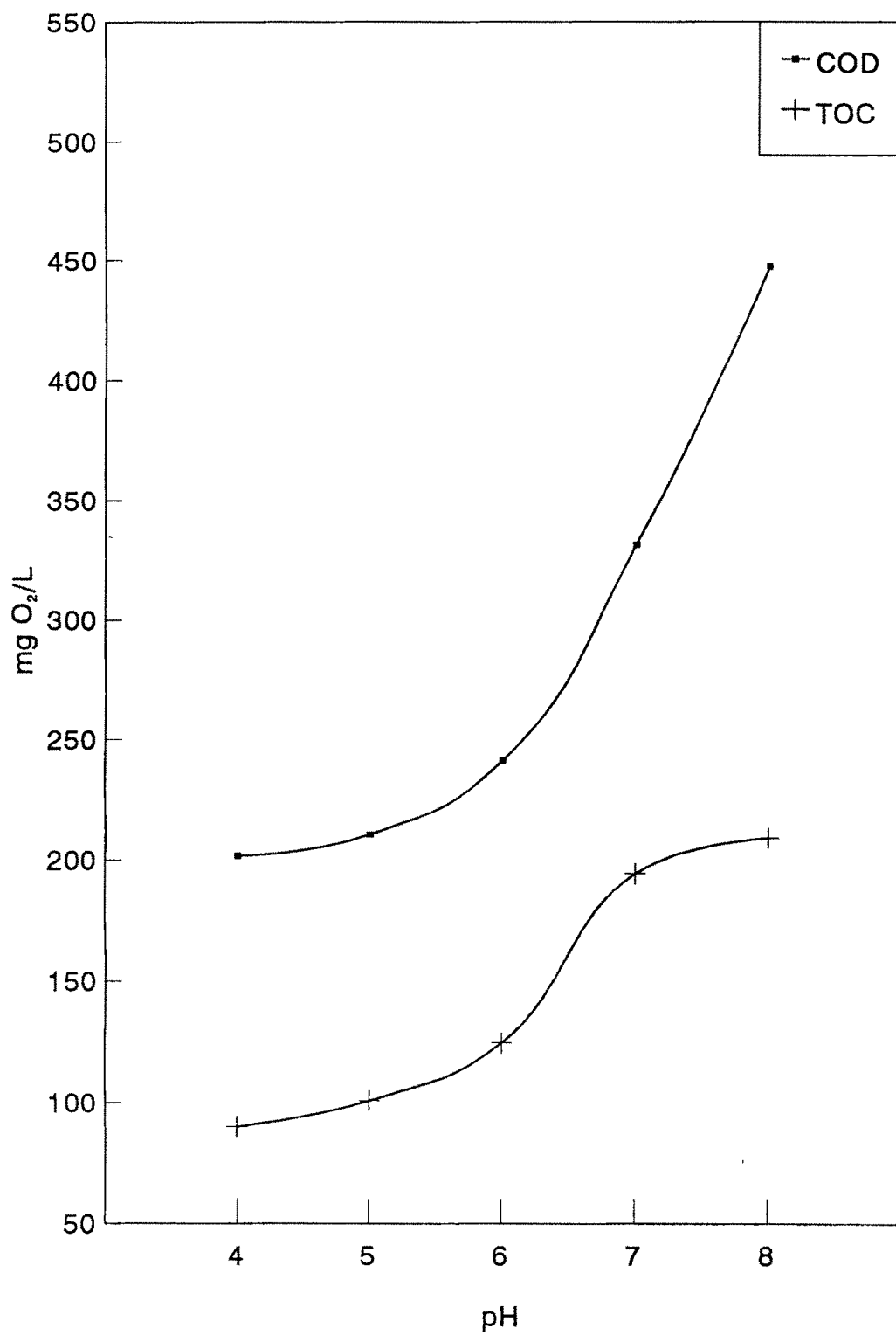Fig.6. Water pollution parameters at varying pH after treatment with 750 mg/L of Na_2SO_4

