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Research Article

Coagulation/Flocculation Process for Produced Water Treatment

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Abstract

*Produced water is a huge waste volume of water associated with crude oil production. It is a combination of formation water that is present in the well and the oil well injection water. Produced water consist of oil content, dissolve solid and suspended solids. This research interested on treated produced water results from Iraqi midland oil company from suspended solid contamination and oil content. The production rate of produced oil and produced water at 2015 were 140*10³bbl/d and 27.56*10³ bbl/d respectively. While the expected produced oil at 2031 were 92.15*10³ bbl/d with corresponding produced water of 307.84*10³bbl/d. If these huge volumes of produced water disposal to the environment without treated, it will cause many serious environmental problems. Coagulation/ flocculation is a widely-used process in industrial wastewater treatment. It's a preference in the primary purification processes due to its simplicity operation, efficient and cheap. The experimental tests were done by a jar test and followed ASTM D2035. Three coagulant materials tests were used KlarAid CDP1326 , KlarAid PC1195 and KlarAid IC1176 and Zetag8140 as flocculent material. The first part in experimental study was to determine the best coagulant material, the second part is to determine the optimum coagulant and flocculent dosages. The results showed that KlarAid CDP1326 had superior efficiency in removing turbidity compared with other coagulants at the same conditions and the best turbidity removal was achieved at dose concentration of 70 mg/l of KlarAid CDP1326 and dose concentration of 2.5 mg/l of Zetag8140, were its decreased from 206 NTU to 1.5 NTU, the oil content decreased from 550 mg/l to 54.6 mg/l at same dose of coagulant and flocculent. Statistical analyses of results gave a general equation described the process.*

Keywords: *Coagulation, Flocculation, Produced water.*

1. Introduction

Oil is a mixture of hydrocarbons including benzene, toluene, ethylbenzene, xylenes (BTEX),naphthalene, phenantherene, dibenzothiophene (NPD), Polyaromatic hydrocarbons (PHAS) and phenols. water cannot dissolve all hydrocarbons, so much of the oil is dispersed in water (ahmadun, et al., 2009). Generally, an oil and water mixture can be classified as free oil with oil droplets larger than 150 µm, dispersed oil, with oil droplets in the range of 20-150 µm and emulsified oil with oil droplets smaller than 20 µm (Wang, 2011). The midland oil company (Iraq) produced a huge volume of produced water .In 2015 the production rate of oil and produced water were 140*103 bbl/d and 27.56*103 bbl/d respectively and increased to 92.15*103 bbl/d and307.84*103 bbl/d respectively in 2031 as expected .These huge volume should be treated from emulsified oil droplets of few micrometers in diameter which were protected from spontaneous coalescence into larger ones due to electrostatic repulsion forces , making oil separation by simple gravity separation a difficult and time-consuming process. Several methods have been applied for the removal of oil from waste waters. such as adsorption , flocculation, electro-coagulation and flotation (Zouboulis, et al., 2000). Coagulation / flocculation is a widely-used process in the primary purification of water and in industrial wastewater treatment. This method has a preference in the primary purification processes mainly due to the ease of operation, high efficiency, cost effective also it uses less energy than alternative treatment (Altaher, *et al*., 2011).

Many researchers studied the coagulation /flocculation process on waste water treatment such as: Altaher *et al*, 2011 (Altaher, *et al*., 2011) optimized the coagulation-flocculation process of Wastewater Streams from Petroleum /Petrochemical. Ramavandi, 2014 (Ramavandi, 2014)evaluated the coagulation potential of FCE(FeCl3-inducedcrudeextract) obtained from P.ovata seeds for the turbidity removal from water. Rincon, 2014 (Rincon, et al., 2014) presented electro-coagulation as a method to treat bilge water, with a focus on oily emulsions and heavy metals (copper, nickel and zinc) removal efficiency. Daud *et al*,

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2015 (Daud, *et al.*) investigated the efficiency of coagulation and flocculation processes for removing suspended solid (SS), color, COD and oil and grease from biodiesel wastewater. Rao, 2015 (Rao, 2015) Treated textile industry waste water used chitosan. Zouboulis (Zouboulis, *et al.*, 2000), Xia (Xiaa, *et al*., 2007), Maleki (Maleki, *et al*., 2009) and Farajnezhad (Farajnezhad, *et al.*, 2012) used jar test for investigated water treatment. In this study , the produced water treated using the following technique and tests the jar test has been the standard technique used to optimize the addition of coagulants and flocculants. The standard practice for coagulation/flocculation Jar Test of Water, ASTM D 2035, was first approved in 1980 and reapproved in 1999. The scope of this practice covers a general procedure for the evaluation of a treatment to reduce dissolved, suspended, colloidal, and non settleable matter from water by chemical coagulation_/flocculation, followed by gravity settling. This standard was utilized to provide a technique to systematically evaluate the variables normally encountered in the coagulation_/flocculation process (Ebeling, *et al*., 2003).A turbidity meter was used (Lovibond, SN 10/1471) , Germany to measure the performance of individual treatment processes as well as the performance of an overall water treatment system.

