

Treatment of Oily Wastewater

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Abstract

The industrial wastewater discharge from the North Oil Company causes a high industrial water pollution to the agricultural lands. The present study aims to find the possibility method for treating such industrial oily wastewater, by coagulation-flocculation and sedimentation.

The experimental test will deal with the characteristics and analysis of wastewater such as turbidity, pH, TDS, T.H, and oil concentration. Also it deals with the effect of coagulation, flocculation, and sedimentation on the removal efficiency of oil in wastewater and other parameters. Four types of coagulation were used. The experimental was carried out by using Jar-test (flocculator laboratory scale). The behavior of flocculent settling was studied in sedimentation column.

It is found from the experimental results of Jar test, the optimum alum dosages are. (25,40,70 ppm), FeCl_3 dosages are (4,8,20 ppm), CaO dosage are (7,15,30 ppm) and clay dosage are (2.5,5,9 g/L) for initial oil concentration (30,58,136 ppm) respectively.

The experimental results are represented by mathematical empirical correlation for used coagulants alone and in combination as follows

$$R\% = 66.23 + 0.326 D_A + 1.17 D_F + 0.85 D_C + 6.342 D_L + 0.383 C_0 - 0.0026 D_A^2 + 0.302 D_F^2 - 0.013 D_C^2 - 0.496 D_L^2 + 0.017 C_0^2$$

From the polynomial equations and graphical figures it was found the oil removal efficiency is a function of alum, FeCl_3 , CaO and clay dosage and initial oil concentration. The result of sedimentation column was indicated that the combination of doses improves the removal efficiency and settling time. The above equation shows the removal efficiency of oil decreases with increases of initial concentration.

معالجة المياه الملوثة بالفضلات النفطية

الخلاصة

ان تصريف المياه الصناعية من شركة الشمال في كركوك تسبب تلوثا عاليا للأراضي الزراعية المطروحة اليها لهذا تهدف الدراسة الى ايجاد امكانية استخدام طريقة لمعالجة هذا التلوث المتمثلة باستخدام التبخير والتليد والترسيب .

درست مواصفات الماء الملوث مخبريا مثل:- العكورة, الدالة الحامضية, مجموع الاملاح والمواد الصلبة الذائبة, العسرة الكلية والمحتويات النفطية, لقد توصلنا من نتائج التحليل بأن المياه المطروحة الى الاراضي الزراعية تتميز بملوثها بتركيز عالية من الملوثات النفطية, اما بقية الانواع الاخرى من الملوثات فانها تقع ضمن مواصفات المياه المستعملة للزراعة.

درس تأثير طريقة التبخير والتليد والترسيب على كفاءة نسبة الازالة من الملوثات النفطية وبقية المتغيرات. وتم استخدام اربعة انواع من المختبرات في هذه الطريقة وباستعمال جهاز فحص الجره المختبري وعمود الترسيب.

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من خلال التجربة بجهاز فحص الجره قد تبين ان الجرعة الامثل للشب هي (٢٥ , ٤٠ , ٧٠) ملغم /لتر والجرعة الامثل لكلوريد الحديد (FeCl₃) هي (٨ , ٤٠ , ٢٠) ملغم /لتر والجرعة للجير (CaO) هي (٧ , ١٥ , ٣٠) ملغم /لتر وكذلك فان الجرعة الامثل للطين الاحمر هي (٥ , ٢٠ , ٩٠) غرام /لتر في حالة كون لتراكيز الابتدائية للنفط في المياه الملوثة هي (٣٠ , ٥٨ , ١٣٦) ملغم /لتر على التوالي.

وقد تم تمثيل النتائج المختبرية بعلاقة رياضية تجريبية باستخدام الحاسبة الالكترونية تمثل طريقة المعالجة بالتخثير والتلبد والترسيب باستخدام المخثرات كل نوع على حدة او معا وكما يلي:

$$R\% = 66.23 + 0.326 D_A + 1.17 D_F + 0.85 D_C + 6.342 D_L + 0.383 C_0 - 0.0026 D_A^2 + 0.302 D_F^2 - 0.013 D_C^2 - 0.496 D_L^2 + 0.017 C_0^2$$

من خلال المعادلة المذكورة والعلاقات البيانية لرسم كفاءة الازالة كدالة من جرعات المخثرات الكيماوية للتراكيز الابتدائية للنفط في المياه الملوثة استنتج ان اضافة الشب مع الجرعات المثالية من المخثرات الاخرى يزيد كفاءة الازالة ويحسن من نوعية الماء الناتج وسرع الترسيب وبنفس الوقت تقل الكفاءة في حالة زيادة تراكيز النفط في المياه الملوثة.

Symbol	Definition	Unit
C	Effluent Concentration of oil	mg/l.
C ₀	Initial Concentration of oil	mg/l.
C _A	Alum dose	mg/l.
D _F	FeCl ₃ dose	mg/l.
D _C	CaO dose	mg/l.
D _L	Clay dose	mg/l.
G	Mean velocity gradient	1/s
NTU	Naphelometric turbidity unit	---
R%	Oil removal efficiency =	((C ₀ - C)/C ₀)*100
TDS	Total dissolved solid	mg/l.
T.H	Total Hardness	mg/l.

Introduction

Petroleum and non- petroleum industries are among major users of water, each petroleum industry produces a large volume of wastewater, varying in composition and pollutant concentration, including oil containing wastewater. For example the industrial wastewater discharge from the North Oil Company is estimated to be 60m³ /hr, which carries high industrial water pollution to the agriculture lands. Oil means liquid hydrocarbons of crude petroleum, tars, vegetable and mineral

oils, animal fats, light and heavy fuel, as well as their mixtures, which are insoluble or poorly soluble in water.

