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Oil Reduction from Durah Wastewater Treatment Plant using Two Types of Coagulants

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Abstract
The Durah Oil Company represents one of the important companies in Iraq that consumes a large quantity of water. The refinery wastewater discharged from the company is evaluated to be 60 m^3/hr, which causes high water pollution to Tiger river and the agricultural lands. The basic aim of this investigation is to modify the methods for treating oily wastewater. Measurements of wastewater such as turbidity, pH, and TDS, COD, TH and oil quantity were achieved during period four months. Two coagulants were used in this experiments including Alum and mixture of Bentonite and Kaolin, the optimum alum dosages are (20, 40 and 80 ppm) and clay dosage is (2.5, 5, and 9 g/l) are required to treat wastewater for initial oil concentration (20, 40, and 136 ppm) respectively.
Keywords: Refinery wastewater, oil removal , Coagulant, Bentonite, Kaolin

1- Introduction

Petroleum and non-petroleum industries are among major users of water, each petroleum industrial produces a large volume of wastewater, varying in composition and pollutant concentration, including oil-containing wastewater. Oil containing wastewater includes petroleum, oil, fats and their derivatives. 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. In wastewater they may be present in one of five forms such as: Free oil (20 μm or larger),Physically emulsified (5-20 μm),Chemically emulsified (less than 5 μm),Dissolved and Oil wet solids (oil that adheres to the surface of particulate) .**Pushkarev, et al., 1983).** Oil and grease content are required to be pretreated these wastes before discharging to the city or storm drain systems. Oil pollution, has many forms **(AL-Maliki, 2001).** Free oil that exists in the form of hydrocarbon films preventing the normal reparation of water. The lighter fractions evaporate more or less rapidly and contribute to atmospheric pollution.The most dangerous are those, which are slightly soluble in water since the most soluble hydrocarbons are these which are most carcinogenic. The intermediate fractions are biodegradable and large quantities of oxygen are consumed and therefore affect the surface waters quality and endangers the life of aquatic animals.The relationship between oil and water in a mixture is well known and governed by two physical properties gravity and surface tension (**Skimming, 2001**).Most hydrocarbons have a lower specific gravity than water. Without agitation, oil separates from the water and floats to the surface. These oils are known as LNAPL's, Light Non-Aqueous phase liquid. Oils (and other compounds) that sink in water have a higher specific gravity and are known as DNAPL's Dense Non-Aqueous phase liquid.The normally oil bonds more tightly to itself and other materials than to water. This affinity and differences in surface tension between oil and water, causes oils to adhere to a skimming medium.One of the principal problems associated with the prevention of pollution of surface water by oil is the range and variety of the sources from which the escaping oil may emanate. The effect all situations involving the production, refining, handling, storage, transportation, use and disposal of oil are potential sources of oil spills. (**Degremont, 1991),(Ellis et al., 1990)**.The source of an oil spill may be an oil refinery, a petrochemical works, a factory, a petrol filling station, an engineering workshop, a garage, a civic dump, a school or domestic premises. In addition, the transportation of oil whether by pipeline ,barge, rail tanker or road tanker poses particular problems, which may arise as the result of an accident to the vehiclemore commonly, a spillage may be caused as a result of human negligence or misjudgment, or of equipment failure, during the transfer of oil from one container to another. In addition, the over-filling of receiving containers as a result of lack of attention on the part of operator or because of alarm and cut offsystems is a continuing cause for concern. Also of concern is the rain water run-off from paved area containing oil tanks, drums or machinery or which is used for the parking and maintenance of road vehicles. (**Ellis, et al., 1990**).The major goals of this investigation tofind suitable treatment of the oily wastewater in Durah oil company characterize the properties of effluent stream from Durah oil company and optimize the coagulant (Alum and Bentonite dose) for improving effluent quality

2- Coagulation

Coagulation is a complex process involving many reactions and mass transfer steps. As practiced in water treatment the process is essentially three separate and sequential steps: -Coagulant formation, Particle destabilization, Inter particle collisions, Coagulant formation, particle destabilization, and coagulant interaction typically occur during and immediately after a chemical dispersal in rapid mixing, inter particle collision that cause aggregate (floc) formation begins during rapid mixing but usually occurs predominantly in the flocculation process. (**Raymond, et al., 1999**).The term coagulation comes from the Latin word coagulation to derive together. Coagulation is a chemical process in which charged particles colloid are destabilized.(**Raju, 1995**)Coagulation is the process of making the particle less stable by neutralizing its charge, thus encouraging initial aggregation of colloidal and finely divided suspended matter. Particles no longer repel each other, and can be brought together (**NSF, 1999), (EM, 2001**).When oil particles suspended in water, the charge on organic and inorganic colloids is typically negative. Because of electrostaticforces the negative colloid charge attracts positive ions. Figure (1)illustrates howcoagulants reduce the electric charges on the colloidal surfaces, allowing colloidal particles to join (**EM, 2001**).

