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Improving Treatment Performance of Dissolved Air Flotation System by Using Ionic Liquids as Surfactants

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Abstract

The effect of three ionic liquids viz., 1-hexyl-3-methylimidazolium tetrafluoroborate (ILE), 1-hexyl-3-metylimidazolium hexafluorophosphate (ILF) and 1-octyl-3-methylimidazolium tetrafluoroborate (ILG) when used as surfactants on the performance of dissolved air floatation (DAF) was investigated.

Experiments were conducted at a temperature of 30-35 ºC, 10ppm ferric chloride as coagulant, 50% recycle ratio, pH 8, and 10 minutes treatment time to find oil and grease (OG) and turbidity removal efficiencies at saturation pressure (2-6) bar.

ILs were used at concentration of 50 µl/liter of treated water in two positions in DAF system; the saturation vessel and the treatment tank. The performance using ILs in the saturation vessel were better than that in treatment tank because ILs reduced the surface tension of water, which lead to an increase in the solubility of air in water and eventually increase the microbubble formation. The OG removal efficiency using ILG as an efficient surfactant in saturation vessel was higher than that in the treatment tank and higher than other ILs (ILG>ILF>ILE). The removal efficiency reached about 90% at a saturation pressure of 5 bar, and 85% at 3 bar, which reduces the operation costs. The treated water oil concentration at 3bar was 9.5 ppm, which meets the Iraqi pre-disposal regulatory limit.

Key Words: produced water, DAF system, ionic liquids

Introduction

Dissolved air flotation technique had gained widespread usage over the last forty years for the removal of suspended solids (TSS), oils and greases (OG), and biochemical oxygen demand (BOD) from wastewater and other industrial process streams.

Produced water is water trapped in underground reservoir rocks, which can be brought to surface along with crude oil and gas. Water produced during oil and gas extraction operations constitutes the industry's most important waste stream. The large amount of water represents a potential problem to the environment and to the oil production industry that needed to be solved. In this situation, produced water can be classified into formation water, injection water and process water, which is extracted along with oil and gas during petroleum production [1].

Basically, produced water contains dissolved and insoluble petroleum fractions, which are similar to that found in crude oil and natural gas [2]. The insoluble petroleum fractions tend to disperse in the form of small droplets in the water. This represents an oily water and most of it is existed in the form of Oil-in-water (O/W) emulsions [3]. A good knowledge of petroleum emulsions is significant for monitoring and improving processes at all steps. Many studies have led to better consideration of these complex systems [4].

Emulsion behavior is largely controlled by the properties of the adsorbed layers that stabilized the oil–water surfaces. In addition other factors can be very effective on this stability like viscosity, produced water type, agitation etc. [5].

Many separation methods were used during the past decades like mechanical, heating, electrical and chemical demulsification. Every technique has advantages and faults.

These methods include: de-oiling (removal of dispersed oil and grease), desalination, removal of suspended particles and sand, removal of soluble organics, removal of dissolved gases, removal of naturally occurring radioactive materials (NORM), disinfection and softening (to remove excess water hardness). Until now there is no technique that could reach complete destabilization without grouping with another one [6].

For many applications of flotation in the wastewater treatment field, it is more efficient to use micro-bubbles generated by nucleation of dissolved air, rather than the dispersed air method used for minerals. Flotation offers process advantages over sedimentation, including better treated-water quality, rapid startup, high rate operation, and thicker sludge. Dissolved air flotation (DAF) is considered not only an alternative to sedimentation plants, but also a clarification method to improve filtration [7].

Dissolved air flotation uses pressure saturation to increase the solubility of air in water to produce fine microbubbles for oil removal. The idea is to develop agglomerates with lower density than water, causing the oil droplets to rise through the water and accumulate at the surface where they can be removed [8]. Dissolved air flotation is an effective method of oil from water separation because the high concentration of microbubbles and their slow rise rates allow for more collision opportunities with the oil droplets [9].

Treatment of produced water is controlled by disposal regulatory limits or beneficial reuse specifications (e.g. agricultural usage, potable purpose and industrial field, etc.); these limits include oil and grease, toxicity, and other constituents [10].

