Crude Oil Desalting by Using Nanocarbon

Hossain Keshavarz and Nadia Esfandiari*

Department of Chemical Engineering, Marvdasht Branch,
Islamic Azad University, Marvdasht, Iran

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Abstract

In the process of crude oil desalination, the aim is to separate dispersed phase of brine from oil phase. The project aim is the use of carbon nano-adsorbent for remov-al of salt from crude oil that, unlike other methods of salt separation from crude oil currently used, is a simple, inexpensive method with good ability to remove salt from crude oil. In this study, first, four types of carbon adsorbent were used for removal of salt from crude oil using dispersion in solution method. Then, the adsorbents that had the best absorption were identified. In continuation, two nano-adsorbents were selected from nano-adsorbents and their effect on the absorption of salt from crude oil was investigated using filtration method. Finally, a survey was carried out on regeneration of multi-walled carbon nanotubes that had the ability to absorb more than 50% of salt from crude oil, which were then selected as the best nano-adsorbents.

Keywords

Crude oil;
Desalting;
Nanocarbon;
Regeneration;
Adsorbent.

1. Introduction

Oil is located over salt water in the underlayers of the earth. Therefore, the fluid produced at the wellhead in addition to oil and gas contains free water and emulsified water (water–oil emulsion), especially in reservoirs that are in the half-life of their production. The oil produced from these wells contains some salt water. The salt water in crude oil causes problems such as reduction in the performance of machinery, clogging of reactors and destruction in their catalytic bed, and decrease in quality of products that will eventually lead to a decrease in export price of crude oil. Thus, there are commercial reasons for removing salt water suspended in the crude oil. Crude oil price is dependent on its quality. For example, every ppm increase in water and salt deposits in crude oil will lead to a fall in the price approximately from 0.85 to 3.1 US dollars. Therefore, carrying out research on purification and increase in crude oil quality is necessary. Two parameters are employed to determine oil quality. The first one is crude oil density, which depends on the amount of paraffin, asphalting, and other hydrocarbons contained in it and is represented by American standard unit API; besides, its heaviness illustrates the lightness of crude oil and its lightness represents the heaviness of crude oil. The other parameter is the percentage of salt deposits and water along with oil that is characterized by BS & W (bottom sediments and water) parameter. In most of the oil fields in the world, oil production is associated with a substantial amount of brine and, currently,

* Corresponding Author.
Tel./Fax: +989173042094
Email: esfandiari_n@miau.ac.ir (N. Esfandiari)

in Iran, in most productive oil wells, it is also associated with quantities of water. Therefore, in order to enhance the quality of crude oil, salt water must be separated [1-2].

Different methods are used for separating salt water from crude oil. Methods include gravity method, method of adding fresh water to wash water, thermal method, the use of emulsion breaker chemicals (Demulsifies), mechanical method, electric method, and hybrid method [3-10]. One of the best methods that is currently used in industry is the hybrid method. However, one of the disadvantages of this method is its high cost. It is obvious that gravity and thermal methods are less expensive than other methods. The isolation using breaker suspension materials is effective on heavy oils. Given the characteristics that crude oils have in each region, a set of the above-mentioned methods are used to separate salt from crude oil.

One of the new methods that is currently used in all fields is nano-technology. Considering the increasing development of nanotechnology, it seems that nano-adsorbents are beneficial in the process of separating salt from crude oil. Nikkhah and Jahanmiri conducted a research on improving the performance of crude oil emulsification using titanic nanoparticles [11]. They showed that titanic nanoparticles were effective in the process of separating salt from crude oil. In their study, different types of nano silica were used to separate salt water; the sample coated by polyvinyl alcohol enjoyed the best performance compared to other particles at an equal concentration. The reason for this was the size of used nanoparticle, which was 12nm for the test sample; with increase in the size of nanoparticles, emulsion stability decreased and by strengthening the hydrophobicity of nanoparticles, percentage of separated water increased, which had the greatest value for nanoparticles with polyvinyl alcohol coating [11].

The methods of synthesizing carbon nanotubes can be divided into three groups of electric arc discharge, laser radiation, and chemical vapor deposition. The third method is more appropriate, because there is a possibility of synthesizing vertically aligned carbon nanotubes. There are several methods for preparing nano-carbon materials, which are used to increase scale in synthesis and carried out with high yield and high purity at relatively low temperatures [12-15].

