OIL REMOVAL FROM WASTEWATER OF AL-BEZERQAN CRUDE OIL FIELDS BY AIR FLOTATION

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ABSTRACT

In the present study, an attempt was made to study the efficiency of dissolved air flotation process to remove the emulsified oil in the wastewater generated from Al-Bezerqan oil fields in Missan Governorate. The experiments were carried out in a continuous dissolved air flotation system. The range of variables that studied in this work were, system gauge pressure of 0.5-2.0 bar, flow rate of air saturated oily water of 0.6-1.2 l/minute, salinity of 10-100 g/l, and water temperature of 25-40°C. In order to study the effect of addition of chemicals on the enhancement of the efficiency of oil from oily wastewater, some experiments were carried out using alcohols as frothing materials at a concentration range of 0.05-0.50% vol. Three types of alcohol (ethanol, propanol, hexanol) were used in this study to investigate the effect of increasing the chain length of alcohol on the oil removal pr°Cess by flotation. It was found that the best conditions of flotation are; 1bar gauge pressure, 1lit/min flow rate (the best space time in pressure vessel = 2 minutes), 100 g/l salinity, 40°C water temperature, 0.5%vol of alcohol concentration. It is found also that the efficiency of oil removal increases with increase the chain length of alcohol from ethanol to hexanol.

INTRODUCTION

Oil water separation techniques have gained increasing attention in recent years because of the need for treating oil polluted waste water (1). Emulsified oil particles of the order of several microns in diameter are protected from spontaneous coalescence into large ones due to electrostatic repulsion, making oil separation by gravity settling very difficult (2). Typically the major portion of free and emulsified oil in refinery effluent is removed by API method i.e., baffle plate separators followed by chemical clarifiers, or by dissolved air flotation (DAF), or using filters (3). Areas where flotation has been successfully applied include algae removal from stabilization pond effluents, waste activated sludge thickening, final clarification of wastewater plant, and waste sludge thickening (4). Oil removal by flotation, is a system for removing trace oil contamination from oil field wastes, it involves adding gas as tiny bubbles to the oily water stream. As the bubbles rise through the water they contact and adhere to small oil droplets. This oil/gas froth rises to the surface where it is skimmed off. The most common gases used for flotation are air, Co2, N2, and natural gas. Natural gas is preferred in oil field service to avoid oxygen corrosion in the flotation cell and down stream equipment (5).

The process of flotation consists of four basic steps: bubble generation in oily water, contact between a gas bubble and an oil drop suspended in the water, attachment of the oil drop to the gas bubble, and rising of the gas/oil combination to the water surface where the oil can be removed by skimming. There are three common methods of bubble generation: dissolution of gas from a supersaturated solution (dissolved gas flotation), mechanical mixing of gas and liquid (dispersed gas flotation) and direct gas injection by means of a sparger (6).

The success of DAF process depends on the use of very fine air bubbles to increase the rate of rise of suspended oil drop (7). The production of very fine air bubbles required for this process can be accomplished by dissolving air in water under pressure and subsequent flashing to normal pressure (8). There are several variables that determine the amount of gas going into solution: total pressure, gas composition, solubility's of gas components (Henry's law constants), temperature, and the efficiency of the saturator (9).

The solubility of air in water is determined by three factors; applied pressure, temperature and absolute air composition. The solubility is directly proportional to the applied pressure but inversely proportional to the water temperature. In other words, with increasing pressure the solubility of air rises, whereas it decreases with increasing water temperature. These facts are embodied into Henry's law, which is applicable to aqueous, non-reacting solutions of low concentration (10). Henry's law predicts a linear relationship between the partial pressure of the gas in the atmosphere above the water to the quantity of gas dissolved in the water (11):

$$C_i = y_i .44.6.\frac{M_i}{H_i}.\left(\frac{273.15}{T}\right).\left(\frac{P_{total}}{101.3}\right) \quad (1)$$

The air transfer or saturator efficiency, defined as the ratio between the actual air mass transferred to the theoretical maximum air mass transferable (12).

$$\eta_i = \frac{actual\,air\,mass\,transfer}{theoretical\,air\,mass\,transfer} = \frac{C_s - C_a}{C_s^* - C_a} \quad (2)$$

Because the air saturation system constitutes approximately 50 percent of the power cost of the flotation process, it is important to optimize the design of the air saturation in order to minimize the operating cost. Various methods are employed for dissolving air under pressure in the water stream. These include sparging the air into the water in a pressure vessel (saturator), trickling the water over a packed bed, spraying the water into an unpacked saturator, entering the air with ejectors, and injecting the air into the suction pipe of the pump (13).