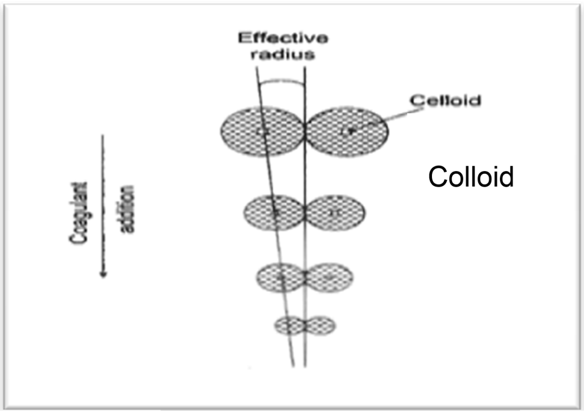

Figure (1): Charge Neutralization (Coagulation) (EM, 2001).

Breaking of oil–in–water emulsion can be achieved by suitable chemical treatment to inactivate the emulsifying substances. This inactivation may be accomplished by the use of chemical coagulating agents such as aluminum salts, ferric salts and calcium salts. (**Lawrence, 1975**).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. For example, iron is sometimes available at no cost as a waste product in the form of pickling liquor, and is heavy and quick setting takes place compared with alum. (**Sheree, 1994**).Common coagulants usealuminum compounds, iron salts, lime and clay (bentonite, fullor's earth, or other clay). (**EM, 2001**) states that inorganic compounds (typically iron and aluminum derivatives) are commonly used as coagulants. During dissolution, the actions serve to neutralize the particle charge and the effective distance of the double layer, thereby reducing the zeta potential. In inorganic coagulants, a trivalent can be as much as 1000 times more effective than a monovalent ion. This is the reason why alum and iron salts are extremely efficient coagulants. Alum (Al^{3+}) relative coagulant power equals 570 but Na^+ equals 1.Excess of coagulant above the electrostatically- neutral point results in excess adsorption of Fe^{3+} and Al^{3+}. The net charge on the colloidal particles is reversal (from negative to positive). The suspension becomes stable again when the electrostatic repulsion overcomes the Van der Waals attractive forces. (**Huang, 2003**).

3- Material and methodology

Two types of coagulants were used in treatment of oily wastewater, which added separately to optimize coagulant dose for high removal efficiency. These types are (Alum, and Bentonite) that were prepared by dissolving a certain weight of coagulant powder (1gm) in a known volume of distilled water (100 ml). The solution was stirred vigorously with magnetic stirrer and kept then in volumetric flask. Thus (1) ml of solution is equivalent to (10) ppm of coagulant. The chemical analysis of the coagulants is used as shown in table (1).

Table (1): Chemical Compassion of Alum.

Chemical	Alumina	Total Iron	Total SO_3	Free SO_3	Basic SO_3	Insoluble
Content (ppm)	15.8	0.004	37	-	0.184	0.15

3-2 Bentonite

Bentonite (CaB) was obtained from the bed in the Al-Anbar region in Iraq and supplied by Iraqi National Company for Geological Survey and Mining. The basic of Bentonite clay mineral is calcium montmorillonite(CaM). Standard Phllipstype PW1877 Automated powder diffractometer was used with Cu-Kα radiation and a pure Silicon powder as a standard for studying the composition and diffraction pattern of Bentonite. Specific surface are was measured using instrument model Q-surf (9600) according to the B.E.T. methods. Apparent bulk density measurement was carried out according to ASTM method D2854-83 as shown in table (2).