Ionic liquids (ILs) are considered one of the promising alternative materials for different applications. They are defined as salts with melting temperatures below 100°C, evolved from traditional high temperature molten salts, consisting of organic cations combined with anions of organic or inorganic nature. The chemical structure of ILs allows many combinations of anions and cations, enabling one to obtain compounds with properties quite varied, which means that tailor-made ILs can be produced for a given application [11,12].

For nearly two decades, ILs attracted the quickly growing attention due to their outstanding properties: wide liquid range, low volatility, high thermal stability, low toxicity, high ionic conductivity, wide electrochemical window, etc. This makes many ILs perspectives for applications in various fields of chemistry and technology and determines their importance for “green” chemistry [13]. ILs are expected as superior environmentally friendly solvent for chemical synthesis, homogeneous catalysis, biocatalysts, separation technologies, nanomaterial preparations, templates for production of porous solids, hydraulic fluids, and lubricants [14].

The aim of this research is to examine a technology to improve the performance of a dissolved air flotation (DAF) system in treating oilfield produced water through pretreatment with coagulants and the use of ionic liquids as surfactants.

Experimental Work

Materials

Raw produced water obtained from Middle Oil Company (Md.O.C) (East of Baghdad fields) with initial oil and grease concentration of (60-80) ppm was used in DAF experiments.

Chemicals used in DAF experiments were hydrochloric acid, sodium sulfate anhydrous, carbon tetrachloride, ferric chloride anhydrous, sodium hydroxide, sodium chloride.

Ionic liquids used were 99% purity supplied by Shanghi Cheng Jie Chemical Co, China. The physical properties of the ionic liquids are listed as given in table (1).

Table (1), Physical properties of ionic liquids

IL Name	Molecular weight	Density g/ml	Melting point ˚C
ILE	254.08	1.15	-181.85
ILF	312.24	1.25	-60.85
ILG	282.13	1.08	-79.85

Batch Dissolved Air Flotation Unit

In the current study, a batch DAF unit located in the Iraqi Ministry of Sciences and Technology was used, as shown in Fig. (1).

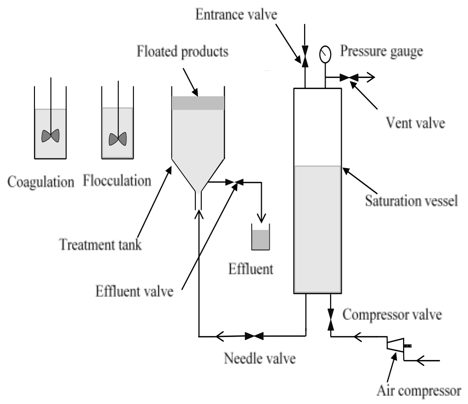

Fig. 1, Batch DAF unit schematic diagram

Ten liters of raw oil field produced water were poured into coagulation vessel. The pH value was controlled to 8 using NaOH (0.5M) and HCl (0.1M). 10ppm of ferric chloride was added to the solution and subjected to rapid mixing (60-100 rpm). The final solution was then poured in flocculation tank after two minutes of mixing. The solution was subjected to low mixing speed (15 rpm) for thirty minutes resulting in an emulsion containing flocks.

In case of using any of ILs in treatment tank, they must be added to the raw produced water before using the coagulants.

The final emulsion was poured in the treatment vessel. The needle valve between saturation tank and treatment vessel and also effluent valve must be kept close at this step.

Ten liters of demulsified produced water (trace oil concentration about 5ppm or less (50% recycle ratio) were added in the saturation tank through the entrance valve. Compressor valve must be kept close at this step.

In case of using ILs in saturation tank, it must be added to demulsified produced water with mixing at (400-500 rpm) before decanting in the saturation tank.

The compressor was switched on and the entrance, vent and needle valves were closed. Then the compressor valve was opened and the pressure gauge controlled to typical values of (2, 3, 4, 5 and 6) bar for control case (which represents DAF unit operation without using ILs) and ILs case (adding any of the three ILs in DAF unit) by controlling the vent valve (the pressure must be constant during running the DAF experiment).

The needle valve was used to control the rate of micro bubbles saturated water that transfer (by acting the of the pressure) from the saturation tank to the treatment tank.