Oil and grease content are required to be pretreated before discharged to the city or storm drain systems. The most common treatment methods for treating oily wastewater are sedimentation, centrifugal separation, coagulation and flocculation, sorption, flotation, filtration ultra filtration, and reverse osmosis. These methods can be used separately or in combinations (Pushkarev et al, 1983). The

coagulation, flocculation and sedimentation were used in present work. Coagulation is a complex process involving many reactions and mass transfer steps. Coagulation is a chemical process in which charged particles colloid are destabilized. Particles no longer repel each other, and can be brought together (Raju, 1995 NHF, 1999 and EM, 2001).

Coagulation of wastewater may be accomplished with any of the common water coagulants including lime, iron and aluminum salts. The choice is based on suitability for a particular waste, availability and cost of the coagulant, and sludge treatment and disposal consideration.(Sheree, 1994).

The purpose of flocculation is to bring particles together to form well settling flocculation. The rate of aggregation is dependent upon the rate of entering particle collisions. When particles aggregate, hydrodynamic shear forces in the water can cause the aggregation to break-up. The two processes can occur simultaneously (Alley, 2000, and EM, 2001) state that there are several factors that affect coagulation, flocculation: - pH, mixing effects (velocity gradient i.e. $G \text{ sec}^{-1}$), time of mixing, coagulation dosage, colloid concentration, cat ions solution nature of the particle surface temperature,

The sedimentation is the most widely used method for removal of floating and coarsely dispersed oils from wastewater. In certain cases it can be a pretreatment stage, and in others it is used for final treatment. (Culp et al., 1968). Therefore the aim of the present work is to study the possibility of using coagulation, flocculation and sedimentation for oil removal efficiency for an industrial wastewater from the North Oil

Company and to find the suitable coagulants for oil removal

Experimental Work

The experimental work was performed in two parts to remove oil pollutants from wastewater. The first part includes standard characteristics of wastewater in the North Oil Company. These standard include turbidity, TDS, total hardness, oil and grease concentration, pH. All the experiment procedures were taken from the standard methods in the examination of water and wastewater manual published in 1988 (ASTM). The second part includes treatment methods of wastewater by coagulation, flocculation and sedimentation with and without chemical coagulants. Four types of coagulants were used: - Alum, FeCl_3 , CaO and clay. These experiments were carried out by using flocculate test (Jar- test) and the procedure of experimental tests shown in (Eman, 2003).The Jar-test apparatus consists of a set of vertical paddles (6-paddles) in a row so arranged that liter beakers of wastewater could be conveniently placed under each paddle. The driving motor has a variable speed control. The speed of meter is in the range (0-400) rpm. A cylindrical settling column of (11.5) cm in diameter and length of (1) m was used as settling column. The column has four sampling points at a depth of (10, 30, 50, 70) cm. The samples were analyzed for turbidity and oil concentration at different times (5, 10, 15, and 20 min) the settling column was filled with the sample of 250 NTU after coagulation and flocculation used optimum does of alum, CaO and FeCl_3 each it combination with alum does.

Results and Discussion

The results and discussion treatment methods of wastewater are presented in the following sections:-

Characteristic and Analysis of Wastewater:- Figures.(1-5) show the relation between the characteristic (pH, TDS, turbidity, oil, concentration and total hardness T.H) from North Oil Company with days of sampling and analysis. These figures. show the rang of wastewater of maximum – minimum value of 7.9- 6.5, 605-210 ppm, 41-1.9 NTU, 17-163ppm and 378-169ppm for pH, TDS, turbidity, oil, concentration and total hardness T. H respectively. All these results are within the allowable range for water used in agriculture expects the concentration of oil; therefore the wastewater must be treated.

Effect of Coagulants Type and Influent Oil Concentration On Oil Removal Efficiency:- Figures.(6-10) show the results obtained with coagulant alone at initial different concentrations of oil in wastewater. Also Figures.(11-16) show the results obtained by combination of coagulants doses. These figures show that the removal efficiency of oil increases with coagulation does increases until reaching the optimum dose, except clay does, until it reaches the saturation. It is found in the Figures.(11-16) that the removal efficiency of oil increases by combination of coagulation. At optimum the removal efficiency of oil at low concentration $C_o = 30$ ppm is (65%, 71.67%, 75% and 82.6%) for (alum alone, alum + optimum $FeCl_3$ alum + optimum Ca O and alum + optimum clay) respectively. The result of combination of alum and clay indicate more efficiency in oil

removal (82.67%, 78.45% and 77.57%) for initial concentration (30, 58, and 136) respectively than other coagulants. The clay coagulation improves the coagulation and flocculation with alum. In general these Figures. (6-15) show that the oil removal efficiency is decreased as coagulants– influent concentrations are increased with in the range of influent concentration given (30-136) ppm, of oil. This means that the quality of residual oil in wastewater is more than the required level then it affect to the quality of the reused water.

The reason for this case is because some particle of oil remains stable or carry polar force with water molecule in high concentration of oil in wastewater.

Effect of Flocculent Settling Column:-The results of settling column test after flocculation. Process are represented by isoremoval curves, each curve represents the removal efficiency at known depth and time. The percent of removal at each depth and time interval is calculated from the concentration and plotted as in Figures.(17-19) for alum, alum + optimum $FeCl_3$ and alum + optimum CaO doses respectively. Settling column tests are used to establish the design parameters for a flocculate suspension, (such as settling time, floc size and capacity).

