Coagulation - Flotation Process for Removing Oil from wastewater using Sawdust+ Bentonite

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ABSTRACT

In many industries especially oil companies in Iraq consumed large quantities of water which will produce oil-contaminated water which can cause major pollution in agricultural lands and rivers. The aim of the present work is to enhance the efficiency of dispersed air flotation technique by using highly effective and cost-efficient coagulant to treating gas oil emulsion. The experimental work was carried out using bubble column made of Perspex glass (5cm I.D, 120cm height). A liquid was at depth of 60cm. Different dosage of sawdust +bentonite at ratio 2:1 (0.5+ 0.25; 1+ 0.5 and 2+1) gm and alum at concentration (10,20and30mg/l) at different pH (4 and 7) were used to determine optimum dosages of coagulant. Jar test experiment has showed that optimum dosage of (sawdust +bentonite) was (1+0.5gm) and alum concentration was 30 mg/l at pH=4.

The present study was conducted to evaluate the effect of various parameters pH (3, 4,7and 9); air flow rate (300, 500, 1000, and 1500 cc/min); initial oil concentration (300 up to 1000 ppm); concentration of Sodium dodecylsulphat surfactants ,SDS (25, 75and 150mg/l); and the effect of the addition coagulant (sawdust + bentonite at ratio 2:1) and alum (30mg/l) in the removal efficiency of oil from wastewater by coagulation –flotation process.

The study has showed that the removal efficiency of COD, oil content and turbidity were related to the initial oil concentration; additive concentration of SDS and dosage of coagulants. It was found that the flotation rate increases when using coagulants, the fastest removal rate was obtained when pH 4 and also the higher removal efficiency achieved was for flotation (87%) and (95.7%) sawdust +bentonite; (97%) for alum in coagulation – flotation process.

Key words: Oily wastewater; Sawdust+ bentonite; Alum; Coagulation -Flotation
1. INTRODUCTION

The threat of oil pollution increases with the expansion of oil exploration and production activities, as well as the industrial growth around the world. The study on the treatment of oily wastewater is a critical issue to the environmental protection as oil caused problems to the wastewater treatment facilities, Wahi et al., 2013.

Oil is one of the important contaminants in water and causes the wastewater problems in environments. In practice, this can form various types of oily wastewaters; for instance, soluble oil in water, emulsion with or without surfactants or floating film, Painmanakul et al., 2009.

Major spills, such as pipeline, tanker or storage tank accidents, create an acute problem of pollution. On the other hand, continuous low-level inputs are rarely noticed, and pose a serious threat to the environment as contamination accumulates. Therefore, diesel hydrocarbons create a world-wide problem of contaminated water and soil that require decontamination.

Diesel causes eye and skin irritation in humans, but otherwise its effects on humans are considered to be poorly investigated, Muzyka et al., 2002.

Standards and regulation were adopted for discharge of oily wastewater into surface water or sewage systems. These regulations may vary from country to country, and even within a country itself. Environment Canada (1976 b) has established a discharge limit for oil and grease of 15 mg/L at federal establishment. The allowable oil concentration for discharge into water bodies...
are 2 to 10 mg/L and 5 mg/L in Germany and Switzerland, respectively. The allowable hydrocarbons and its derivatives discharge into water bodies about 3 mg/L in Iraq, Iraqi preservation law, Law No. 2, 2001.

Flotation separation is a primary water treatment process. Numerous studies on the potential of using flotation unit to remove oily emulsions have been reported, Weltz et al., 2007. Xiao et al., 2007. and Painmnakul et al., 2009. Gas flotation units work by introducing small gas bubbles into the wastewater being treated. The gas bubbles acquire a small electronic charge, opposite that of the oil droplets. As the gas bubbles rise through the oily wastewater, oil attaches to the bubbles, Bradley, 1990. and Arnold, and Stewart, 2008. Flotation units use two distinct methods for producing small gas/air bubbles needed to contact with water: pressurized gas/air injection and induced gas/air, Cline, 2000.

Flotation units typically serve as a preliminary step for water treatment in removal of suspensions and emulsion due to small differences in the density of continuous phase and of particulate phase. Flotation is an alternative as it has high efficiency as well as low operating cost, Rubio et al., 2002.

Generally, flotation separation can be divided into two types: (1) dispersed air flotation and (2) dissolved air flotation, (DAF).

