

Optimization of Operating Parameters of Oil Desalting in Southern Treatment Unit (HMD/Algeria)

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Abstract

Crude oil often contains fine saline water droplets, salt crystals, suspended solids and traces of metals. To meet business requirements, the salinity of the latter is limited to 40 mg/L and (BS&W) Basic Sediment and Water must be lower than 1%. For this reason and to prevent corrosion, plugging, and fouling of equipment, electrical desalting plants are often installed in crude oil production units.

This paper presents the results of a laboratory work conducted regarding the impact of important key parameters of oil desalting, namely: the rate of wash water, oil temperature, and injected chemical demulsifier amount in aim to achieve their optimum value and thus to reach the lowest oil salinity and (BS&W) without applying electrical field.

Experiments conducted in South Crude Treatment Unit laboratory (UTBS/Hassi-Messaoud/Algeria), showed that the salts removal efficiency (SRE) increases with increasing the wash water rate, demulsifier amount and operating temperature. For 5% of wash water rate and 0.5% of demulsifier at 52°C, the (SRE) was 96.94%. Applying these parameters values to electrical desalting vessel with electrical field supply, would increase the (SRE) to a remarkable extent. The mean value recorded for (BS&W) during experiments was only 0.5%.

Keywords: Oil desalting; Dewatering; Salinity; Demulsifier; Droplets; Emulsion

Abbreviations: BS&W: Basic Sediment and Water; HMD: Hassi Messaoud region (South-east of Algeria); SRE: Salts Removal Efficiency; UTBS: South Crude Treatment Unit (Unité de Traitement de Brut Sud); WRE: Water Removal Efficiency

Symbols: v: The volume of fresh wash water (ml).

Introduction

Crude oils are complex mixtures obtained from many parts of the world, and all crudes contain dilute dispersion/emulsion of ultrafine water droplets containing a variety of salts, solids and metals. These emulsions might be quite stable due to the presence of natural surfactants in oil such as asphaltenes, resins, naphthenic acids, fine solids, etc. [1]. Adverse effects of these impurities can result in shortened unit run lengths and reduced equipment reliability. To prevent corrosion, plugging, fouling of equipment, electrical desalting plants are often installed in crude oil production units in order to remove water-soluble salts from an oil stream. The refiners often wash the crude oil with fresh water, add chemical (demulsifier), and use electrical desalting vessel to remove the added water and most of the inorganic contaminants from the crude oil [1].

Electrical desalter is the typical method of crude-oil desalting [2]. After separation by gravity settling, crude oil can be desalted by following the steps:

- The crude oil is preheated to decrease its viscosity for easy separate water from crud and hence easy desalt. Preheating also increases demulsifier reactivity, and destabilizing emulsion, however, the crude temperature is limited to avoid its vaporization in the desalter, and prevent damage to the electrical grid insulator bushings.
- The chemicals (demulsifiers) used are surfactants which migrate to the oil/water interface to rupture the stabilizing film around the water droplets and allows them to merge and coalesce. Chemical

usage rates vary widely with crude type, and desalter equipment. Chemicals are more efficient with basic pH water, while electrical desalters function much better in acid pH range. Low pH result in excessive corrosion, while high pH permits NH_4OH (added to increase pH) to migrate into the crude. Excessively high pH can aid in stable emulsion formation; So typical pH control will be required.

- Addition of fresh water (wash water), increase coalescence and destabilizing emulsion. The volume of wash water can be fixed from 3 to 10%; its value is governed by the refiner's needs.
- Wash water mixing is applied to ensure that the added fresh water is dispersed well so that it can be available to combine with the contaminants in the crude. Wash water mixing is accomplished by a mixing valve with adjustable pressure drop.
- Finally, high electrical field is applied in desalter vessel to coalesce and group the salty water droplets as a flow of water which settles under the effect of its weight.