Table (2): Properties of Bentonite

Property	Bentonite
Actual density, kg/cm^3	2018
Apparent density, kg/cm^3	748.8
BET Surfacearea, m2/g	224
Particle porosity	0.37
Bed porosity	0.42
Average particle diameter, mm	0.2
Pore volume, cm3/g	0.3
pH	9.8
Ash content, %	-
CEC, meq /100g	32.4

The chemical analysis and physical properties and XRD of Iraqi Bentonite, were determined in the labs of Ministry of industry (State Company of Surveying and Mining).The composition of Iraqi Bentonite and Kaolin is given in tables (3) and the physical properties of Bentonite are shown in table (4) respectively . As shown in table (4-3), the bentonite is mainly composedof(SiO_2,Al_2O_3,Fe_2O_3,CaO,MgO,Na_2O_3,K_2O,P_2O,SO_2,Cl,LiO_3,Na_2O and CaO) which reflects the content so fcationic inter layer in monomorillonite as well as the different contents of CaO and Na2O can classify abentonite as either Ca-bentonite or sodium bentonite. Iraqi bentonite shows high content ofCaO(4.48)andNa_2O/CaOratioislessthan1,which indicatesthepresenceofCa-bentonite.Thediffractogramofrawsampleindicatedthatthe sample consisted of predominantly, substantial amount of quartz, feldspar, calcite, and Dolomite.

Table (3): Chemical Composition ofIraqi Bentonite.

SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	K2O	P2O	SO2	CL	LiO3
56.77	15.67	5.12	4.48	3.42	1.11	0.6	0.65	0.59	0.57	9.49

Table (4):Physical Properties Bentonite.

ClayType	Surface area(m2/g)	Density (Kg/m3)	Oil Retention (%)	pH	Adsorption of water vapor %
Bentonite	220	750	35	10.1	11.8

3-3 Sampling Test: -

Wastewater sampling is a necessary condition for obtaining reliable and trust worthy data on analysis. Errors in sampling procedure cannot be corrected in the subsequent analysis.Sampling points should be chosen where the oils couldn't separate in the water from special sample collection. Samples cannot be collected for analysis from flooded sumps or other low flow places because of non-uniform distribution of oil in water. The sample is collected under the surface of the water at a depth of 20-50 cm to avoid the surface film of polluting material getting in to it. A sample of 5-liter should suffice for most physical and chemical analysis. In general, the shorter the time that elapses between collection of sample and its analysis, the more reliable will be the analysis results.

3-4 Laboratory-Scale Jar Test: -

In initial test of wastewater from source, experimental tests should were be carried out by using Jar-test to determine: -

- The optimum coagulants after pH adjustment.
- The optimum of settling time.
- The effects of addition of coagulants alone or together on oil removal efficiency.
- The effect of coagulant addition on pH value.
- The effect of coagulants addition on turbidity and TDS removal efficiency.

The Jar-test apparatus shown in figure (4.2) consists of a set of six vertical 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 motor in the range (0- 400) rpm.

4- Results

Effects of coagulants type on removal efficiency of oil have been investigated .Two common coagulants, Alum and Bentonite were selected and added to refinery wastewater as primary treatment. Effect of alum and bentonite doses separately on removal efficiency of oil from refinery wastewater has been obtained.

4-1 Coagulants dose

A set of experiments are carried out during period (Oct.2013 to April 2014) to optimize the alum and bentonite dose for different oil concentrations. The removal efficiency of oil increases when alum dose increase until reaching the optimum dose. Results explains that the optimum dose of alum was (25, 40, and 50 ppm) for initial oil concentration (C_o = 20, 40, and 136 ppm) respectively. The alum over- dosing causes decreases in oil removal efficiency because of destabilization state the over dose of alum which causes stability again .The increasing of bentonite dose causes decreasing in oil concentration of treated water until it reaches the saturation state. Analysis of water samples for different oil concentrations appears the optimum dose is (2500, 5000, and 9000mg/l) for initial concentration (C_o = 20, 40, and 136 ppm) respectively. The over-dosing of bentonite increases oil removal by causing sludge removal problem (large production of biomass sludge). The bentonite as coagulant is more efficient than alum producing higher rate of sludge.

4-2 Oil Concentration Measurements

Many attempt were achieved to improve the efficiency dosing by adding alum dose (25,40, and 50 ppm) to oily wastewater with initial concentration (20, 40, and 136 ppm).The best removal efficiency is 65% when (25 ppm) of alum dose is added at initial oil concentration approach to (20 ppm) as shown in figure (2).