Coagulation is the addition of chemicals and the provision of mixing so that particles and some dissolved contaminants are aggregated into larger particles that can be removed by solids removal processes such as sedimentation, dissolved air flotation, rapid filtration or membrane filtration. Fig. 1 illustrates the process of coagulation, flocculation and flotation, Dempsey, 2006.

Saatci et al., 2001. studied the efficiency of treating vegetable oil factory wastewater by using the DAF coagulation with lime and alum; their analyses have shown that COD concentration of wastewater depends on its oil and grease content. This means that COD load could be importantly decreased with a decrease in oil and grease concentration.

The efficiency of wastewater treatment increased depending on the reduction of pH. And they concluded that the amount of sludge produced was reduced to 58% compared to lime treatment and it was shown that clay could be an alternative to lime.

Soletti et al., 2005. studied the effect of ferric sulfate Fe (SO₄)₃ on pH values in dissolved air flotation of oily wastewater treatment by flotation column and obtained increase in coagulant concentration decrease pH value and enhance removal efficiency.

Welz et al., 2007. investigated the flotation of oil from wastewater in a laboratory scale mechanically agitated flotation cell and explores the effect of chemical factors (coagulant and flocculants) on flotation performance based on coagulant and flocculants dosages of (0.5 mg/l) when using Al₂(SO₄)₃ and 1.5mg/l when using lime. They found that the effect of coagulant dosage is more economical with the use of Al₂ (SO₄)₃ is the further justified due to lower cost as well as lower dosage and higher efficiency.

Mohammed, and Zain-al-albideen 2007. studied the effect of coagulant (alum, clay) on removal efficiency of oily wastewater treatment by dissolved air flotation. They found that the removal efficiency of oil increase with alum until reaching the optimum dosage (25, 40, 70) ppm for initial oil concentration (30, 58, 136) ppm respectively, and the over dosage causes a
decrease in the oil removal efficiency, but the other coagulant (clay) having higher removal efficiency of oil the optimum dose of it was (2.5, 5, 9) ppm for the same initial oil concentration, but disadvantage of higher amount of sludge caused.

The removal of oil emulsion in wastewater had also been studied by Painmanakul et al., 2009, utilizing the induced air flotation on the study of the effect of bubble hydrodynamic such as bubble size and addition of chemical coagulant (alum) to induced air flotation process and chemical dosage for the treatment of oily wastewater. They reported optimum pH value between the values of 8-10. This research study showed some similarity with the study of Xiao et al., 2007, though the former used induced air flotation while the latter used DAF.

AlMaliky et al., 2009. studied oil and grease removal from two types of industrial wastewaters; Sweets and Dairy Industries wastewater by induced air flotation. Their results have shown that (3-5 l/min.) air flow rates are the optimal for having separation efficiencies between (77%- 80%) for effluent of Sweets industry, and (66%- 70%) for effluent of Dairy industry. The addition of (0.5 g/l) alum has proved significant influence on oil/ water separation efficiency, which could reach the values of (96%- 99%), using the air flow rates mentioned above, for Dairy and Sweets industrial effluents respectively.

Sulaymon, and Mohammed 2010. studied the effect of coagulant Al₂(SO₄)₃.17H₂O and surfactant on separation efficiency of the emulsified kerosene in water in bubble column. The results indicate that the rate of the flotation enhanced when using SLES (sodium laurel ether sulfate) where the surface tension was reduced which leads the improvement of the separation efficiency, and found that adding Al₂ (SO₄)₃.17H₂O and SLES together have a high coagulant effect than individually.

Tansel, and Pascual 2011. investigated the removal of emulsified fuel oils from brackish and pond water by dissolved air flotation (DAF) with and without use of coagulants and they concluded that coagulant addition initially increased the petroleum hydrocarbon (PHC) removal by about 5–15%.

SEIN, 2011. concluded that dispersed air flotation (DIAF) unit was efficient as a primary water treatment process in treating synthetic wastewater containing suspended solids and oily emulsions, also the addition of alum (coagulant) and anionic polymer (flocculent) is necessary to improve flotation via destabilization of colloids and agglomeration of destabilized particles. Oil and grease removal required a more agitated system compare to total suspended solid (TSS) and turbidity removal which suggest that a more turbulent system had a beneficial rather than disruptive effect on oil flotation.

Fu, and Chung, 2011. concluded that the use of a mixture of bentonite and sawdust, with sawdust being the vast majority, is highly effective for the coagulation of oil in water, giving coagulation efficiency 92% or above.