Bratby and Marais (14) developed an efficient dissolved-air (pressure) saturation system. The saturator dissolved the air into the water under level. Air is bubbled through the water by means of an air-circulating pump which withdraws air above the water level and introduces it through the sparger near the bottom of the saturator.

Ward et al. (15) and Takahashi et al. (8) studied the nucleation and growth of microbubbles. They stated that energy must be imparted to a liquid supersaturated with air, before bubbles will form. This energy Δf is usually provided by liquid turbulence. Its value, in joules, is given by:

$$\Delta f = \frac{16}{3}\pi\sigma^3 / (p_0 - p_a)^2 \quad (3)$$

Equation 3 may be used to deduce the effect of pressure and surface tension on bubble size. It shows that the energy necessary for bubble formation can be decreased by decreasing the surface tension or by increasing the pressure. For the same concentration of dissolved air it is reasonable to assume that a larger number of smaller bubbles will be generated as the energy required for bubble formation is reduced.

The aim of the present work was to study the factors affecting the dissolved air flotation for the oil recovery from the oily wastewater generated from Al-Bezerqan oil fields. The important factors affecting this process are pressure, temperature, solution salinity, water flow rate and oil concentration. These variables were studied in order to achieve the best operating conditions. A chemical additive (Alcohol) was used to enhance the oil removal. Three types of Alcohols (ethanol, propanol, hexanol) were used to show the effect of increasing of the chain length of alcohol on the oil removal.

EXPERIMENTAL WORK

The first approach in the present study involved with studying the effect of some variables on the dissolved air flotation to get maximum recovery of oil from waste oily water. The ranges of these variables were selected according to the following reasons; the pressure range was used to be suitable for the equipment used, the temperature range was selected according to the Henery's law, the flow rate range was used to study the best space time in the pressure vessel, the salinity range was selected to study the effect of the highest possible salinity on oil removal, while the oil concentration range was chosen according to it's concentration in the wastewater of Al-Bezerkan oil fields. Table 1 shows the range of each variables used in the present experimental work.

Table 1 Range of variables used in the present work

Variable	*Range*
Pressure, bar gauge	0.5-2
Flow rate, lit./min.	0.6-1.2
Salinity, g/lit.	10-100
Temperature, °C	25-40
Oil concentration, mg/lit.	100-600

The second approach deals with the enhancement of the oil removal using chemical additives in the dissolved air flotation. Different chain length alcohols, namely; ethanol, propanol, and hexanol with different concentrations (0.025-0.5% vol.) were used in the experiments to investigate the effect of these additives on the oil removal.

A schematic diagram of the experimental system used in carrying out the experimental work is shown in Fig. 1, and the description in details can be found somewhere (16). A cylindrical QVF. vessel with inner diameter of 0.22m and height of 0.7m was used to prepare the oil water emulsion of different oil contents. The mixing was carried out by air bubbles emerging from an air Sparger fitted at the center of the vessel. Ring ,type air sparger was used with compressed air flowing through it. The number and size of holes was calculated according to the pressure drop limitation.

A plexi-glass cylindrical vessel with internal diameter of 0.12m, and height of 0.22m was used for dissolving air in the oily water. Fig. 2 shows the schematic diagram of this vessel. The pressure tank was supplied with a pressure gage a safety valve to regulate the pressure inside the vessel. The tank has two inlets, one for entering the pressurized water to the tank and the other for entering the compressed air. The oily water with dissolved air leaves from an outlet opening to the flotation vessel.