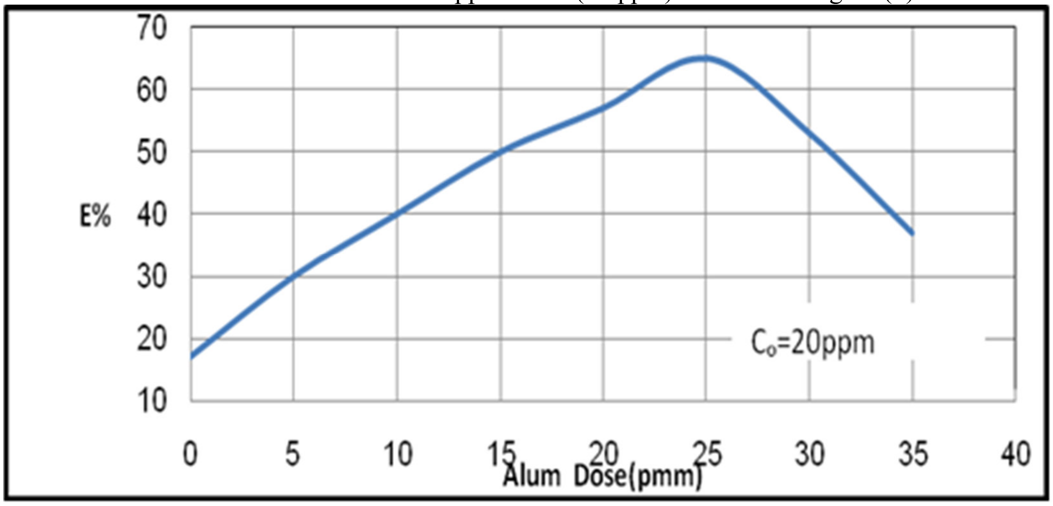

Figure (2): Effect of Alum Dose on Oil Removal Efficiency at C_o=20 ppm

Regarding to many trails of coagulant dose, the maximum removal efficiency was 64% when (40 ppm) of alum is add to refinery wastewater of initial concentration (40 ppm) as shown in figure (3).

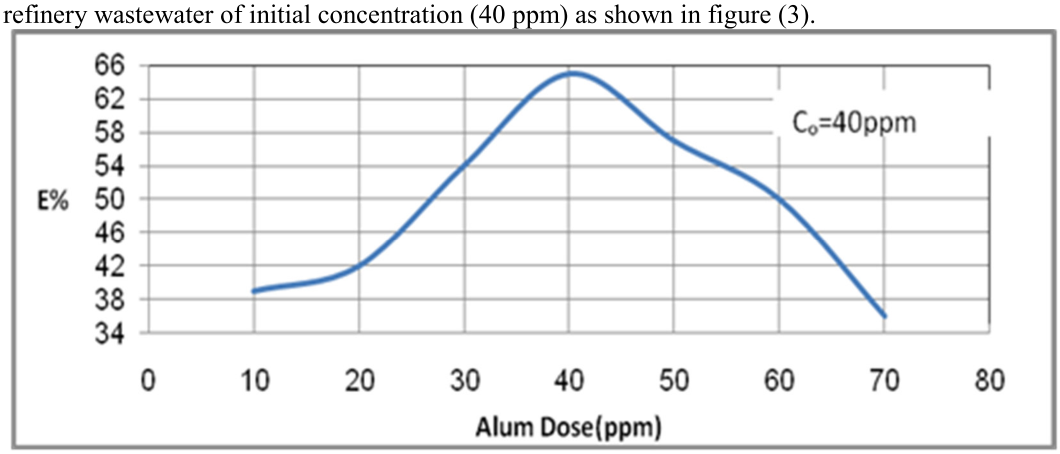

Figure (3): Effect of Alum Dose on Oil Removal Efficiency at C_o=40 ppm

The removal efficiency of oil is 67% when (50 ppm) alum was added to refinery wastewater of initial oil concentration 136 ppm as shown in figure (4).