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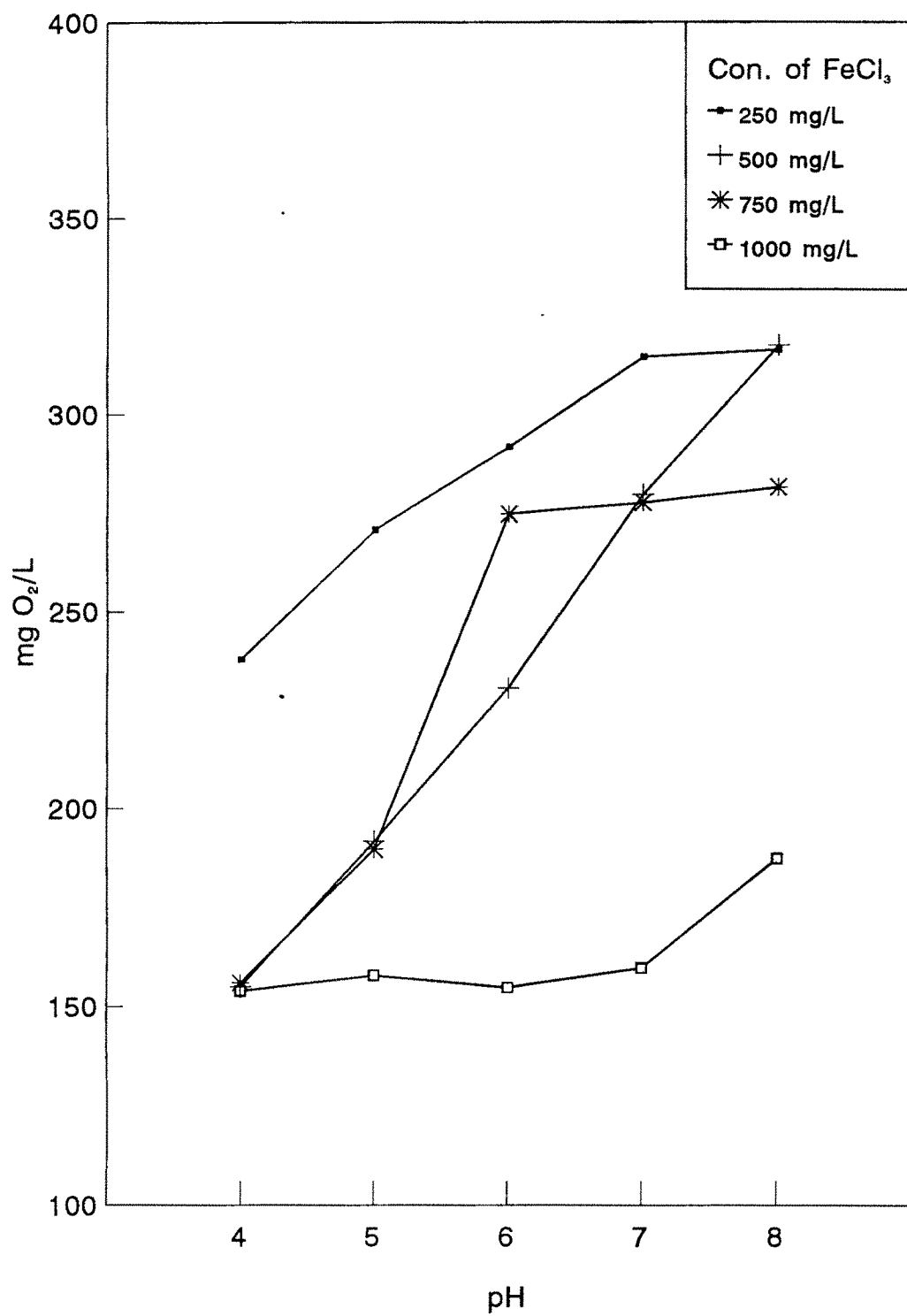Fig.7. COD values of oil waste water after treatment with different concentrations of FeCl₃ at varying pH