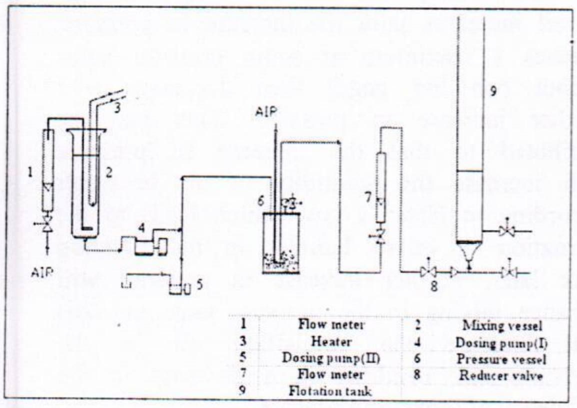

Fig. 1 Schematic diagram of equipment used for oil removal by flotation

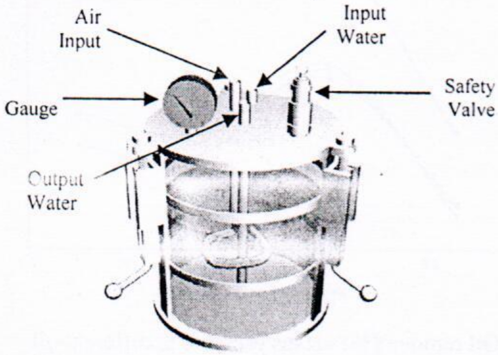

Fig. 2 Schematic diagram of the pressure vessel

The flotation tank is the vessel at which the dissolved air flotation takes place. It is a QVF glass vessel with inner diameter of 0.15m and height of 1m. The flotation vessel works under atmospheric pressure at which the air micro bubbles emerges at the bottom of the vessel. The flotation vessel contains a glass tap using for drawing samples for analysis. A globe valve was used for releasing the effluent of the pressurized tank into the flotation tank. The globe valve has three functions; it controls the process pressure, provides pressure drop to facilitate the formation of air bubbles, and it provides the turbulence necessary to create the minute air bubbles.

Two dosing pumps were used in the experiment, one is used to draw the emulsion from mixing tank and push it to the pressure tank, the other is used for injection the chemical additives into the pressure tank by conjunction with stream of oily water coming from the mixing vessel.

A heating element with a power supply of 3 kW connected with temperature regulator was fitted inside the mixing vessel in order to control the temperature of the solution at the desired value.

The oil-water emulsion was prepared with a desired oil concentration ranged from 100 to 600 PPM by addition of a suitable amount of crude oil to 15 liters of water. The salt content of the solution was adjusted by adding a certain amount of sodium chloride solution. Also the temperature was adjusted and controlled at the desired value by means of the heater and temperature regulator.

After preparing the required feed of oily water in the mixing vessel, the compressed air was allowed to flow through the air sparger at a rate sufficient to mix the content thoroughly. When the oil-water emulsion was prepared in the mixing tank, it is pumped through the dosing pump to the pressure vessel at a desired flow rate. A compressed air was injected into the pressure tank through a ring-type distributor at which it bubbled and dissolved in the solution. The effluent from the pressurization tank is released through the pressure release valve into flotation tank. The retention time in the flotation tank varies according to the flow rate used. In the flotation tank, very large number of minute air bubbles were emerged through the emulsion, and when rising up, carried the oil drop to the surface of the solution. Samples of solution were taken for analysis to show the removal percentage of oil. To find the effect of some chemicals on the efficiency of the removal process, three types of alcohols; ethanol, propanol and hexanol with different concentrations were added to the solution in the pressure vessel by a dosing pump and the same procedure was followed.