Common water treatment processes intended to remove suspended solids and reduce turbidity include: coagulation, flocculation, sedimentation and filtration (Al-Sameraiy, 2012). Removal of turbidity by coagulation depends on the type of colloids in suspension, the temperature, PH, chemical composition of the water, the type and dosage of coagulants, the degree and time of mixing provided for chemical dispersion and floc formation. A large variety of turbidity-producing substances found in polluted waters do not settle out of solution, for example, color compounds, clay particles, microscopic organisms and organic matter from decaying vegetation or municipal wastes. these particles, referred to as colloids , range in size from 1 to 500 millimicrons and are not visible when using an ordinary microscopic. A colloidal dispersion formed by these particles is stable in quiescent water since the individual particles have such a large surface area relative to their weight that gravity forces do not influence their suspension (Ali, 2004).TD-500 oil in water analyzer (Revision: C , P/N 100668), United States of America measures the oil content in the oily water containing crude oil or gas condensates using UV fluorescence.

It works on produced water, de-salter water, and crude storage tank water and in any application where crude oil may be in contact with the water. TD-500 oil in water meter uses an easy to use solvent extraction procedure with high accuracy and repeatability. The standard procedure of solvent extraction is specified by EPA-1664A method better known as FastHex method of analysis. The analysis method is compatible with all popular solvents including n-Hexane, Freon, Xylene and others. The sample analysis time is less than 4 minutes (Patel, 2004). A second order polynomial equation is used to describe the relationship between the factors (Xi and Xj) and the investigated response (Y).

$$Y=\beta 0 + \Sigma\ \beta i\ Xi + \Sigma\ \beta ii\ Xii2 + \Sigma\ \beta ij\ Xi\ Xj \quad (1)$$

where Y is the response model (residual turbidity removal and residual oil content); β0 is the constant coefficient; βi is the coefficient of the linear term; βii is the coefficient of the square term; βij is the different interaction coefficients between the input factors Xi and Xj; Xi and Xj are the coded values of the independent variables(coagulant and flocculent dosages).

This study interested on removal suspended solid contamination and oil content from produced water using coagulation /flocculation process, studying the ability of three coagulant materials (KlarAid CDP1326, KlarAid PC1195 and KlarAid IC1176) and Polyelectrolyte Zetag8140 flocculent material, Find the optimum value of coagulant and flocculent dosages and obtained a general equation relating coagulant and flocculent dosages with residual turbidity and residual oil content respectively.

2. Materials

The materials used in the present study can be illustrated as the following:

2.1 Coagulant and Flocculent materials

Three coagulant materials used in the study are:

2.1.1 KlarAid CDP1326 is a strongly cationic, high charge and molecular weight, liquid coagulant. Its chemical name is ferric sulphate 25%.

2.1.2 KlarAid PC1195 is a strongly cationic, medium molecular weight, liquid coagulant. Its chemical name is 1,2-Ethanediamine, polymer with (chloromethyl)oxirane and N-methyl methan amine 25%.

2.1.3 KlarAid IC1176 is a strongly cationic, low to medium molecular weight liquid coagulant. Its chemical name is Aluminum chloride 10%. Commercial flocculent used is Polyelectrolyte Zetag8140, has Physical and Chemical Properties show in table 1.

Table 1 Polyelectrolyte Zetag8140 Physical and Chemical Properties

Property	Specification
Form	Powder
Odour	Odourless
Odour threshold	No data available.
Colour	off-white
pH value	3.5 - 4.5 (10 g/l)
Melting point	The substance / product decomposes therefore not

	determined
Boiling point	not applicable
Bulk density	approx. 700 kg/m3
Solubility in water	Forms a viscous solution

3. Experimental Tests

3.1Choice of coagulant

In order to determine which coagulant is suitable for produced water treatment, Three experiments were done separately includes addition of 50ppm of coagulant in 250 ml produced water (oil content= 550ppm and turbidity=206NTU) using jar test followed ASTM D2035. A sample from the upper layer of treated produced water was take and analyzes for turbidity using turbidity meter. The objective of this experiment was to determine the best coagulant that can be used to reduce turbidity to the permissible level for such wastewater. It is well known that the behavior of coagulant may change from waste- water to another according to different constituents of wastewater.