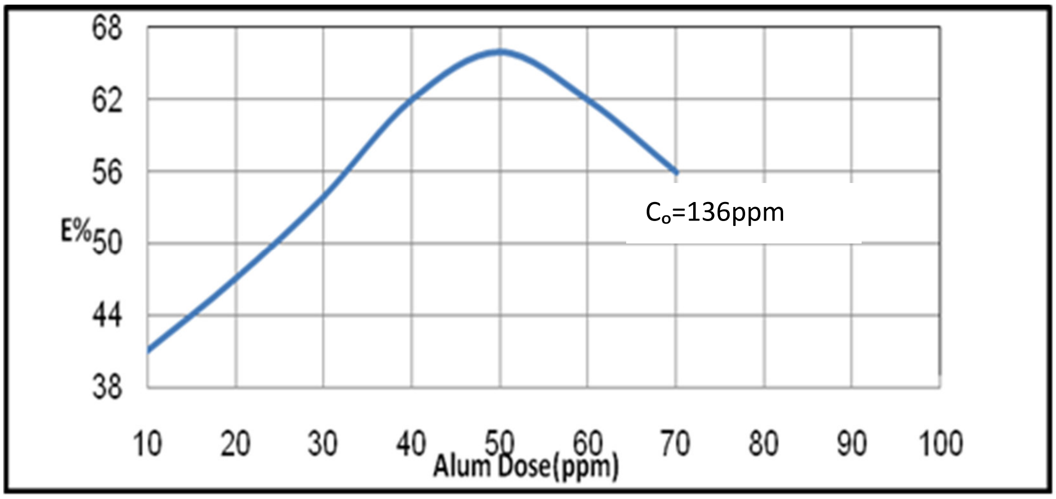

Figure (4): Effect of Alum Dose on Oil Removal Efficiency at C_o=136 ppm

The best removal efficiency is 75% when (2.5 g/l) of bentonite dose is added at initial oil concentration approach to (20 ppm) as shown in figure (5).

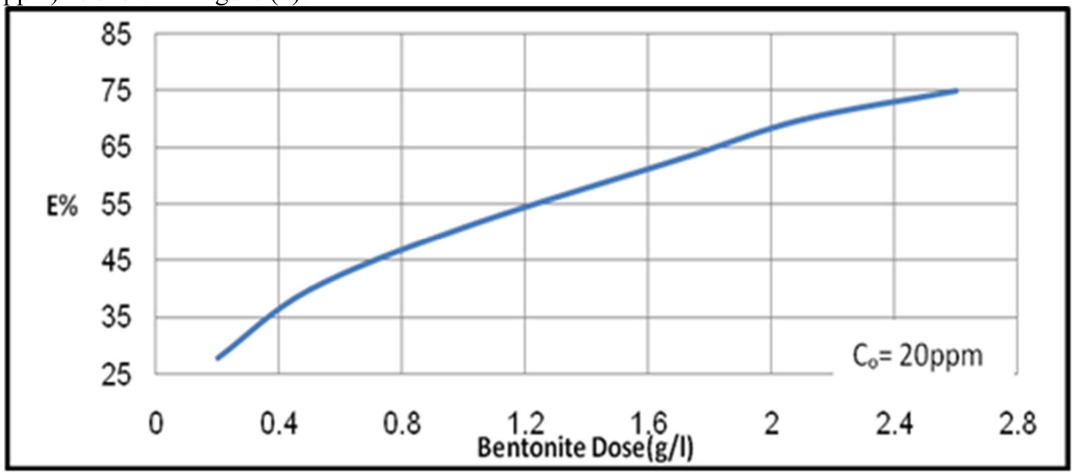

Figure (5): Effect of Bentonite Dose on Oil Removal Efficiency at C_o=20 ppm

The maximum removal efficiency of oil with initial concentration (40 ppm) was 75% when bentonite was added by (5 g/l) as shown in figure (6).