Determination of Oil Concentration

There are two methods used in this work to determine the oil concentration, these are:

1. U V Analysis

The oily matter is extracted from the water with carbon tetrachloride, then the absorbance of the extracted is determined with the use of ultraviolet spectrometer and the oily matter concentration is taken from the calibration curve shown in Fig 3. 200 ml of waste water sample was taken from flotation tank and put in a separating funnel. 1 gm of NaCl was added in order to break the emulsion of oil. 20 ml of carbon tetrachloride was added and followed by vigorous shaking for one min. After 15 min., when the solution separates into two distinct layers, the lower (organic) layer was taken for the absorbance measurement, and then from the calibration curve Fig 3.2 the concentration of oil in the effluent was obtained (17).

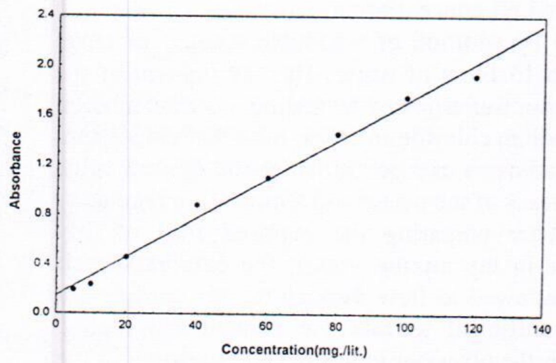

Fig. 3 Calibration curve of Crude Oil in CCl4 Measured at 311nm in U. V. Spectrometer Model 160

2. Evaporation method

Oil field wastewaters contain all the hydrocarbons of natural gas and oil from methane up, plus asphaltic and resinous materials, fatty acids, and other organic matter. When the oil is separated by solvent extraction, either with or without the aid of flocculation, there is no practical way of separating the solvent from the extracted oil without the loss of highly volatile fractions. The highly volatile oils do not contribute to oily films on the surface of polluted streams. In this practical analytical procedure, the oil was separated in the form of a dilute solution in an organic solvent. The solvent then was removed by evaporation. The emulsified oil was extracted from water using solvent (carbon tetrachloride) in separating funnel, when the solution separates into distinct layers, the lower (organic) layer filed into a glass dish. After evaporation the solvent then weighing glass dish to determine oil concentration(18, 19).

RESULTS AND DISCUSSION

The effects of studied variables on the oil removal in dissolved air flotation will be will be discussed in the following paragraphs.

1. Effect of Pressure

Figure 4 shows the effect of operating pressure in the pressure tank on percent removal of oil in the flotation tank at different values of oil concentrations. It can be seen clearly that the percentage removal of oil increases with the increase in pressure, reaches a maximum at some pressure value (about one bar gage) then decreases with further increase in pressure. This may be attributed to that the increase in pressure will increase the solubility of air in water according to Henry's law, which leads to the formation of micro bubbles in the flotation tank later. Further increase in pressure will enhance mixing in the pressure tank and this will increase the emulsified oil in the pressure tank resulting in a decrease in the efficiency of separation process.

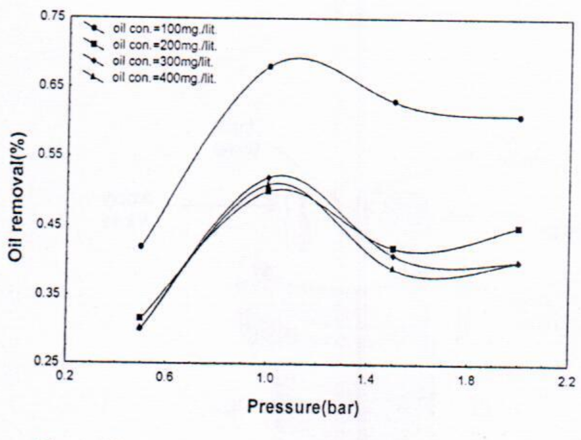

Fig.4 Oil removal(%) versus pressure at different oil concentrations (flow rate = 1l/min., salinity = 10 g/l., and temperature = 25°C)

2. Effect of Water Flow Rate

Figure 5 shows the effect of flow rate of air-saturated oily water from the pressure tank to the flotation tank. It is clear that increasing flow rate will increase the percent removal of oil. Until this removal reaching a maximum at some flow rate (about 1 l/min.) then the removal decreases with flow rate increase. At low flow rate there is no sufficient turbulence for the bubbles to form or move from the outlet of the releasing valve to these flotation tank. On the other hand, at high flow rate, large bubbles form at the distributor in the flotation tank which may result from the coalescence of the small bubbles because of turbulence.