The needle valve was opened, allowing the water saturated with air micro bubbles to flow to the treatment tank, raising the oil layer over the surface of treated water. When the first large bubble appeared in the treatment tank, the needle valve was closed (ending DAF operation) and operating time was recorded. The minimum operating time was not less than ten minutes and was controlled by the needle valve. The DAF operating temperature range was (30-35) ˚C. The sample was decanted from effluent valve and subjected to analysis. Total oil and grease concentration was measured by oil content analyzer (OCMA – 350, Horiba Ltd, Japan), the water turbidity was measured using turbidity meter (TB300IR, Lovibond, Germany), and the surface tension was measured by Sigma 703a tensiometer (KSV instrument Ltd, Finland).

Results and Discussion

Ils Effect on the Removal Efficiency

In this study three-imidazolium type ILs were tested as new demulsifiers for Iraqi oil field produced water. They were used as surfactant in the treatment of produced water in the batch DAF unit. They were tested in the treatment tank and the saturation vessel as illustrated in the experimental procedure. The removal efficiencies were varied from one type to another according to the chemical composition, physical properties, and the usage position (treatment tank, or saturation tank).

Fig. (2) Shows that ILG is the most effective IL among the others, where removal efficiency reaches about 86% at saturation vessel pressure of 3 bar, while ILE at the same conditions had the lowest performance with a removal efficiency not exceeding 76%. The increase in the OG removal efficiency with respect to the control when using ILG in this case will be about 13% at a pressure of 3 bar.

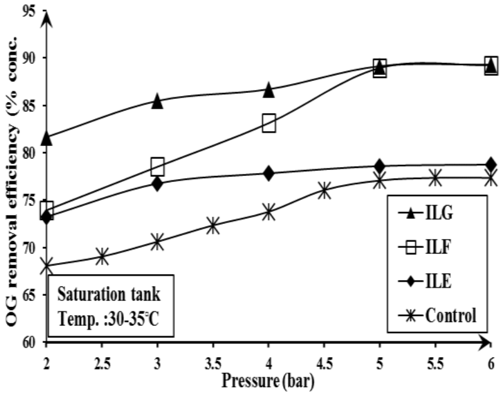

Fig. 2, Oil and grease removal efficiency using ILs in the saturation vessel

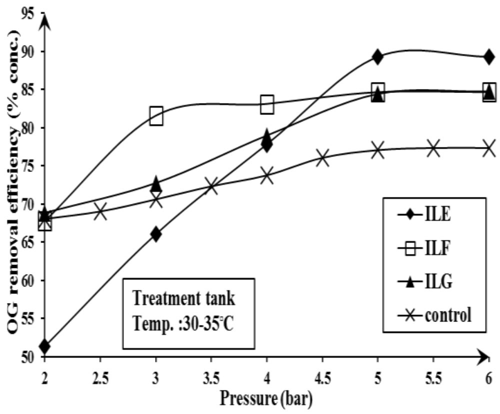

Fig. 3 Oil and grease removal efficiency using ILs in treatment tank

From fig. (3), it can be concluded that ILF was the most effective among other ILs, where separation removal efficiency in treatment tank reached about 82% at saturation vessel pressure of 3 bar, while it was (72% and 66%) for ILG and ILE respectively.

Final OG Concentration Due To Used Efficient Ils in Saturation Vessel and Treatment Tank

The final OG concentrations due to the use of efficient ILs in saturation vessel and treatment tank are shown in Fig. (4) and Fig. (5).