3.2 Choice of optimum coagulant and Flocculent dosages

Jar test apparatus with 4 beakers of 1.0 L capacity each was used. Each beaker was filled with 250ml of produced water with identical turbidity (206 NTU). Different dose of coagulant (10, 30,50and 70) ppm and flocculent (1,1.5,2,3) ppm reagent were added to 4 beakers, . The beakers were agitated at various mixing time and speed, which consist of rapid mixing (120 rpm) for 1 minutes and slow mixing (50 rpm) for 20 minutes, After the agitation being stopped, the suspension was allowed to settle for 15 minutes. Finally, a sample was withdrawn using a pipette from the top centimeters of supernatant to analyze for turbidity and oil content.

3.3 Turbidimeter Sample analyses

After using jar test, Pipet water out of the first beaker and place it in a sample tube, making sure that no air bubbles are present in the sample(air bubbles will rinse while turbidity will sink.). Place the sample tube in a calibrated turbidimeter and read the turbidity. Repeat for the water from the other beakers.

3.4 Calibration of TD 500 and sample analysis

3.4.1 Sample Preparation: A 50 ml volume of the sample to be analyzed is collected in a graduated cylinder. The pH of the sample is adjusted below value of 2 by adding hydrochloric acid. n-Hexane is added as 1 part in 10 parts of the sample on volume basis. The cylinder is rigorously shacked for Two minutes. Solvent extracts soluble oil present in the sample and the two layers are formed. The extract layer contains solvent and oil extracted from the sample. The extract is carefully separated and collected into a separate cylinder or flask. The extract is analyzed by TD-500.

3.4.2 Sample Analysis : Before analyzing a sample, the TD-500 meter is calibrated using standard samples. First of all the standard samples of known oil content are prepared. As a starting point, we prepared a mixture of 1 ml of oil in 9 ml of n-Hexane. This mother solution is diluted with various volumes of n-Hexane to create samples with different oil concentrations. TD-500 meter is set on calibration mode. A appropriate volume (0.075 ml) of extract is collected in clean minicell cuvettes . The cuvette filled with the extract is placed in a cuvette adapter. The adapter fits into the sample compartment of the analyzer. The analyzer responds within 5 seconds

4. Results and Discussion

4.1 Best Coagulant Choice Results

The turbidity of produced water used in this study was 206 NTU, a three substance of coagulants were used (KlarAid CDP1326, KlarAid PC1195 and KlarAid IC1176). The results show that the residual turbidity were 18.9 NTU, 95.6 NTU and 28 NTU respectively. It was found that KlarAid CDP1326 had superior efficiency in removing turbidity compared with other coagulants at the specified conditions.

4.2 Optimum coagulant and flocculent dosages Results

It has been stated that oil droplets in water have a negative charge on their surface. This negative charge is probably due to preferential adsorption of hydroxyl ions from the dissociation of water molecules (Zouboulis, *et al.,* 2000). In order to assure maximum effectiveness of oil removal, it is necessary to add chemical coagulation and flocculation which can destabilize oil particles or emulsions.

From figure 1 it is clear that as the coagulant dose increase, residual turbidity decreased until reach the lower value at the optimum coagulant dose, then the increased due to high positive charge results from higher coagulant dose added. while figure 2 shows that the oil concentration decreased as the coagulant dose increased. When coagulant of positive electric charge are added, it neutralizes the electric negative charge, precipitate the oil particles and other presented pollutants in the wastewater, as hydroxides and facilitate their removal by physical separations through the sedimentation process. The results obtained indicated that best turbidity removal was achieved at dose concentration of 70 mg/l of KlarAid CDP1326 and dose concentration of 2.5 mg/l of Polyelectrolyte. were its decreased from 206 NTU to 1.5 NTU, and for oil concentration its decreased from 550 mg/l to 54.6 mg/l at same dose of coagulant and flocculent. The concentration of the chemical additive is an important factor that significantly affects the separation efficiency (Zouboulis, *et al*., 2000).Figure 3 explain the process of coagulation, the added coagulant reacts relatively quickly with colloid particles in water to cause neutralization of the surface charge. The particles then coagulate to form primary micro-floccules. During the flocculation process, micro-floccules continue increasing in size to form settling floccules with large size and density.