The Analysis of Empirical Correlation:-The experimental results of this study are used to develop empirical correlation. The statistical program was used on high-speed personal computer (Pentium 4). The method of developing the present model is by introducing equations of different forms into computer

program. The calculated values of the dependent variables are compared with the actual values and the procedure is repeated until excellent agreement is obtained. Equation (1) correlates the best developed fitting for the performance of flocculation unit with combination dose of coagulants for effects on oil removal efficiency.

$$R\% = 66.23 + 0.326 D_A + 1.17 D_F + 0.85 D_C + 6.342 D_L + 0.383 C_0 - 0.0026 D_A^2 + 0.302 D_F^2 - 0.013 D_C^2 - 0.496 D_L^2 + 0.017 C_0^2 - 1$$

The absolute average error (4.6%) and correlation coefficient is 0.81. A correlation between the experimental and calculated results for oil removal is given in Figure (19).

Conclusions

In general, the following conclusions are extracted from the present work:-

- It is found that this wastewater is polluted with oil in the range (17- 36) ppm.
- The clay coagulation improves the coagulation and flocculation treatment with alum and increased in oil removal efficiency more than other coagulants. The oil removal efficiency is equal to (82.67, 78.45, 77.57%) at $C_0 =$ (30, 58, 136ppm) respectively with optimum clay doses equal to (2.5, 5, 9) g/l. and combination with alum.
- The experimental results indicate the coagulation, flocculation and sedimentation process have poor efficiency in

oil removal when initial concentration increase. Therefore it is required other method treatment such as dissolved- air processes

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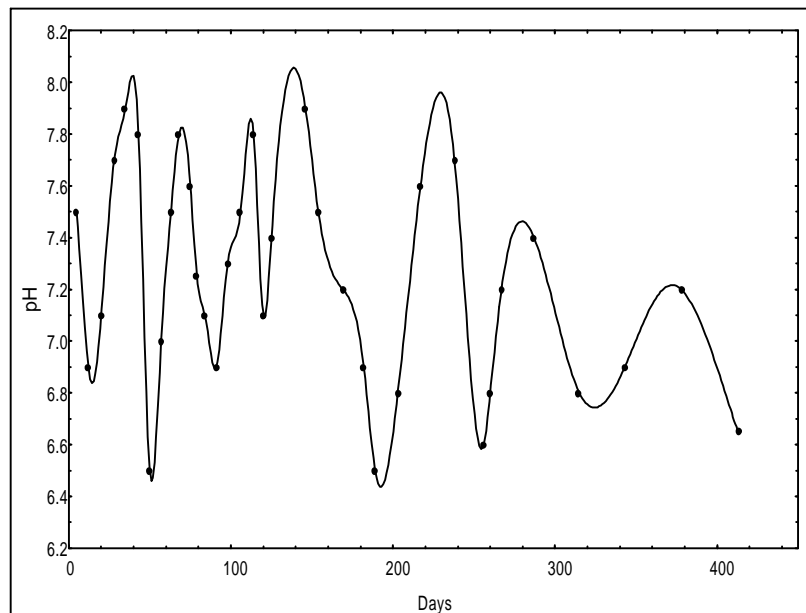


Fig.(1) The Relation Between pH Value and Days of Sampling and Analysis.

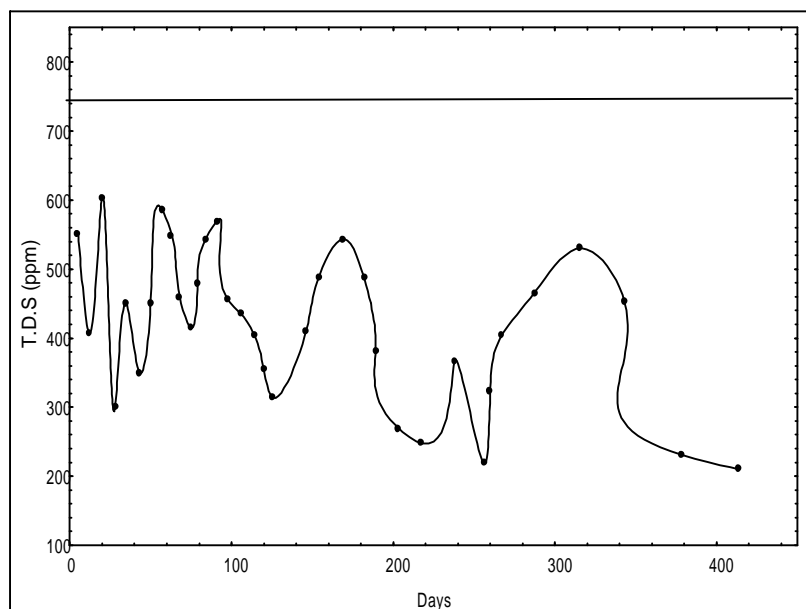


Fig.(2) The Relation Between TDS Value and Days of Sampling and Analysis.