Figure 1 shows a schematic cross-section of one stage electrostatic desalter of crude oil (Figure 1). Generally, the corrosion which occurred in heat exchangers and distillation column, was caused by hydrochloric acid (HCl) which is formed by hydrolysis of the magnesium and calcium chloride salts at high temperatures ($T > 110^\circ\text{C}$). In addition,

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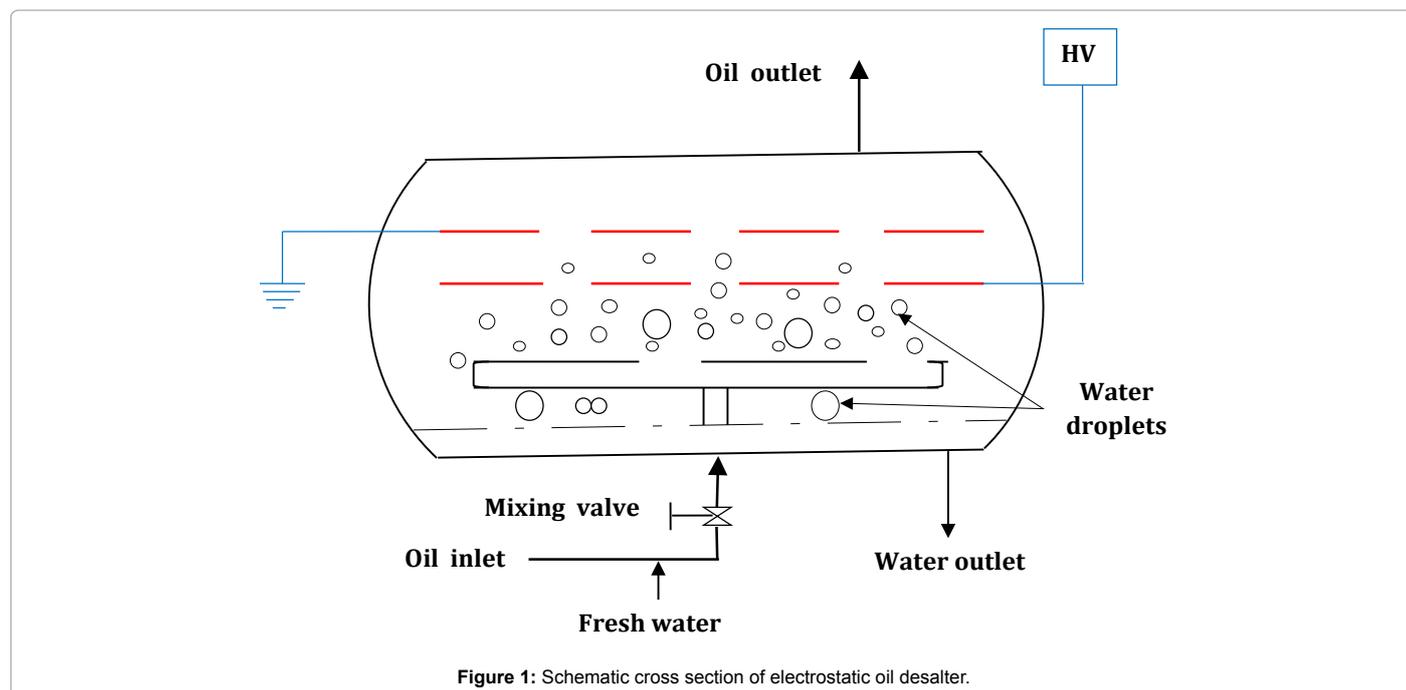
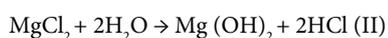
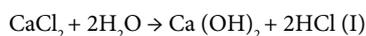


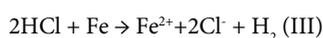
Figure 1: Schematic cross section of electrostatic oil desalter.

if hydrogen sulfur (H_2S) is also present, this corrosion becomes strong and dangerous. The main reactions are summarized by the following steps:

Hydrolysis of salts:



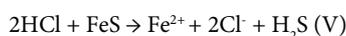
Corrosion:



Presence of (H_2S):



In presence of (H_2S), (HCl) produced by (I) and/or (II) reacts with (FeS) formed by (IV) as follows:



Reproducing (H_2S) by reaction (V) feeds reaction (IV) and increases corrosion.