Fig.8. COD values of oil waste water after treatment with different
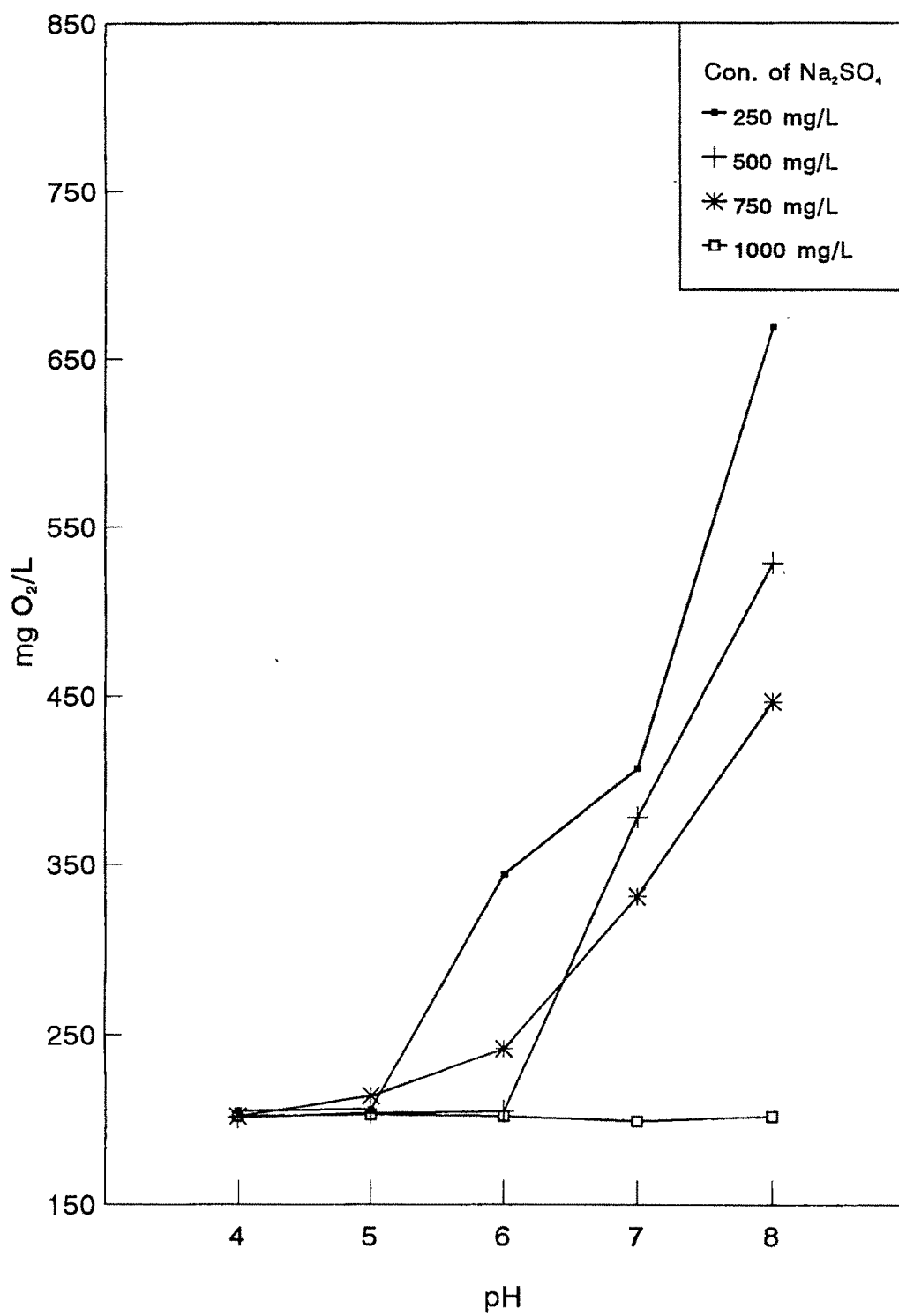