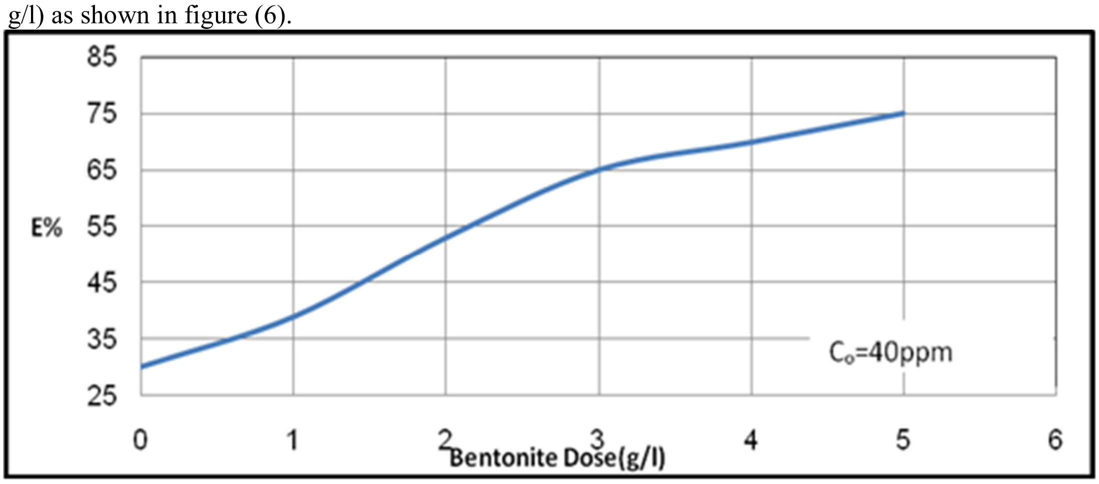

Figure (6): Effect of Bentonite Dose on Oil Removal Efficiency at C_o=40 ppm

Reference to various experiments of coagulant dose, the maximum removal efficiency was 70% when (9000mg/l) of bentonite is add to refinery wastewater of initial concentration (136 ppm) as shown in figure (7).

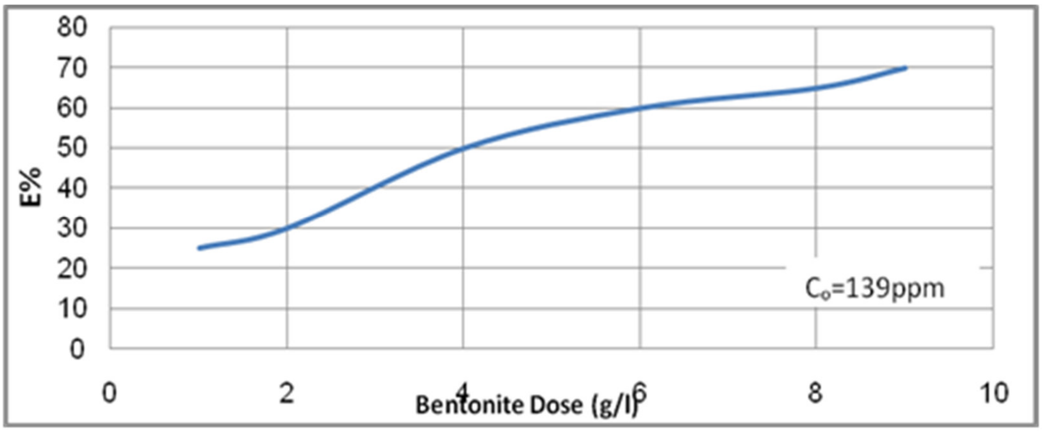

Figure (7): Effect of Bentonite Dose on Oil Removal Efficiency at C_o=136 ppm

4-3Effect of Coagulant Dose on the pH Value

The optimum dose of bentonite was (2.5, 5, and 9 g/l) to make the pH of wastewater approach 7 for oil concentration (20, 40, and 136 mg/l).The pH value decreases when increasing alum dose, as shown in figure (8). Continuous measurements of (pH) for refinery wastewater after adding bentonite show that the effect of bentonite dose on the pH value is very low (low reduction in pH value with increasing in bentonite dose), as shown in figure (9). The pH values of wastewater around seven are required after dose addition and at optimum dose the pH value is in the range of (7 - 7.5). The empirical Equation between pH and dose alum for refinery waste water treatment can be correlated as the form below: -