Several researchers in the axis of oil desalting have developed studies and gave their suggestions and investigations in the aim to improve the efficiency of desalting and dewatering of crude oil, and hence to troubleshoot encountered problems in order to save processing facilities and increasing the selling price of a crude barrel. Some of them [3-7] established a mathematical model to study theoretically the key parameters of electrostatic oil desalting in aim to apply them in treatment units for decreasing amounts of water and salts in outlet treated crude. Mahdi [8] has used a statistically designed approach to evaluate desalting performance by calculating the Salt Removal Efficiency (SRE) and the Water Removal Efficiency (WRE) based on the five process parameters. They found that for the (SRE), the optimum values of demulsifier agent amount, temperature, wash water ratio, settling time and mixing time with wash water were found to be: 15 ppm, 77°C, 10%, 3 min and 9 min respectively. As a result the

optimum value of 93.28% (SRE) was found. This value was 94.80% and 89.57% for (WRE) proposed models.

Other researchers developed the studying of non-electrical desalting and acquired many achievements recently, including different methods namely: centrifuge method [9], filtration method, [10,11] hydro-cyclone method [2,12], microwave radiation method [13] and so on. But those techniques were less used in industrial production because of the complex of the equipment and low reliability.

Vafajoo et al. [14] have studied the effect of three parameters namely: temperature, injected chemicals and the pH of oil associated water. They found that for high performance the temperature between 115°C and 120°C is required. The amount of injected chemicals which gives a high desalting efficiency is (50 to 100) ppm of demulsifiers noted (C and F). Suitable pH range of crude oil associated water is between 9 and 12.

They have also compared between theoretical calculations performed and experimental results, a satisfactory agreement have been obtained.

Forero [15] have studied the effect of the Instituto Colombiano del Petróleo (ICP) contactor and the mixture valve on the desalting process evaluated as a contact system in the crude oil washing process in two different refineries. The pressure drop was measured and the efficiency of the desalting processes was calculated based on the (BSW) measurement, and oil salinity. Results showed that the contactor improved desalting, water in the crude oil was reduced and crude carry over in the wastewater was reduced between 50 and 92% in one refinery and between 40 and 95% in the other. The pressure drop was reduced between 88 and 94% in relation to the mixing valve.

In another research axis with relation to crude desalting, Bahadori and Zeidani [16] studied scale formation and well plugging due to the incompatibility of injected wastewaters collected from desalting plants. They illustrated that formation damage in wastewater disposal wells may occur mainly due to the reaction between Iron ion (Fe^{2+}) and

Hydrogen sulfur (H_2S) to form Iron Sulfide (FeS) which is an insoluble product. They have developed a new correlation estimating the critical concentration of (Fe^{2+}), which will stay in solution at various pH values despite the existence of (H_2S) in disposal wastewaters. This correlation eliminates the need for solubility calculations or experimental testing for water mixtures that contains (Fe^{2+}) and dissolved H_2S .

Experimental Procedure

This paragraph presented the experiments conducted in laboratory regarding the impact of important key desalting parameters, namely: the rate of wash water, oil temperature, and chemical demulsifier amount on the oil salinity and (BSW). Firstly, we present the method how to determine the (BSW) and the oil salinity, and then show the experiment of each parameter effect.

Analysis for basic sediment and water (BS&W)

Materials and solutions needed: For analysis of Basic Sediment and Water in the crude oil, we have used the following materials and solutions:

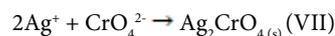
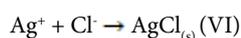
- Two bottles of 100 ml volume.
- Pipette of 20 ml volume.
- Water bath; (up to 90°C, accurate up to +/- 2°C.).
- Centrifuge.
- Beakers for rinsing.
- Demulsifier.
- Solvent (xylene).

Procedure: For determine the (BS&W), the steps must be followed:

- Fill two centrifuge tubes to 50% mark with xylene.
- Mix oil sample thoroughly and fill the tubes remainder to the 100% mark and mix.
- Add 1 ml of demulsifier to each tube and mix.
- Place tubes in water bath at (70-80°C) for about 10 min until they reach the chosen temperature.
- Centrifuge the tubes for 5 min.
- Record observations to include volume of saline water, solids and oil.