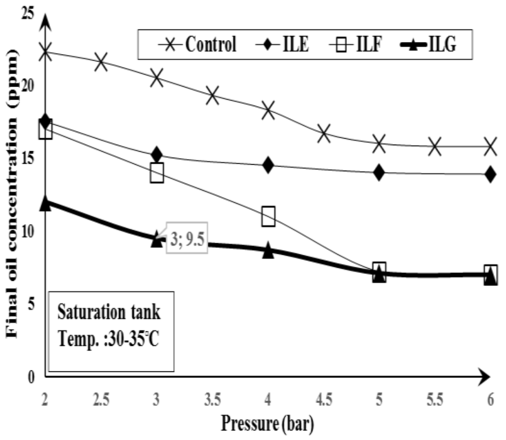

Fig. 4, Final oil concentration when using ILs in saturation vessel

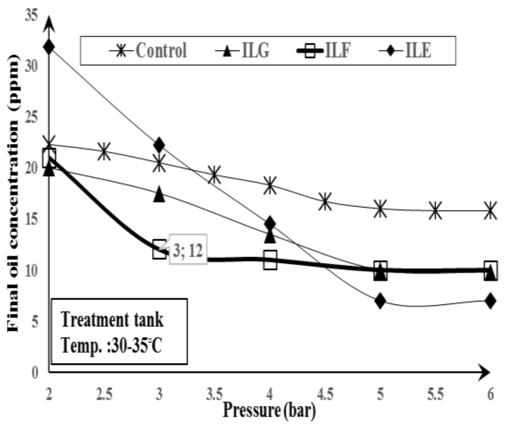

Fig. 5, Final oil concentration when using ILs in treatment tank

The bold curves in Fig. (4) and Fig. (5), represent the two efficient ILs, ILG (1-octyl-3-methylimidazolium tetra fluoroborate) and ILF (1-hexyl-3-metylimidazolium hexafluoro-phosphate) in the saturation vessel and treatment tank respectively.

This study was focused on operating the batch DAF unit to reduce pressure below 5 bar in order to decrease the operating costs. Clearly, it was indicated that the treated water OG concentrations due to using the efficient ILG in the saturation vessel and efficient ILF in the treatment tank were 9.5ppm and 12ppm as shown in Fig. (4) and Fig. (5), respectively when operating saturation pressure was 3bar.

The treated water OG concentration value (9.5ppm) at operation pressure 3bar (when using ILG as surfactant in the saturation vessel) was in agreement with Iraqi rule No. 25 in 1967 [15] which stated that the oil and grease in wastewater effluent should not exceed 10 ppm. Therefore1-octyl-3-methylimidazolium tetrafluoroborate (ILG) was the most efficient surfactant among the other ILs (ILE and ILF) when used in saturation vessel.

Effect of Using Ils on Bubble Growth and Nucleation

The results of testing surface tension of treated Md.O.C produced water in saturation vessel were used to calculate the energy required to form bubbles. Takahashi relation [16] was used for this purpose:

$$\Delta F = {}^{4}\!/_{16} \times \pi \times \gamma^{3} (P_0 - P_a)^{-3} \ldots (1)$$

Where

ΔF: minimum energy to be transferred to the liquid phase to form bubbles by a cavity phenomenon (arising from the liquid turbulence), J

γ: Air/Water surface tension (Nm^{-1})

P_o *and* P_a: the saturation and atmospheric pressure (Pa), respectively.

Fig. (6) Shows that increasing air pressure in the saturation vessel leads to raising air solubility in liquid phase and providing the energy for bubbles nucleation and surface formation.

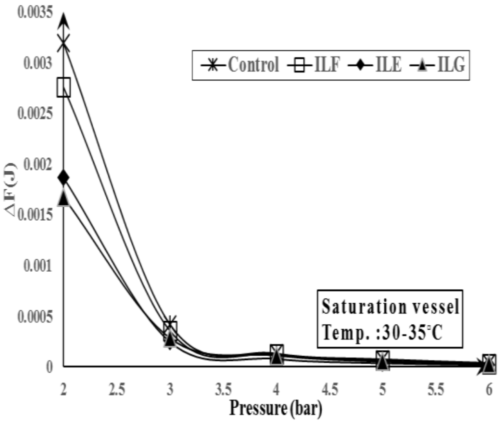

Fig. 6, Effect of pressure upon bubbling energy when using ILs in saturation vessel

In the case of using low oily content produced water in the saturation vessel (control case) large bubbles are formed but the addition of a trace amount of any of ILs (ILE or ILF or ILG) provides low energy nucleation sites such that very minute bubbles, with a cloud-like appearance are generated. Using any of the two ILs (ILE and ILG) required less nucleation energy (ΔF) than that of the ILF and the control during the applied pressure range (2-3) bar as illustrated in Fig. (6). These results are in agreement with those of Féris et al. [7], who showed that the energy transferred to form micro-bubbles will be smaller when the air/liquid interfacial tension is lower and the pressure difference of the liquid phase with respect to the atmospheric pressure is higher. Thus, by lowering the air/liquid interfacial tension, the fluid velocity will be higher and the kinetic of bubble formation will be faster. These results are also in agreement with the results of Dupre et al. [17], who reported that DAF users observe a reduction in the diameters of the bubbles in the tanks when using "polyelectrolytes" and consider this and the use of surfactants a complex matter.