Sawdust by itself sinks in water. However, the coagulated aggregates float on water when sawdust is used with the bentonite. These aggregates are sheet-like, with the oil–bentonite–sawdust serving as a continuous matrix and apparently no upper limit to the aggregate sheet size. Without sawdust, the aggregates sink in water and the coagulation efficiency is only 37%. The sawdust functions as a fibrous framework for the attachment of the coagulating oil and bentonite, thus facilitating floating aggregate formation and the subsequent removal of the aggregates.
Mohammed et al., 2013, studied experimentally the use of induced air flotation (IAF) to treat the oily wastewater of Iraqi North Oil Company and they showed that the removal efficiency of oil was increased with increasing initial oil concentration, it reached up to 76%. While it became 89% when using stirrer. The experimental results were translated to a computer program to predicate empirical correlation.

Vasseghian et al., 2013, investigated the efficiency of Dissolved Air Flotation (DAF) for the treatment of refinery wastewater. The effect of several parameters on flotation efficiency namely, saturator pressure, and coagulant dose, on COD removal was examined experimentally. Experiments were done by using poly aluminum chloride coagulant (PAC) at pressures 2bar up to 5bar and in three doses 15mg/l, 20mg/l and 25mg/l. The data obtained from COD experiments using neuro-fuzzy systems have been modeled. The correlation coefficient ($R^2$), root mean square error (RMSE) and sum of square error (SSE) of predicted values by using neuro-fuzzy systems are obtained 0.9991, $6.35 \times 10^{-3}$ and $4.04 \times 10^{-5}$ respectively, which shows the high accuracy of neuro-fuzzy systems.

The aim of the present study is to studying the enhancement of oil removal by induced air flotation using sawdust + bentonite clay as coagulant.

2. EXPERIMENTAL WORK

2.1 Gas Oil

Commercial gas oil was used in this study as the model pollutant. Gas oil was analyzed in Petroleum Research and Development Center/Ministry of Oil; the chemical compositions are as follows: 62.5% Paraffin's; 18.7% Aromatics and 18.8% Naphthenes.

The functional groups present in gas oil were detected by FTIR analysis; Fig 2. The physical properties of gas oil were shown in Table 1.

2.2 Materials

- Surfactant type Sodium dodecyl sulphat (SDS) from Fisher Scientific was used as anionic collectors and is a white powder material with a chemical structure of $(C_{12}H_{25}OSO_3Na)$, molecular weight 288.38 gm/mol.
- pH adjustment was done by using (NaOH molecular weight is 40 gm/mole and purity of 100%, HCl molecular weight is 98.08 gm/mole and purity of 100%).
- Sawdust was 100% recycled from solid wastes. It is collected, cleaned, milled, and then sieved to obtain grain sizes of (0.6-1) mm in diameter (effective diameter $d_e = 0.63 mm$, uniform coefficient, $U_c = 1.5$).
- Bentonite clay Ca-Montmorillonite % (70min) CEC (65min)-pass from sieve 0.075mm (98%min) (Ministry of Industry and Minerals, Iraqi Geological Survey).
- Aluminum sulfate (Alum): commercial alum was used in the experiments, it is a white dry powder, has a formula of $(Al_2(SO_4)_3.18H_2O)$ and molecular weight of (594.4 gm/mole).

2.3 Apparatuses

2.3.1 Flotation column

The experiments were performed into a cylindrical Perspex glass flotation column with the dimensions (5 cm inner diameter and 120 cm in height), samples were drawn from tap of 0.2 cm inside diameter, at the middle of column, and the column was operated in a semi- batch mode.
(batch wastewater, continuous air). Fig.3 and Fig.4 show a schematic and photographic diagram of experimental apparatus.

2.3.2 Jar test

The sedimentation jar test (Aztec environmental control LTD) was used to simulate conventional clarification, coagulation, flocculation and sedimentation steps. It consists of six beakers (volume of 1L) and stirrers, which could be adjusted to the same stirring conditions for all the beakers. The beakers were filled with 1L of sample and the coagulant was added simultaneously to all beakers.