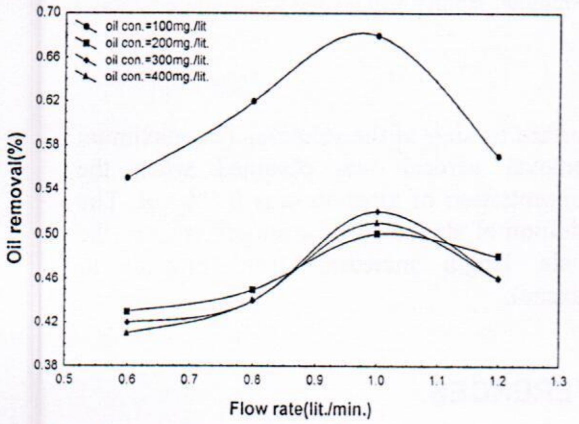

Fig. 5 Oil removal (%) versus flow rate at different oil concentration (Pressure = 1bar, salinity = 10 g/lit., and temperature = 25°C)

3. Effect of Salinity

Figure 6 shows the effect of salinity on percent oil removal. It is obvious that the removal percent increases with increase in the salinity. There are two reasons; the first reason is the reduction in bubble diameters with the increase in salinity due to the reduction in surface tension of the solution. This ensures a long residence time in the flotation tank allowing more opportunities for collisions between bubbles and oil drops. Similar effect was obtained by Strickland (6). The second reason is due to the presence of NaCl in solution changes the electrical and surface properties of the system. This could (and probably does) change the attachment efficiency.

4. Effect of Temperature

There are two contradictory effects of increasing the temperature of the solution in the

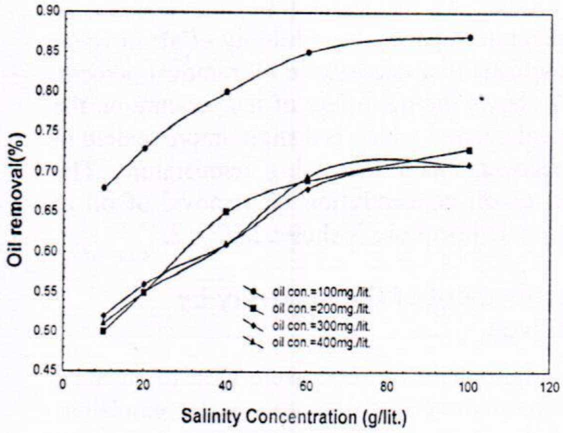

Fig. 6 Oil removal(%) versus salinity concentration at different oil concentration pressure = 1bar, flow rate = 1l/minute and temperature = 25 oC)

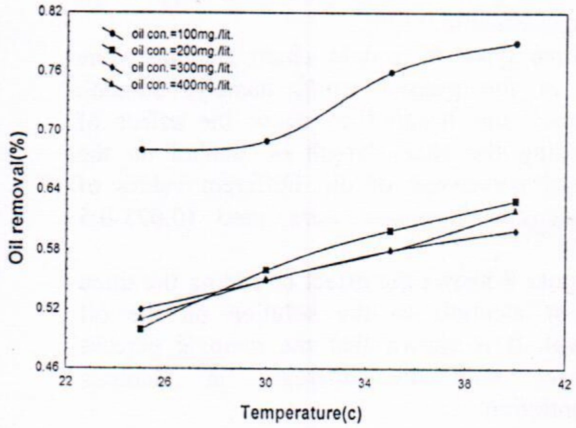

Fig. 7 Oil removal(%) versus temperature at different oil concentration (Pressure = 1bar, flow rate = 1lit./min. and salinity concentration = 10 g/l)