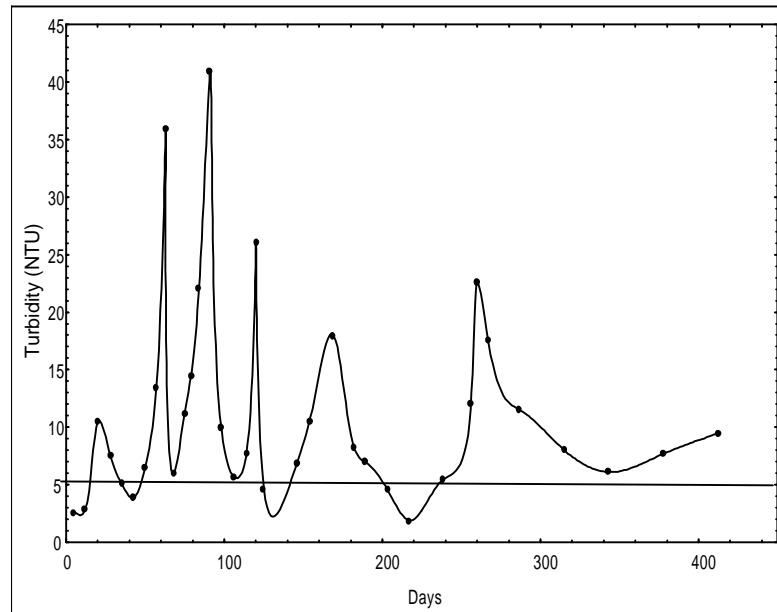


Fig.(3) The Relation Between Turbidity Value and Days of Sampling and Analysis.

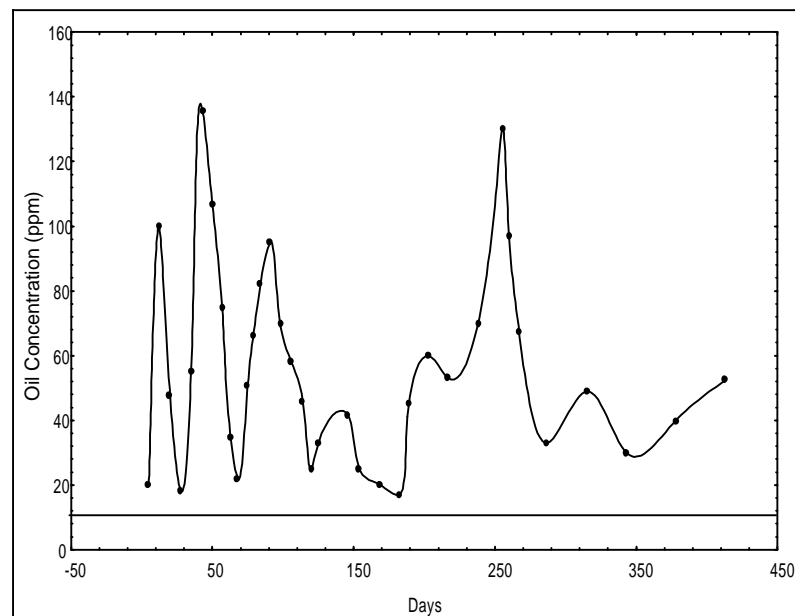


Fig.(4) The Relation Between Oil Concentration Value and Days of Sampling and Analysis.

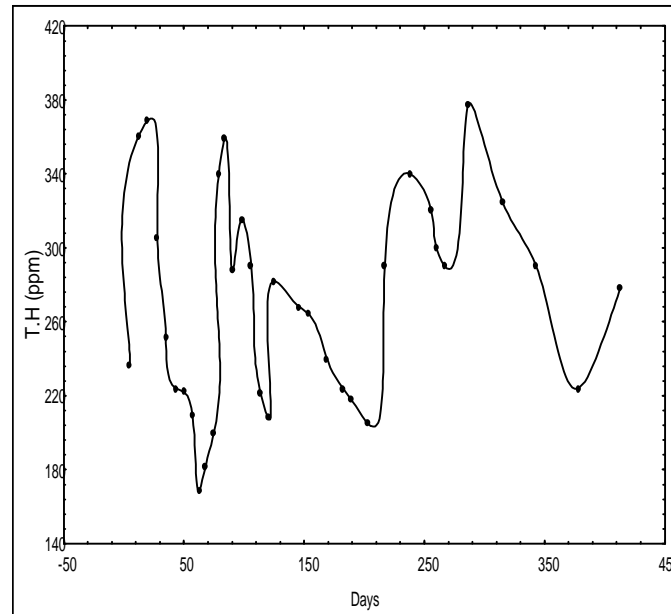


Fig.(5) The Relation Between Total Hardness Value and Days of Sampling and Analysis.