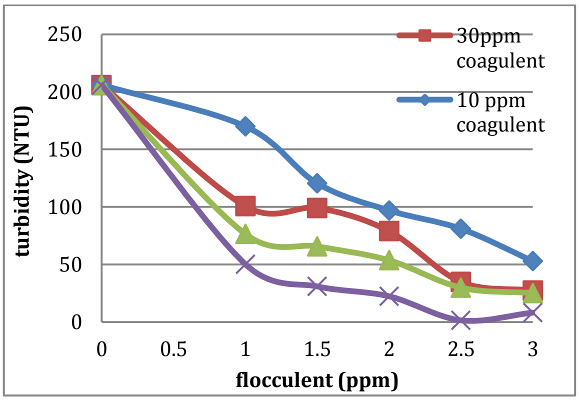

Figure 1 the effect of coagulant and flocculent dosage on turbidity

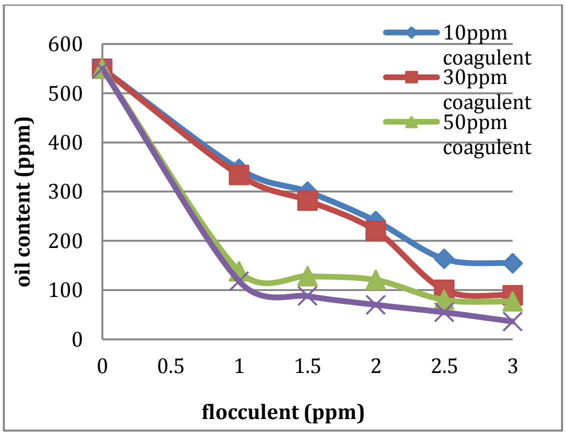

Figure 2 the effect of coagulant and flocculent dosage on oil concentration

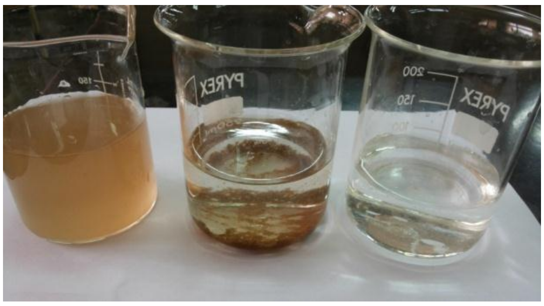

Figure 3 produced water initially and after adding coagulant and flocculent materials

Analysis of variance has been calculated to analyze the convenience of the model. The analysis of variance for the response has been shown in Tables 3 and 4. The larger magnitude of F-test value and the smaller magnitude of P-values, the higher significance of resultant coefficient. Values of P less than 0.05 indicate that the model terms are significant. The empirical relationship between the residual turbidity and the independent variables in the coded units based on the experimental results was given by:

$$Turbidity=231.7428-2.4181X_1-58.9041X_2+0.5519X_1X_2 \quad (2)$$

and for residual oil content, the empirical equation is:

$$Oil\ content =550.358 -5.938X_1-136.869X_2+1.472X_1X_2 \quad (3)$$

where X_1 is coagulant dose and X_2 is flocculent dose. Figures 4 and 5 show the Response surface of 3D plot indicating the effect of interaction between coagulant and flocculent dosages on residual turbidity and residual oil content respectively.

Table 3 ANOVA test results for residual turbidity

Effect	Sum of squares	DF	Mean squares	F-Value	P-Value
Regression	107664.6	4.00000	26916.16	311.4678	0.000000
Residual	1382.7	16.00000	86.42		
Total	109047.3	20.00000			

Table 4 ANOVA test results for residual oil content

Effect	Sum of squares	DF	Mean squares	F-Value	P-Value
Regression	653393.5	4.00000	163348.4	180.2384	0.000000
Residual	14500.7	16.00000	906.3		
Total	667894.2	20.00000			

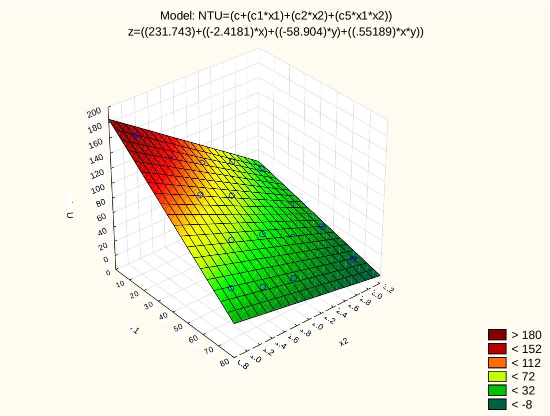

Figure 4 Response surface of 3D plot of residual turbidity.

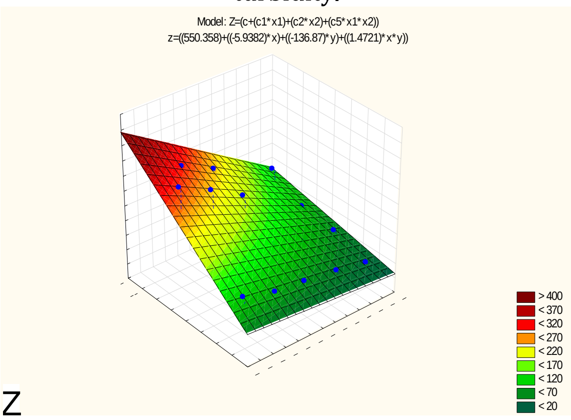

Figure 5 Response surface of 3D plot of residual oil content

Conclusion

KlarAid CDP1326 suitable for Produced Water Treatment, it can decreased the turbidity higher than KlarAid PC1195 and KlarAid IC1176.

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