Determination of chloride ion concentration by titration (Mohr's Method)

The crude oil salinity is expressed in (mg of Cl^- / Liter of crude oil). The well-known Mohr's method in which alkaline or alkaline earth chlorides react with silver nitrate ($AgNO_3$) in the presence of a few drops of potassium chromate solution (K_2CrO_4) as indicator is a simple, direct and accurate method for chloride determination. Potassium chromate can serve as an end point indicator for the Mohr's method determination of chloride ions by reacting with silver ions to form a brick-red silver chromate (Ag_2CrO_4) which precipitate in the equivalence point region. About 1 ml of (K_2CrO_4) was added and the solution was titrated to the first permanent appearance of red (Ag_2CrO_4). Followed reactions have been occurred:



The titration was carried out at pH between 7 and 10; a suitable pH was achieved by saturating the analyzed solution with sodium hydrogen carbonate ($NaHCO_3$). In order to adjust the pH of the solutions, small quantities of ($NaHCO_3$) were added until effervescence ceased.

Materials and solutions needed:

- Burette and stand
- 10 and 20 ml pipettes
- 100 ml volumetric flask
- 250 ml conical flasks
- 10 ml and 100 ml measuring cylinders
- Silver nitrate solution: (0.1 mol/ L) (8.5 g of dry ($AgNO_3$) dissolve it in 500 ml of distilled water)
- Potassium chromate solution (The concentration is approximately: 0.25 mol/L, it means that 1 g of (K_2CrO_4) is dissolved in 20 ml of distilled water).

Effect of wash water rate: In this experiment, we'll regard the effect of the rate of wash water on the amount of removal salts from oil sample and hence the oil residual salinity with keeping other parameters (oil temperature and demulsifier amount) as constants.

During studying the effect of wash water rate, the temperature in the laboratory was 22°C, so the samples will take the same temperature which was adjusted by putting them for about 10 min in water bath well-ordered at 22°C. Demulsifier volume was maintained at 0.5%.

Titration: Before titration followed steps would be done:

- Put 0.25 ml of demulsifier into each 100ml of two volumetric flasks
- Add a volume (v) of fresh water to each flask. ($\frac{v}{\text{Total volume}}$: represents the wash water ratio).
- Fill each flask by crude oil until 50 ml and mix. (Here, total volume = 50 ml).
- Pour the mixture in two centrifuge tubes and place them in water bath at 22°C for 10 min.
- Centrifuge the tubes for 5 min. 3 phases appear (Sediments, removed water and oil).
- Aspire carefully with a syringe the total volume of removed water centrifuged, record it exactly and pour it in a beaker.
- Dilute removed saline water by pipetting the volume (v) ml into a 100 ml volumetric flask and making it up to the mark with distilled water.
- Pipette a 10 ml aliquot of dilute removed water into a conical flask and add distilled water until total volume of about 50 ml, then add 1 ml of chromate indicator.
- Titrate the sample with 0.1 (mol/L) silver nitrate solution. Although the silver chloride that forms is a white precipitate, the chromate indicator initially gives the cloudy solution a faint lemon-yellow color.
- Repeat the titration with further aliquots of dilute removed saline water until concordant results (agreement volume within 0.1 ml) are obtained.

Result calculations:

- Determine the average volume of silver nitrate recorded.
- Calculate the moles of silver nitrate reacting.
- Determine the moles of chloride ions reacting.
- Calculate the concentration of chloride ions in the dilute removed water.
- Deduce the concentration of chloride ions in the volume (v) of removed water, and then in centrifuged water.
- Calculate the concentration of chloride ions in the crude oil in (mg/L), or (mol/L). (The concentration of chloride ions in fresh wash water has been taken in consideration)

The same titration has been down with a new volume (v) of wash water. In this experiment, the rates of wash water which have been chosen were: 5, 10, 15, 20, 25, and 30% of fresh water (the same water used in desalting unit).