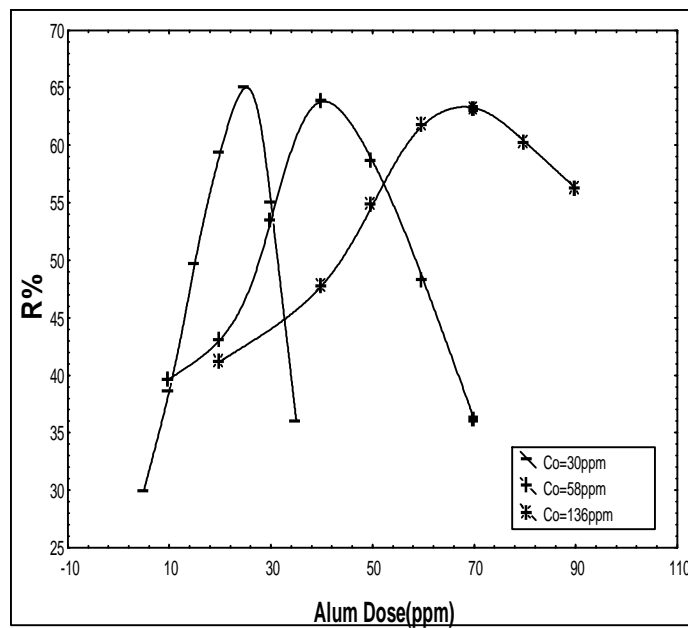


Fig. (6) Effect of Alum Dose on the Removal Efficiency of Oil

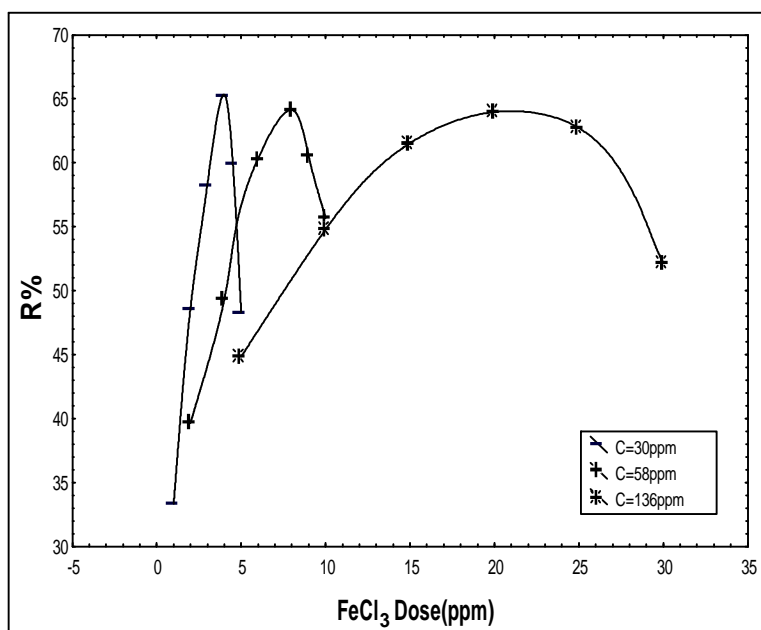


Fig. (7) Effect of FeCl_3 Dose on the Removal Efficiency of Oil

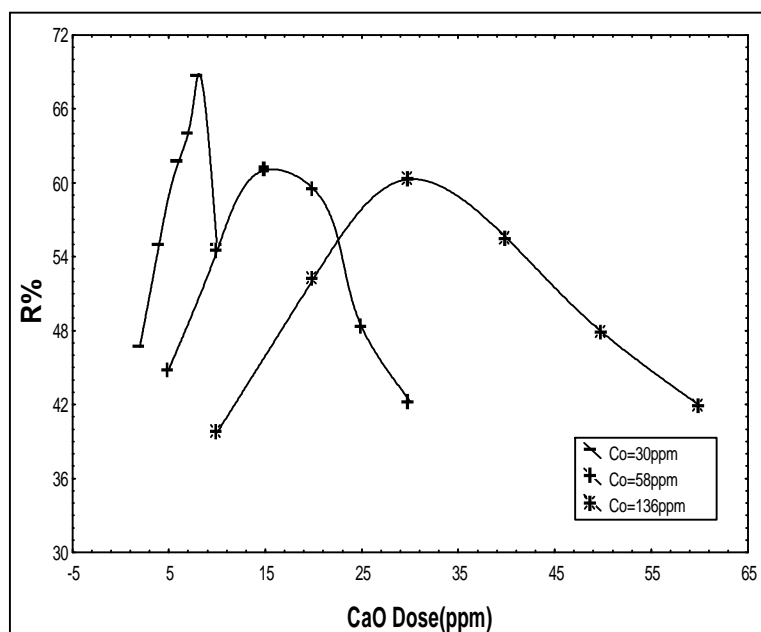


Fig. (8) Effect of CaO Dose on the Removal Efficiency of Oil

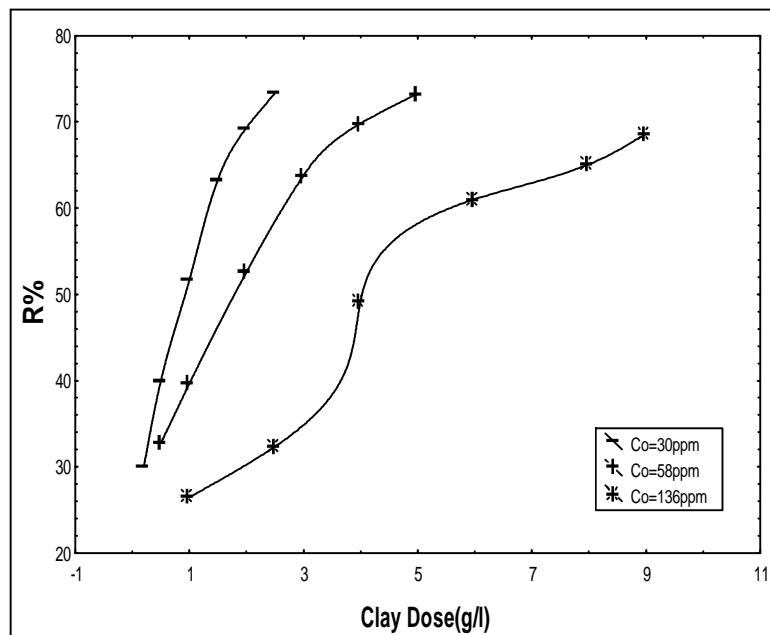


Fig. (9) Effect of Clay Dose on the Removal Efficiency of Oil