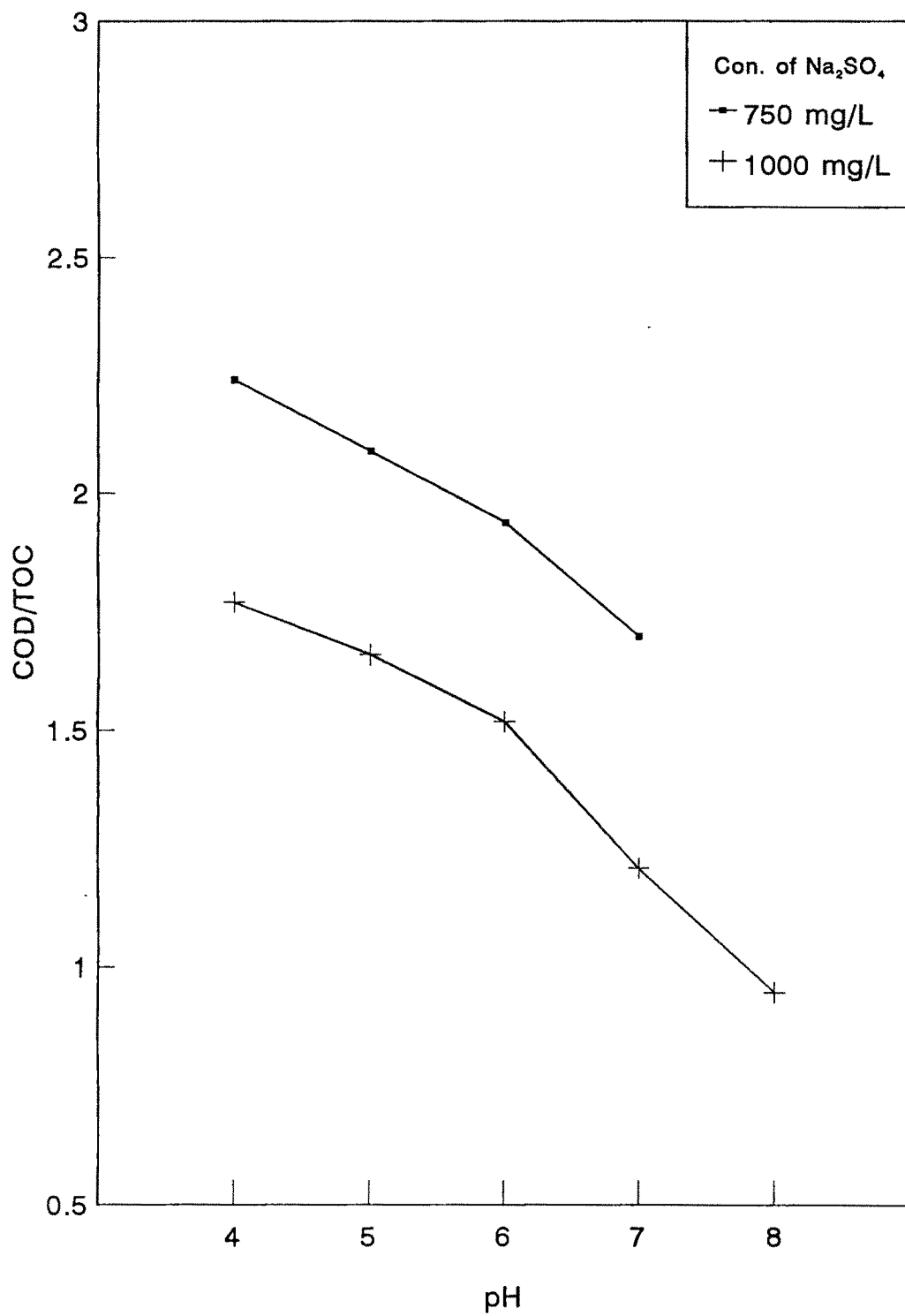concentrations of Na₂SO₄ at varying pH