2.4 Experimental Procedure

- The oil emulsion was prepared with the desired concentrations (300 up to 1000 ppm) by injection the required volume of oil into specific volume of distilled water. Agitation was achieved by bubbling air into the solution for half hour in a tank. The drop oil sizes distribution were found by using microscope type (novex) and the mean drop diameter was found to equal to 20μm

- After oil emulsion was prepared at different concentrations, SDS surfactant (25, 75 and 150 mg/l) was added then poured gently at the top of the column, air was fed to the column at different velocity (0.25, 0.424, 0.849 and 1.273cm/s) by rotameter and then samples were taken at different time intervals 10, 20, 30 and 40 min. pH was adjusted to a desired value using HCL or NaOH.

- Jar test constituted the preliminary test to determine optimum dosage of coagulant for (sawdust + bentonite at ratio 2:1 (Fu and Chung, 2011) (0.5+ 0.25; 1+ 0.5 and 2+1) gm , and alum concentration (10, 20, 30 mg/l) and determine its optimum pH from (pH=4 and pH=7) for optimum removal efficiency of oily wastewater. The jar test speed was set to be 300 rpm for at least 1 min to mix the synthetic wastewater then coagulation was allowed to take place for at least 25 min or until the suspended solids form colloids. Jar test was stopped when coagulation was completed.

- Optimum dosages of coagulant will be added to oil emulsion at its best conditions , then it will be stirrer at speed 300 rpm for 1 min , then it will allowed to take place, coagulated oil emulsions were drained into the flotation tank, then the flotation process was allowed to take place for 40 minutes.

2.5 Analysis

2.5.1 Chemical oxygen demand (COD)

Chemical Oxygen Demand of samples was analyzed by using COD photometer apparatus. The appropriate amount of sample (2ml) was introduced into commercially available digestion solution (MR-Rang: 150-1500mg/L) containing potassium dichromate, sulfuric acid and mercuric sulfate. The mixture was then incubated for 120 min at 150°C in a COD reactor (model RD-125, Lovibond Company, Germany). After oxidation is complete, the COD concentration was measured colorimetrically at 605 nm using a DR/2010 spectrophotometer.

2.5.2 Oil content

Oil content analysis was carried out using the oil content analyzer based on infrared analysis. It includes a single-beam, fixed wavelength, non-dispersive infrared filter-based
spectrophotometer. Infrared radiation from a tungsten lamp is transmitted through a cylindrical, quartz curette containing a sample extract. The radiation which passed through the extract enters a detector containing a filter that isolates analytical wavelength in the 3400- to 3500-nanometer range (Model: HORIBA OCMA-350).

2.5.3 Turbidity

The turbidity of the samples was measured using turbidity meter (laviboid meter with NTU unit).

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH plays an important role in the removal of oil emulsion by flotation method. Different values of pH were examined in this study (3, 4, 7 and 9) keeping the other parameters constant (initial oil concentration 500 mg/l, flow rate 500cc/min and SDS= 20mg/l). By plotting the concentration ratio (C/Co) versus time at various pH values, Fig.5, it can be seen from this figure that concentration ratio (C/Co) of COD; oil content and turbidity decreases suddenly at the beginning of the run then the ratio began to increase slowly with time and it was found that the highest removal is achieved at pH= 4, which suggests that the repulsion between bubble and oil particle is lost and that adhesion between them is promoted.

3.2 Effect of Initial Oil Concentration

Different concentrations of initial gas oil concentrations (300, 500, 700 and 1000) mg/L were studied keeping other parameters constant (pH=4, air flow rate 500cc/min and SDS= 20mg/l). By plotting the concentration ratio (C/C_o) versus time at various initial gas oil concentration, Fig. 6.

It can be seen from this figure that concentration ratio (C/C_o) of COD, oil content and turbidity increases with increasing initial oil concentration that because when the initial concentration of oil increased the contact of air bubble and oil droplet was increased, this result are in agreement with the results of, Mohammed et al., 2013.

3.3 Effect of Air Flow Rate on the Removal Efficiency

Different air flow rates were studied (300, 500, 1000, and 1500 cc/min) that is at gas velocity equal to 0.25, 0.424, 0.849 and 1.273cm/s respectively, with keeping the other parameters constant (pH=4, initial oil concentration=1000ppm and SDS= 20mg/l) in order to show the effect of air flow rate on the concentration ratio.

This effect is shown in Fig.7. by plotting (C/Co) versus time at different airflow rate and from this figure, it can be seen that as gas flow rate increased, the concentration ratio increased. This is because increasing gas flow rate causes early bubble detachment, large fluid activities (stress) at the bottom section and bubble coalescence and (mostly) break up. This results in a large number of small bubbles which facilitates collision with oil, Sulaymon and Mohammed, 2010.