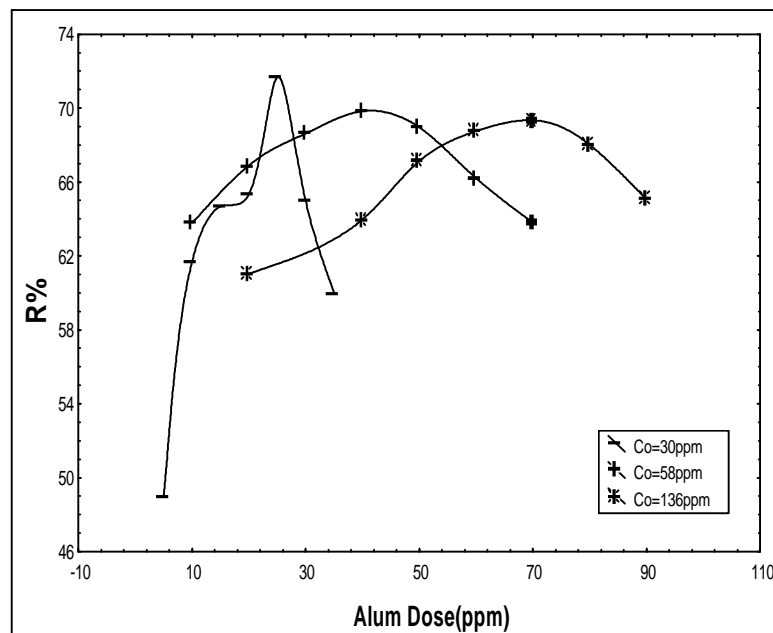


Fig. (10) Effect of Alum Dose with Optimum FeCl_3 Dose on the Removal Efficiency of Oil

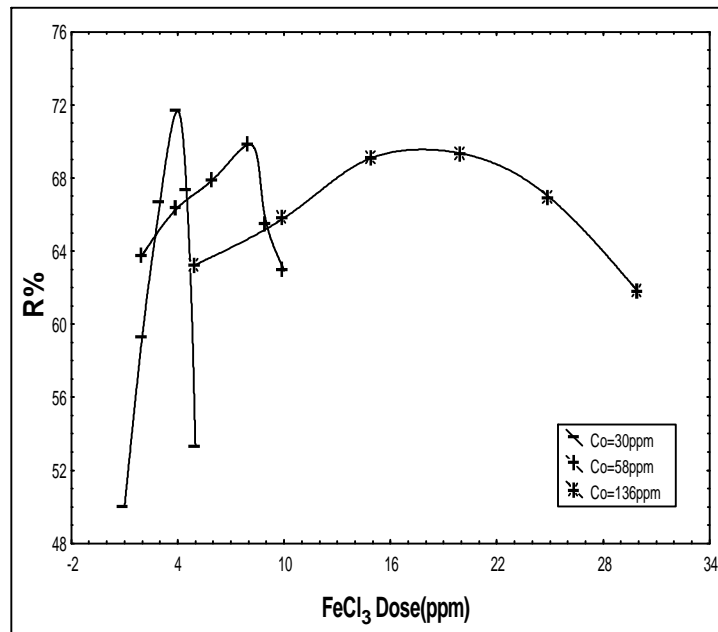


Fig. (11) Effect of FeCl_3 Dose with Optimum Alum Dose on the Removal Efficiency of Oil

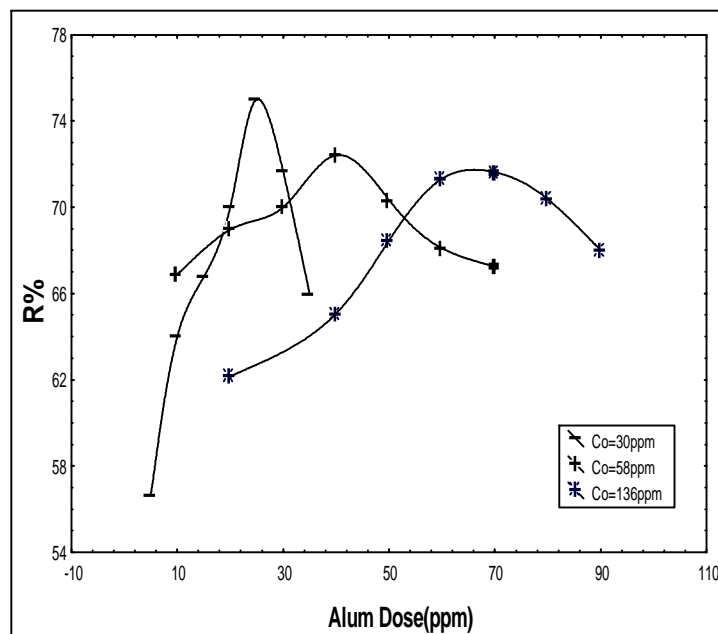


Fig. (12) Effect of Alum Dose with Optimum CaO Dose on the Removal Efficiency of Oil