$$pH = \frac{8.723}{(D_a)^{0.05}} \text{..........} \quad ...(5.1)$$

Where D_a : Alum Dose

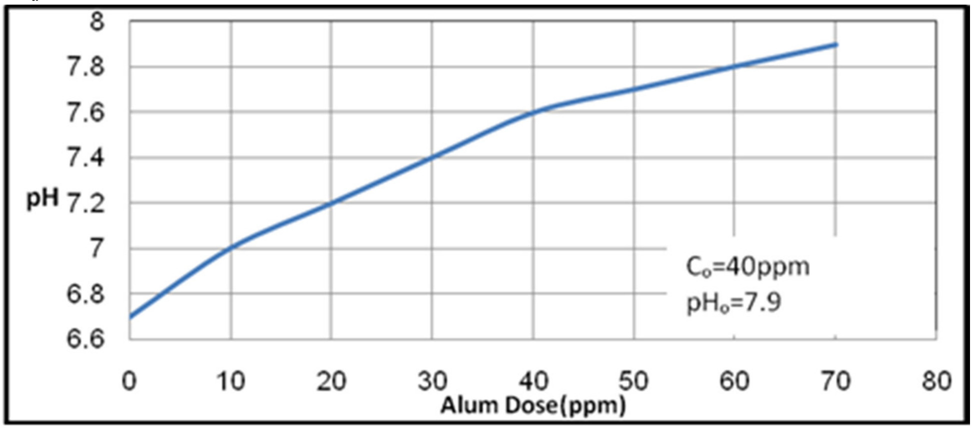

Figure (8): Effect of Alum Dose on pH Value.

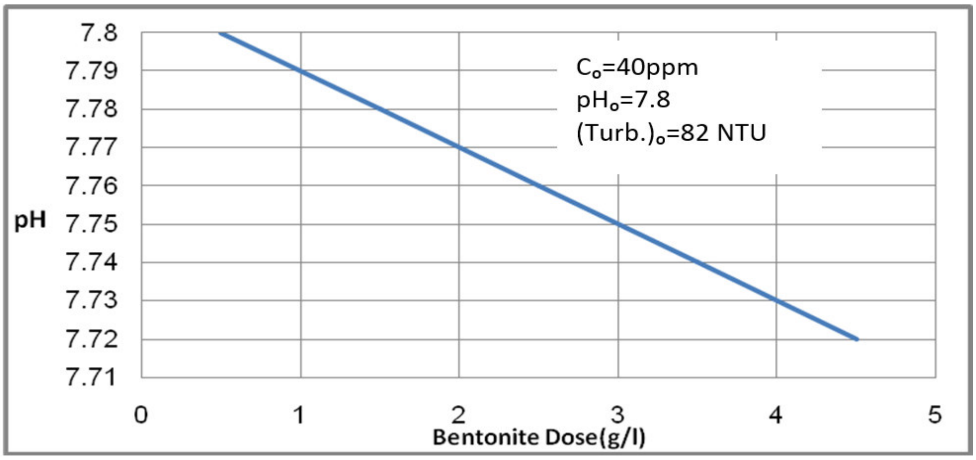

Figure (9): Effect of Bentonite Dose on pH Value.

4-4Total Dissolve Solid Measurement:-

Many experiments indicate that the effects of coagulants on TDS of refinery wastewater are very low for total dissolved solid ranged (540-590 ppm) the range of reduction is (0.03% to 9.6%) as shown in figures (10) and (11). The removal of TDS decreases slightly with increase in coagulants dose.

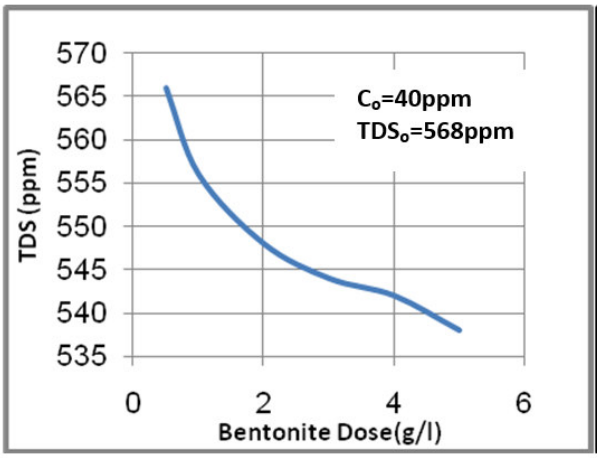

Figure (10): Effect of Alum Doseon TDS Value.

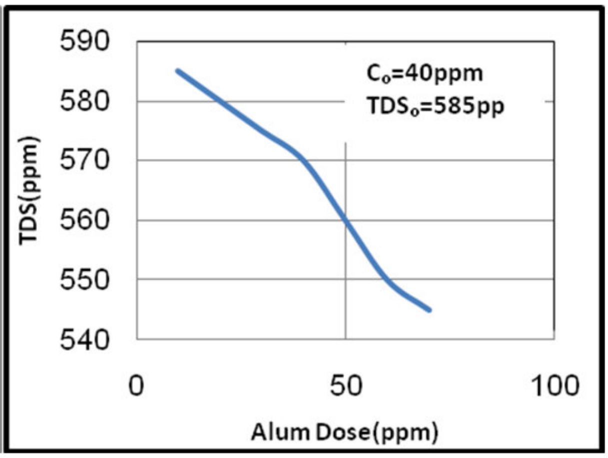

Figure (11): Effect of Bentonite Dose on TDS Value.