3.4 Effect of Surfactant

The removal rate of oil from water was studied at different of SDS surfactant concentrations (20, 75, 150 mg/l) in order to show the effect of adding anionic surfactant on the removal rate of
oil. Fig. 8 shows the effect of (SDS) concentration on the concentration ratio of (COD, oil content and turbidity).

The explanation of this improvement is that surfactant reduces surface tension and reduces the bubble diameter and increases the coalescence of larger diameter droplets which are more easily removed, that result is in agreement with, Gregory and Zebal, 1990. They concluded that chemical pre-treatment of oil-water emulsions is based on the addition of chemicals that destroy the protective action of the emulsifying agent, overcoming the repulsive effects of the electrical double layers to allow the finally sized oil droplets to form larger droplets through coalescence.

3.5 Effect of Coagulant

In order to study the effect of natural coagulant on the removal efficiency of gas oil emulsion by flotation process,(sawdust +bentonite) at its optimum dosage (1+0.5gm) was added to flotation process and compare the results with alum at concentration 30mg/l, Fig. 9, it can be seen from this figure that there is slight difference between natural coagulant (sawdust+bentonite) and alum, higher removal efficiency achieved was 87% for flotation only and 95.7%; 97% for sawdust +bentonite and alum respectively in coagulation – flotation process.

4. Conclusions

1. The emulsified oil with concentration (300-1000 ppm) can be removed by dispersed air flotation; higher removal rate was achieved at 40 minutes, and it was increased with increasing flow rate.
2. The best removal efficiency by dispersed air flotation was 87% at pH 4
3. In coagulation – flotation process, the use of a mixture of bentonite and sawdust with sawdust being the vast majority for the coagulation of oil emulsion, increase the removal efficiency to 95.7% while when using alum ,the removal efficiency was 97%.

5. Recommendations

1. Utilization of other types of coagulant and using industrial or domestic wastewater for comparison purposes in terms of removal efficiency of oil emulsion.
2. Studying the oily wastewater treatment by fibrous coalescer process
3. Using two or three columns in order to enhance the removal efficiency.
4. Studying the effect of temperature.
5. Studying other bubble rise characteristics gas hold up trajectory and drag coefficient produced acceptable and consistent results

References


**Table 1.** Physical properties of the gas oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Density (Kg/m^3)</td>
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<tr>
<td>Viscosity (Kg/m.sec)</td>
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<td>API</td>
<td>35.1</td>
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<tr>
<td>Surface tension (N/m)</td>
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</table>

**Fig.1** Process of coagulation, flocculation and flotation, Dempsey, 2006.
Fig. 2: The functional groups of gas oil detected by FTIR analysis, Ibn-Sina labs.

Fig. 3: Schematic diagram for the experimental apparatus

Fig. 4: Photographic diagram for the experimental apparatus
Fig. 5 Effect of pH on the concentration ratio at different time intervals at initial oil concentration 500mg/l, flow rate 500 cc/min and SDS=20mg/l

(a) Effect of pH on concentration ratio of COD
(b) Effect of pH on the concentration ratio of oil content
(c) Effect of pH on the concentration ratio of turbidity

(a) Effect of the initial oil concentration on the COD ratio
(b) Effect of the initial oil concentration on the oil content ratio
(c) Effect of the initial oil concentration on the turbidity ratio

Fig.6: Effect of the initial oil concentration on the concentration ratio at different time intervals at pH 4, flow rate 500 cc/min and SDS=20mg/l

(a) Effect of the flow rate on the COD ratio
(b) Effect of the flow rate on the oil content ratio

(c) Effect of the flow rate on the turbidity ratio

Fig 7: Effect of flow rate on the concentration ratio at different time intervals, initial oil conc. =1000mg/l, pH=4 and SDS=20mg/l
Fig. 8: Effect of SDS on the concentration ratio at different time intervals at initial oil conc. $=1000\text{mg/l}$, pH=4 and flow rate=1500 cc/min

(a) Effect of the SDS on the COD ratio

(b) Effect of the SDS on the oil content ratio

(c) Effect of the SDS on the turbidity ratio
(c) Effect on the turbidity ratio

**Fig. 9:** Effect of coagulant on the concentration ratio at different time intervals, initial oil conc. = 1000 mg/l, pH = 4 and flow rate = 1500 cc/min and SDS = 150 mg/l