Fig.9.Ratio of water pollution parameters at varying pH after treatment with 750 and 1000 mg/L of Na_2SO_4

RESULTS AND DISCUSSION

The influence of sodium sulphate concentrations and the effect of different pH levels on the removal of residual oil from oil- in- water emulsion in O.N.G.C. Mehsana effluents can be seen from the data presented in Tables 1 and 2 and also in the Figures 1 and 2. The results of gravimetric and spectrophotometric methods of analysis are in close agreements and it has been observed that increasing sodium sulphate levels from 250 to 1000 mg/L, reduced the oil content of the effluent from 85 to 54 mg/L at pH 8.0. A maximum of 80% oil removal was obtained in presence of 1000 mg/L of Na_2SO_4 at pH 4, and the aqueous phase became very clear.There are indications that at extremely low pH levels a slightly better oil removal can be effected. However, these effluents would then become unfit for disposal according to regulations of Water Pollution Control Board. The pH effect and the sodium sulphate effect are independent of each other and appear synergistic.

The results of oil removal trials with trivalent and divalent iron salts are presented in in Tables 3- 6 and in figures 3 and 4. The results obtained by using the above salts were different from those obtained by using sodium sulphate.The optimum pH for demulsification is 5.0 . With decrease in pH from 5 to 4 resulted in retention of higher levels of oil. However, in case of iron salts higher concentration of salts reduces the oil content effectively. These results are presented in tables 5 and 6, and are in agreement with the results obtained by Deepak et al[9].

Use of combinations of $FeSO_4$ and Na_2SO_4 results in lower residual oil content than when corresponding single electrolyte wasemployed Concentrations of both 250 mg/L and 500 mg/L were effective (Table-7) 250 mg/L treatment reduced the oil content to 13 mg/L at pH 5.0 and 500 mg/L treatment reduced it to 12 mg/L at the same pH. The maximum oil removed in these trials was 92% of the original amount. The

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synergistic action of these electrolytes is clearly indicated and suggests a certain degree of site specificity for effective electrolyte action.

The sludge formation during demulsification is highest with ferric chloride and lowest with sodium sulphate. Figures 5 and 6, shows the results of COD and TOC analysis of Mehsana effluents after treatment with sodium sulphate, ferrous sulphate and ferric chloride. They run parallel to the results obtained in oil content reduction studies. When sodium sulphate was used, both COD and TOC values were lowest at pH 4; but when either ferrous sulphate or ferric chloride were used the optimum pH for lowest COD and TOC determination was 5.0.

The results of the effect of different concentrations of these electrolyte on COD and TOC are shown in figure 7 to 9 With increasing concentration of all these electrolytes, there is increae in the emulsion breakdown and larger amounts of oil is liberated from emulsions. These results can be explained on the basis that the colloidal nature of the emulsified droplet is lost when the charges of the particle are neutralized by the opposite charges of the electrolyte ;thus the oil droplets form bigger free oil droplets which separate out from water. The actual mechanism of such a mode of action is a matter of speculation but it can be safely assumed that processes of charge neutralization, coagulation, flocculation and precipitation as well as those of phase separation are involved.

The COD/TOC ratio of waters is often used as anindicator of the degree of pollution. The lower the ratio, the lesser the pollution.The graph (fig 9) shows that at 1000 mg/L Na_2SO_4, the COD/TOC ratio averaged to 2.08. This and the pH relationship indicate that there is a close relationship between COD, TOC and the results obtained in oil removal studies.

From the obtained results it can be concluded that by increasing the concentrations of these electrolytes , there is increase in the demulsification of oil-in-water emulsion. pH 4 is optimum for removal of oil when sodium sulphate is used and pH 5 and 6 is optimum for $FeSO_4$ or $FeCl_3$. By using Na_2SO_4 the sludge problem can be reduced and this in turn would reduce the filtration and sludge disposal problems. But incase of $FeSO_4$ and $FeCl_3$, sludge formation is more. At higher pH large amount of sludge is found. Filtration and sludge disposal can be very problematic when $FeSO_4$ and $FeCl_3$ are used as electrolytes for treating oily waste water.

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