The removal of turbidity by adding coagulants is shown in figures (12) and (13). The removal of turbidity increases when alum or bentonite dose increase until reaching the optimum value, the turbidity removal decreases at over-dosing state because of destabilization of the colloid particles.

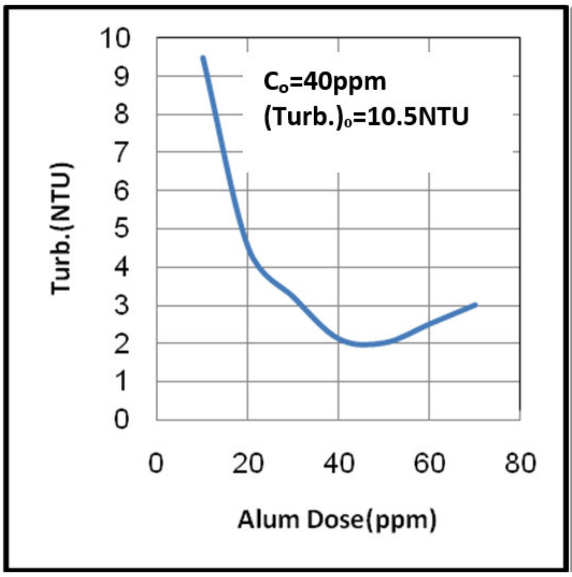

Figure (12): Effect of Alum Dose on Turbidity Value

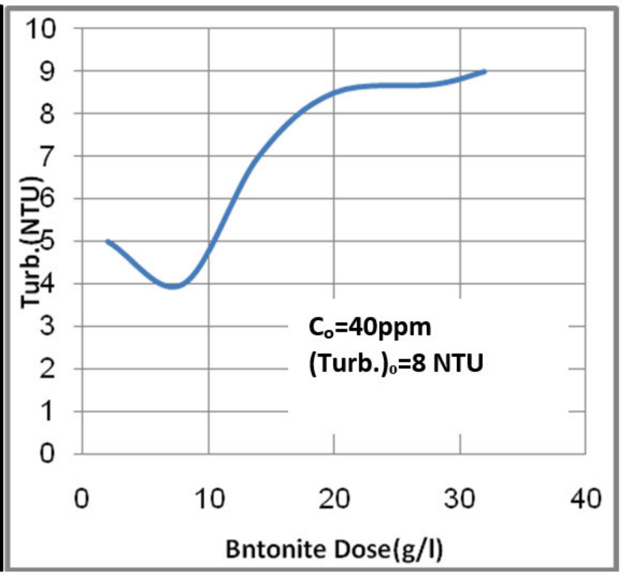

Figure (13): Effect of Bentonite Dose on Turbidity Value

5. Conclusions

The experimental study on oily wastewater treatment for the Durah Oil Company has given some basic information. In general, the following conclusions are extracted from the present study: -

5-1 Industrial wastewater discharged from the Durah Oil Company is polluted with oil in the range (17-136) ppm, COD = (9-97) ppm, turbidity = (1.9- 41) NTU, pH = (6.5- 7.9), TDS = (210-605) ppm, T.H = (169-378) ppm.

5-2 For coagulation flocculation treatment, alum, mixture of bentonite and kaolin were used as coagulants.

The optimum alum dosage was found by jar test to be equal to (25, 40, 80 ppm), and bentonite with kaolin optimum dosage equal to (2.5, 5, 9) g/l, for initial concentration of oil equal to (30, 58, 136 ppm) respectively.

5-3 The oil removal efficiency for coagulation and flocculation treatment is equal to (65, 64, 67%) at Co = (30, 40, 136 ppm) respectively with optimum alum dose.

5-4 The oil removal efficiency for coagulation and flocculation treatment is equal to (75%, 75% and 70%) at Co = (30, 58 and 136 ppm) respectively with optimum (alum + clay) dose.

5-5 The Bentonite as coagulant is more efficient than alum producing higher rate of sludge.

6 Reverences

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