Effect of demulsifier amount: During this experiment when studying the effect of demulsifier rate, the temperature of samples was maintained at 22°C, so the samples was putted for about 10 min in water bath well-ordered at 22°C. The fresh wash water rate was maintained at 5%. The percentage of chemical demulsifier was varied as follows: 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0%.

Titration

- Put the volume (v = 2.5 ml) of fresh water into each 100 ml of two volumetric flasks
- Add 0.25 ml of demulsifier into each flask.
- Fill each flask by crude oil until 50 ml and mix. (Here, total volume = 50 ml).
- Pour the mixture in two centrifuge tubes and place them in water bath at 22°C for 10 min.
- Centrifuge the tubes for 5 min. 3 phases appear (Sediments, removed water and oil).
- Aspire carefully with a syringe the total volume of removed water centrifuged, record it exactly and pour it in a beaker.
- Dilute removed saline water by pipetting the volume (v) ml into a 100 ml volumetric flask and making it up to the mark with distilled water.
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- Repeat the titration with further aliquots of diluted saline water until concordant results (agreement volume within 0.1 ml) are obtained.

Result calculations: The same steps of paragraph (2.2.2.2) have been followed. The same earlier titration has been repeated with a new volume of demulsifier according to the percentage chosen and so on.

Effect of mixing temperature: During this experiment, the

rate of wash water and the volume percentage of demulsifier have been maintained respectively in 5% and 0.5% although the mixture temperature has been varied as follows: 22, 28, 33, 42, 47 and 52°C.

For titration, the same steps of earlier titration have been followed, but before any centrifuge, the mixture should be placed in water bath at desired temperature. Result calculations have been carried out following the paragraph (2.2.2.2).

Results and Discussion

Analysis for basic sediment and water (BS&W)

After 3 analyzes of basic sediment and water (BS&W), the mean value recorded was about 0.5%. This value is acceptable, so the crude doesn't need further (BS&W) treatments because generally good oil quality is < 1% BS&W.