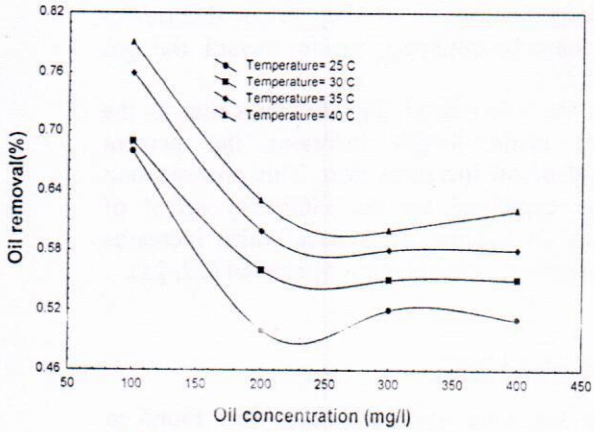

Fig. 8 Oil removal (%) versus oil concentration at different temperature (pressure = 1bar, flow rate = 1lit./min., and salinity = 10 g/l)

dissolved air flotation process. The increase in temperature may resolve the oil-water emulsion and this enhances the oil removal percent for the oily water. At the same time, the increase in temperature reduces the solubility of air in water which leads to a decrease in oil removal percent. Fig 7 shows the net effect of temperature on the removal percent which is a slight improvement in oil recovery with increasing temperature. The effect of oil concentration on removal of oil at different temperature is shown in Fig. 8.

Enhancement of Oil Recovery by Additives

Straight-chain alcohols were used to enhance the oil recovery from the oily water emulsion. Alcohol acts as a frother which reduces the surface tension of the solution and promote bubble formation at the water-air interface where large and stable surface foam can support the particles lifted in it (20).

Three type of straight chain alcohols were used in the present work, namely; ethanol, propanol and hexanol to show the effect of increasing the chain length of alcohol on the removal percentage of oil. Different values of alcohol concentrations were used (0.025-0.5 vol %)

Figure 9 shows the effect of adding the three type of alcohols to the solution on the oil removal. It is shown that the removal percent increases with the increase in alcohols concentration.

The addition of alcohols to the oil-water emulsion causes a reduction in surface tension of the solution. This reduction in surface tension will reduce the energy required to form the bubble (Equation 3); as they orient themselves with their hydrophobic group toward the gas phase (21).

On the other hand, Fig. 6 shows that as the alcohol chain length increases the percent removal of oil increases also. This phenomenon can be explained by the inhibitory effect of alcohols on bubble coalescence which increases with increasing chain length of alcohol (22, 23).

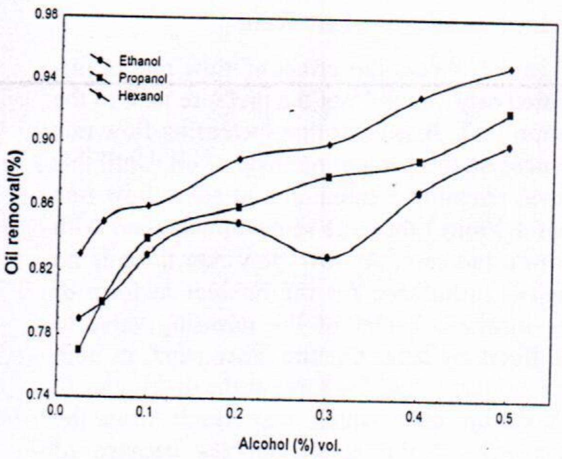

Fig. 9 Oil removal (%) versus alcohol vol. (%) at oil con. =600 mg/l (pressure = 1bar, flow rate =1 l/minute, salinity =10 g/l and temperature =25oC)

CONCLUSIONS

1. The best operating conditions were found to be; pressure of 1 bar gauge, salinity concentration of 100 g/lit, resident time in pressure vessel of 2 min, and a temperature of water of 25- 40 OC.
2. The oil removal percent can be enhanced by the addition of frother materials such as straight chain alcohols which decrease the surface tension of the solution. The maximum removal percent was obtained when the concentration of alcohols was 0.5% vol. The addition of alcohols was more effective as the chain length increased from ethanol to hexanol.

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