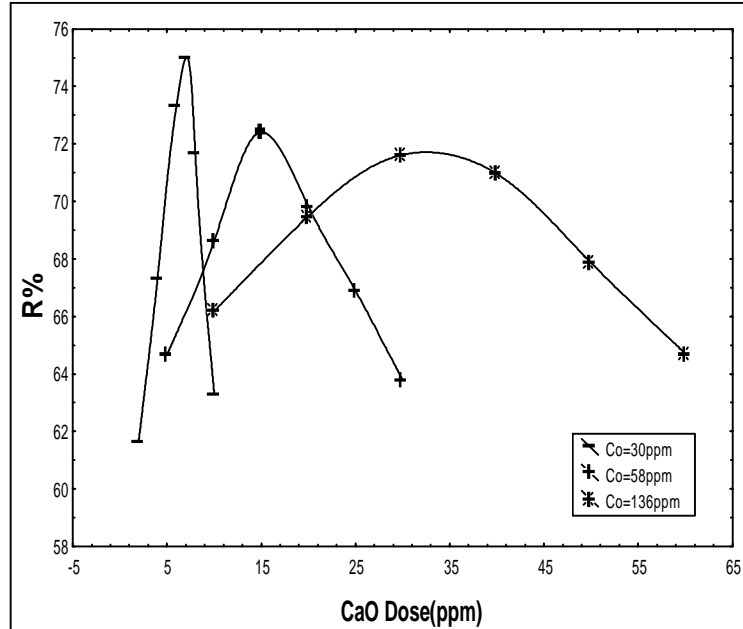


Fig. (13) Effect of CaO Dose with Optimum Alum Dose on the Removal Efficiency of Oil

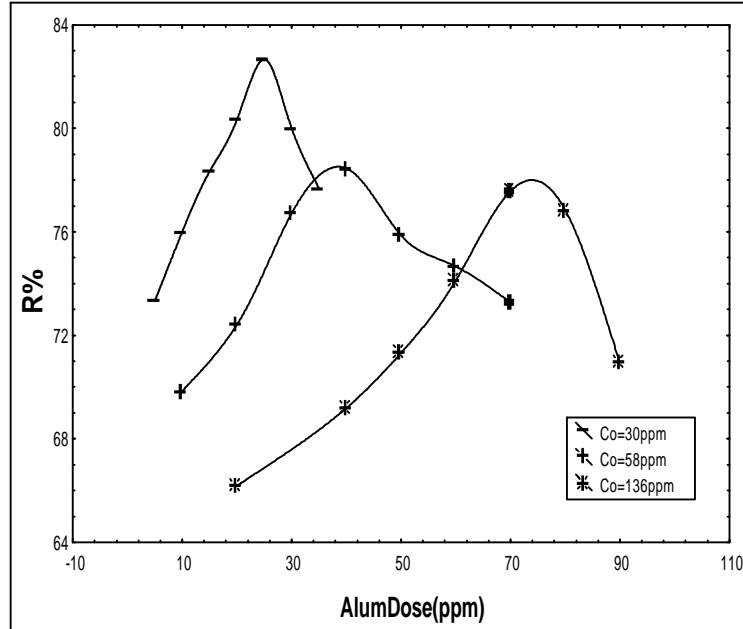


Fig. (14) Effect of Alum Dose with Optimum Clay Dose on the Removal Efficiency of Oil

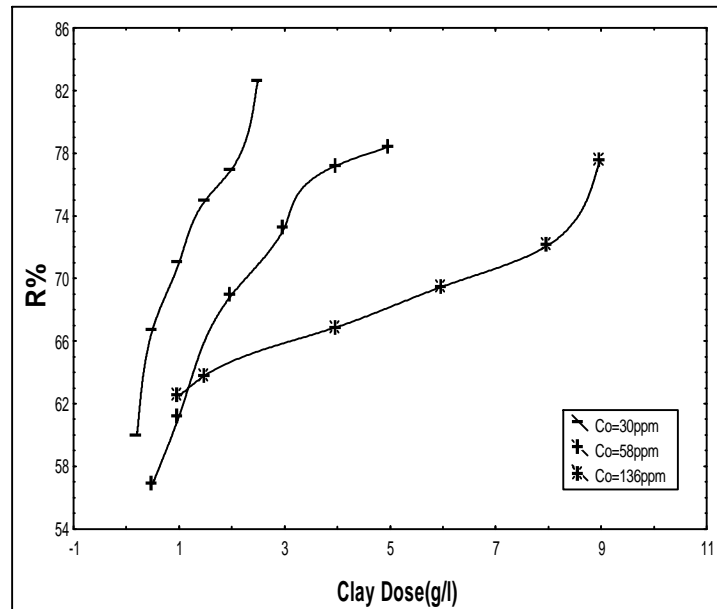


Fig. (15) Effect of Clay Dose with Optimum Alum Dose on the Removal Efficiency of Oil