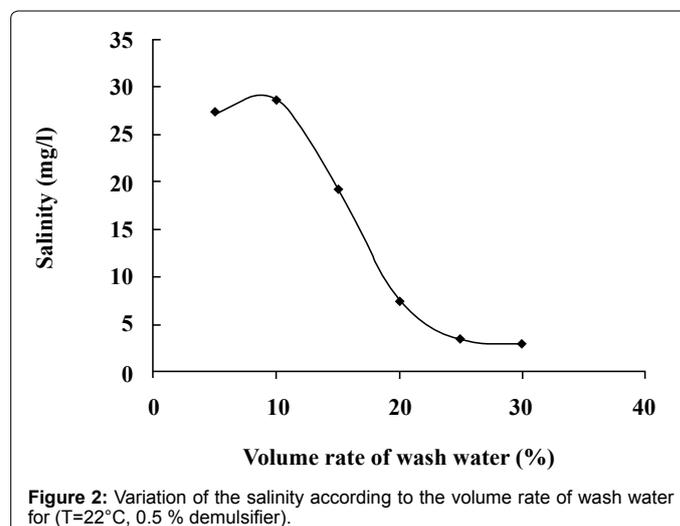
Effect of wash water rate

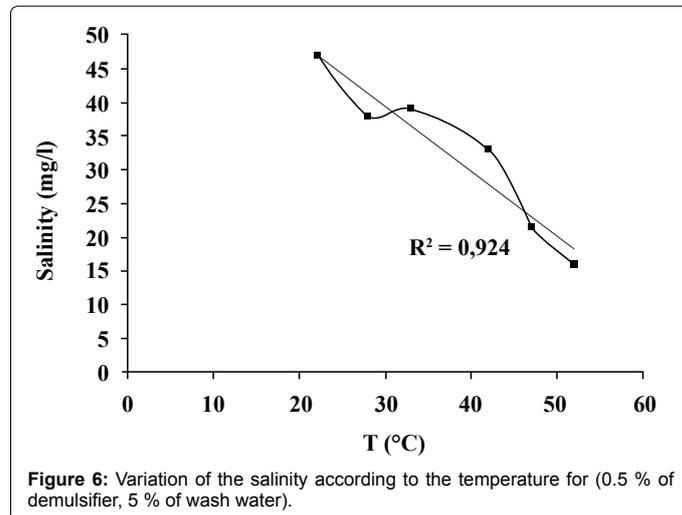
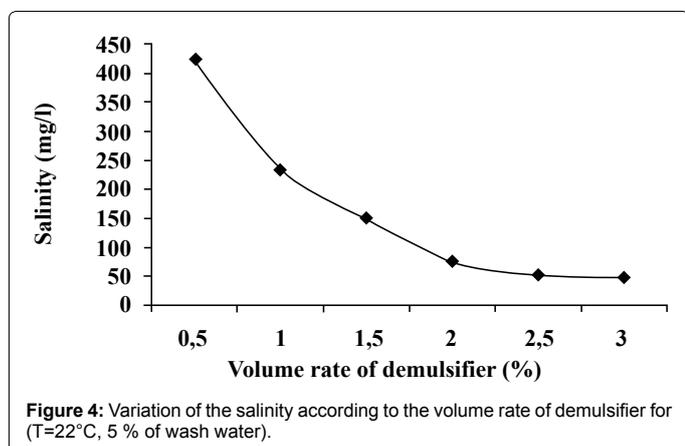
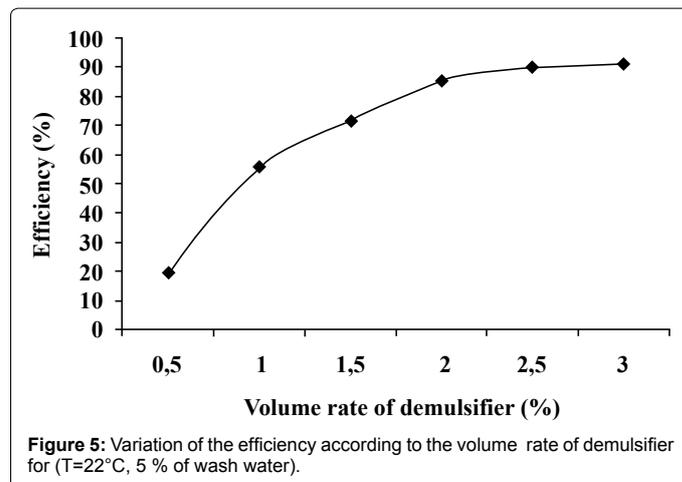
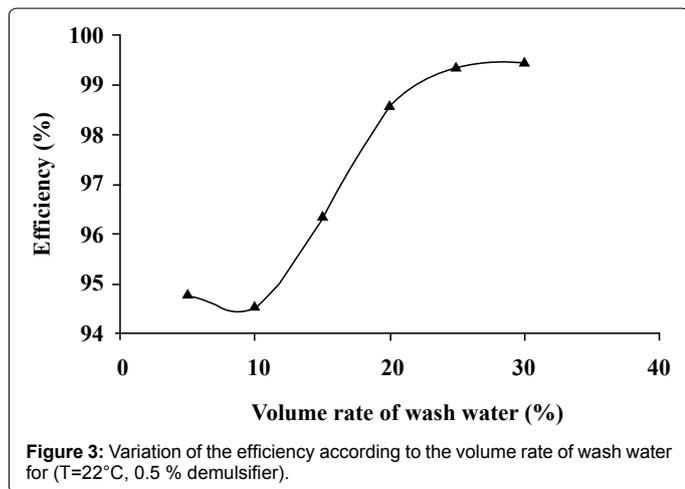
Figure 2 displays the variation of salinity according to the rate of wash water for 0.5% of chemical demulsifier at 22°C. It is clear that removal salts from crude oil are directly proportional to the amount of wash water although the lower values of demulsifier amount and operational temperature. The better salinity (lower value) recorded is 2.8 mg/L for 30% of wash water rate, however, and for economic and security reasons, this rate of wash water must not be applied in desalting plant. Generally (3-10%) of wash water rate is required. The rate of wash water would be lower if its salinity is low and vice versa.