Conclusions

1- The imidazolium group, ionic liquids showed good performance in demulsification process in batch DAF unit. The OG demulsification rate due to use the ILs in the saturation vessel was higher than that when using the ILs in treatment tank, this means that the pressure has a good impact upon the physicochemical properties of the ILs and eventually increases the OG removal efficiency.
2- In the present study, the ILG (1-octyl-3-methylimidazolium tetra fluoroborate) is used in the saturation vessel for the first time and is an efficient demulsifier for oil field produced water emulsion. The OG removal efficiency approximately increased by 13% above that in the normal case (when using $FeCl_3$ with dose of 10ppm, pH8) at optimum pressure (5 bar). At 3 bar the OG removal efficiency reached 85% and final effluent concentration of OG was 9.5 ppm. This value was in agreement with the Iraqi produced water discharge regulations, which indicates that OG concentration in wastewater effluent to rivers should not exceed 10 ppm.
3- Using ILs (ILE, ILF and ILG) in saturation vessel as surfactant allowed micro bubbles generation at operating pressure lower than 3 bar with high-energy savings.

References

1- Veil, J.A. and Clark, C.E., (2009), “Produced Water Volumes and Management Practices”, U.S. Department of Energy Technology Laboratory, pp. 7.
2- Tellez, G.T., Nirmalakhandan, N. and Gardea-Torresdey, J. L., (2005), “Comparison of Purge and Trap GC/MS and Spectrophotometry for Monitoring Petroleum Hydrocarbon Degradation in Oilfield Produced

Waters", Microchemical Journal, Vol. 81, pp. 12-18.

3- Fanchi, R. and John. (2006), "Petroleum Engineering Handbook: General Engineering", USA: Society of Petroleum Engineers, Richardson, Vol. 1.

4- Langevin, D., Poteau, S., Henaut, I. and Argillier, J., (2004), "Crude Oil Emulsion Properties and their Application to Heavy Oil Transportation", Oil & Gas Science and Technology, Rev. IFP, Vol. 59, No. 5, pp. 511-521.

5- Abdel-Raouf and El-Sayed Manar, (2012),"Crude Oil Emulsions Composition Stability", Croatia: Intech, Rijeka, pp. 185.

6- Ebenezer, T. I. and George, Z. C., (2014), "Produced Water Treatment Technologies", International Journal of Low-Carbon Technologies, Sep., pp. 160.

7- Féris, L., Gallina, S., Rodrigues, R. and Rubio, J.,(2000), "Optimizing Dissolved Air Flotation Design System", Braz. J. Chem. Eng., Vol. 17, pp. 4-7.

8- Lundh, M., (2000), "Experimental Studies of the Fluid Dynamics in the Separation Zone in Dissolved Air Flotation", Wat. Res. 34(1), pp. 21-30.

9- Al-Shamrani, A., James, A. and Xiao, H., (2002), "Separation of Oil from Water by Dissolved Air Flotation". Colloids and Surfaces A: Physicochem. Eng. Aspects 209, pp. 15–26.

10- Veil, J. A., Puder, M. G., Elcock, D. and Redweik, R. J. J., (2004), "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane", USA: U.S Department of Energy National Energy.

11- Huddleston, J. G., Visser, A. E., Reichert, W. M., Willuer, H. D., Broker, G. A. and Rogers, R. D., (2001), "Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cution", Green Chem., Vol.3, No. 4., pp. 156-164.

12- Kadokawa, J. I., (2013), "Ionic Liquids - New Aspects for the Future", Rijeka, Croatia : In-Tech,.

13- Smirnova, N. A. and Safonova, E. A., (2010), " Ionic Liquids as Surfactants", Petersburg, Russia : Russian Journal of PhysicalChemistry, Vol. 84, No. 10, pp. 1695–1704.