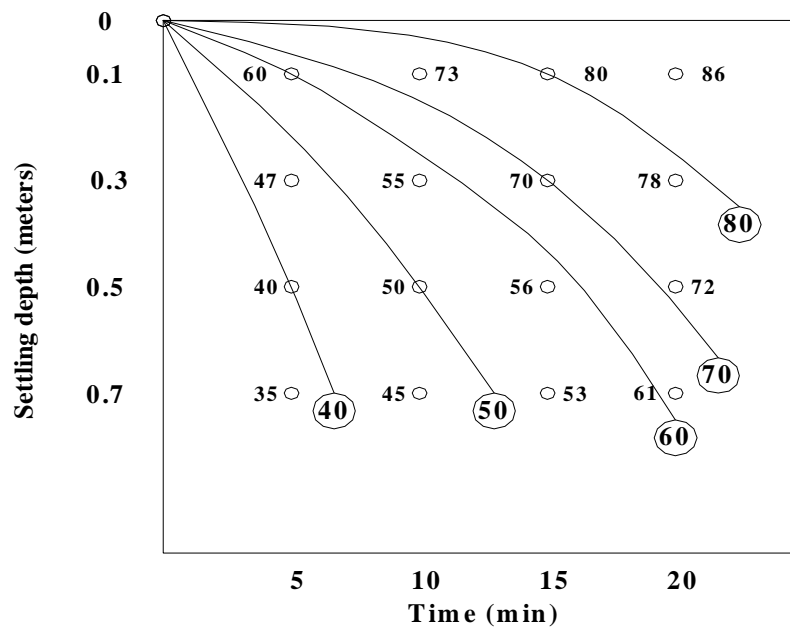


Fig.(16) Effect of Flocculate Particle in the Settling Column by using Alum Dose

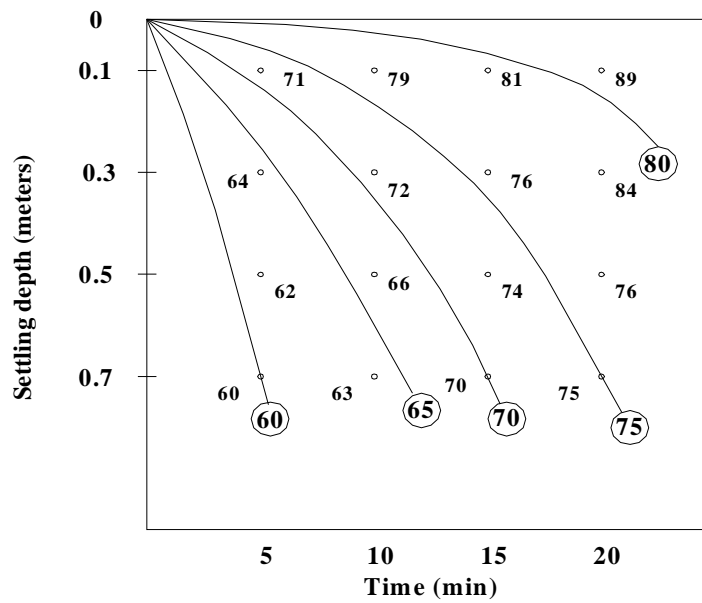


Fig.(17) Effect of Flocculate Particle in the Settling Column by using (Alum + FeCl₃) Dose

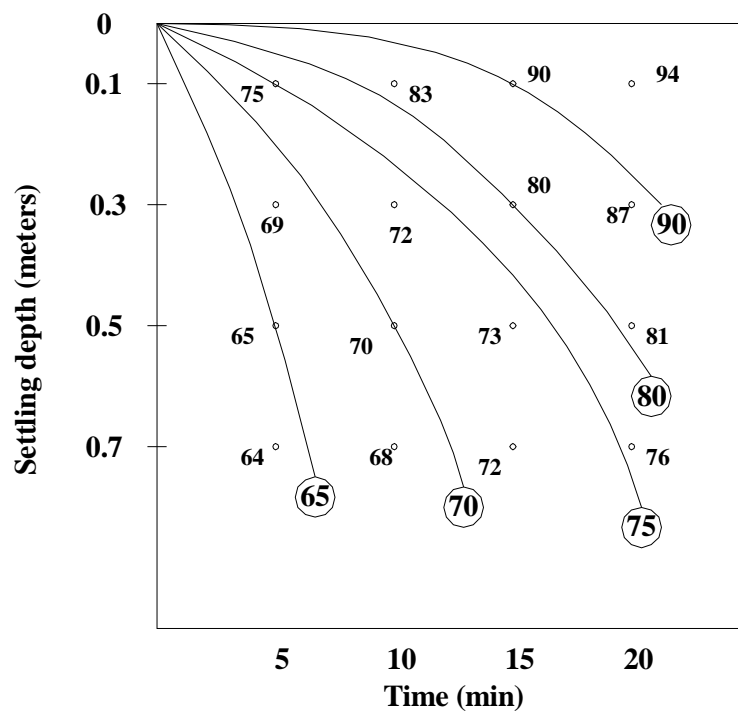


Fig.(18) Effect of Flocculate Particle in the Settling Column by using (Alum + CaO) Dose

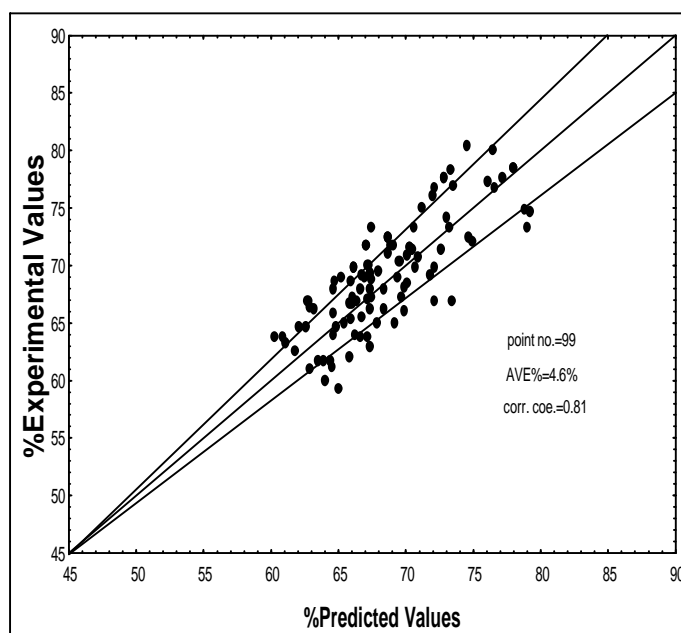


Fig.(19) Experimental Versus Predicted Values for Equation (1)