Figure 3 shows salts removal efficiency (SRE) according to the rate of wash water. It is clear that salts removal efficiency was higher than 94.54% for any wash water ratio. The maximal (SRE) recorded for 30% of wash water ratio was 99.46%. We note that if distilled water were used, the results recorded would be better, but to be near the same industrial conditions, we have used the same water which used in desalting plant.

Effect of demulsifier amount

As shown in Figure 4, the oil salinity decreases remarkably with the increasing of chemical demulsifier rate for 5% of wash water ratio at 22°C. The lowest salinity recorded in this conditions was 48 mg/L for 3% volume rate of demulsifier. The effect of demulsifier is very intense because from 0.5 to 3% of demulsifier rate, the salinity decreased from 442 to 48 mg/L. Generally demulsifiers are expensive, so in our case





and for economic reasons, the used demulsifier rate is limited between 0.25 and 2%.

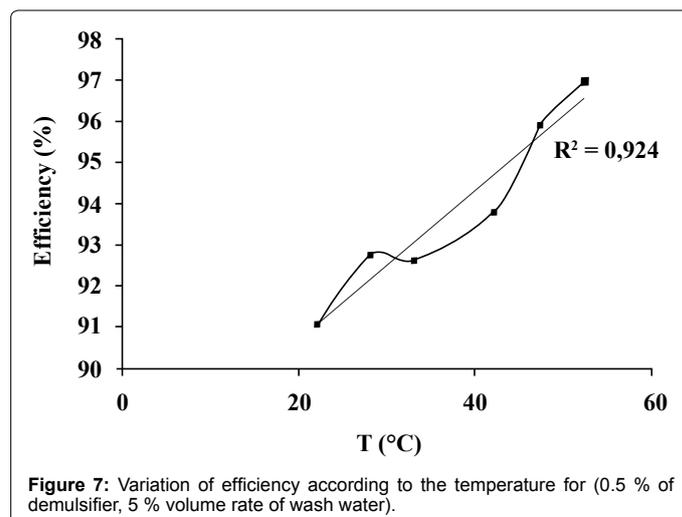
Figure 5 displays the variation of (SRE) for 5% wash water rate at 22°C according to demulsifier rate. As shown, salts removal efficiency increases from 19.08 to 90.84% respectively for 0.5 and 3% of demulsifier rate.

Effect of the mixture temperature

As shown in Figures 6 and 7, increasing the temperature of the mixture decreases the oil salinity and hence enhancing the salts removal efficiency. For the mixture temperature of 52°C, the oil salinity was 16 mg/L with salts removal efficiency of about 96.94%. Generally the oil preheating decreases its viscosity, also decreases drops settling time, increases demulsifier efficiency, and destabilizing emulsion, but the crude temperature is limited to avoid its vaporization into electrical desalter, and prevent damage to the electrical grid insulator bushings. In our case, desalting vessel operating temperature is limited to 70°C.

Conclusion

Crude oil often contains fine saline water droplets, suspended solids, salt crystals, and traces of metals. To meet business requirements, the salinity of the crude is limited to 40 mg/L and (BSW) Basic Sediment and Water must be lower than 1%. For this reason and to prevent corrosion, plugging, and fouling of equipment, electrical desalting plants are often installed in crude oil production units.



This research presents the results of a study conducted regarding the impact of important key desalting parameters, namely: the rate of wash water, oil temperature, and injected chemical demulsifier amount on oil dewatering/desalting.

Our aim is to achieve the optimum of each parameter for reaching the lowest values of oil salinity and (BSW) in laboratory without applying electrical field.

Experiments conducted in South Crude Treatment Unit laboratory (UTBS/HMD/Algeria), showed that the salts removal efficiency (SRE) increases with the increasing of wash water rate, demulsifier amount and the operating temperature.

For 5% of wash water rate and 0.5% of demulsifier at 52°C, the (SRE) was 96.94%. Applying these parameters values to electrical desalting vessel with the supply of electrical field effects, would increase the (SRE) to a remarkable extent.

The mean volumetric ratio of (BS&W) recorded during experiments was only 0.5%, so the crude treated is high quality.

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