The functionalization of carbon nanotubes changes their physical and chemical properties and results in unique nanotubes [16, 17]. In general, the presence of oxygen-containing functional groups such as OH, C = O and COOH increases polarity, hydrophobicity, and ion-exchange capacity in CNTs. Since the aim of this research was to isolate the salt water, carboxyl functional group (COOH) was selected.

In order to provide carbon nanotube modified with carboxyl functional groups, 5gr of multi-walled carbon nanotubes was added to 250mL of mixture of sulfuric acid and nitric acid with volume ratio of 1:3. The mixture was stirred for 2 h at a temperature of 60-50 ºC in an ultrasonic bath. Then, the mixture was diluted with distilled water at a ratio of 1:5. By centrifugation, functionalized carbon nanotubes were separated from acid and rinsed several times with distilled water until pH was 7. Next, the material was completely dried in vacuum hot-house at a temperature of 70 ºC for 24h [18].

Sad et al. [19] studied the heavy oil desalination. They investigated density, viscosity, total salinity index, total sulfur, and total acid number before and after the crude oil desalination. Kim et al. [20] studied the modeling of desalting process. Their simulation was based on module modeling. Check and Mowla [21] investigated the desalting of crude oil by ultrasonic irradiation. They studied the effect of irradiation input power, irradiation time, temperature, and injected water on the desalting efficiency. The effect of demulsifying agent concentration, temperature, settling time, mixing time, and wash water dilution ration on desalting efficiency was investigated [22].

With regard to a research study that was conducted on the desalination process of crude oil, this study has examined the effect of carbon nanotubes on the process of separating salt from crude oil. First, four carbon nano-adsorbents, namely, single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), carbon nanotube with carboxyl factor (MWCNT+ COOH), and 1-3-layer Graphene using dispersion in solution were tested in different weights and, by investigating the results, two nano-adsorbents, namely, SWCNT and MWCNT, that had high absorption compared to others were selected for further investigation. Two nano-adsorbents selected in different weights were studied using filtration method.

2. Experimental

Among the methods available to evaluate the amount of salt in crude oil, IP-77 method was selected to measure the effect of nano-adsorbents used in this study due to its simplicity, low cost, and quickness.

2.1. Materials

All carbon nano-adsorbents used in this study have been synthesized with chemical vapor deposition (CVD) and include SWCNT, MWCNT, (MWCNT + COOH), and 1-3 layers of Graphene that were purchased from Oil Industry Research Institute. Xylene, toluene, 30% hydrogen peroxide, potassium chromate, and 2-propanol were purchased from Merck. Crude oil was prepared by Iranian Offshore Oil Company, Soroosh oil platform. The produced water properties are shown in Table 1.

Table 1. Produced water properties.

Salinity (mg/NaCl)	192000
Density @ 3700 psia, 84 °C (Kg/m^3)	1100
Stock tank density (Kg/m^3)	1128
Compressibility (l/psi)	2.2×10^{-6}
Viscosity @ 3700 psia, 84 °C (cP)	0.55

2.2. Experimental procedure

At the beginning of each stage, to evaluate quantity of primary salt in crude oil, control test (IP-77 test) was performed on the primary crude oil. Then, at the first stage, four nano-carbon adsorbents, namely, SWCNT, MWCNT, MWCNT with carboxyl factor, and 1-3 layers of Graphene, were tested in different weights by dispersion in a solution method. Then, results were analyzed and highly absorbable nano-adsorbents were compared and selected for further investigation. At the second stage, two nano-adsorbents selected in the previous stage (SWCNT and MWCNT) were tested in different weights using filtration method. Finally, with respect to analysis of filtration method results, regeneration testing was carried out over the best nano-adsorbent (MWCNT).

2.3. Control test

The 50mL of crude oil from Soroosh platform was loaded into a 250mL-beaker. Then, 50mL of xylene, 50mL of alcohol (2-propanol), and 100mL of deionized water were added to the beaker. The materials inside the beaker were boiled at 80 °C for 30min. Next, the solution was cooled and allowed to form in a two-phase water and oil solution. After separating the aqueous phase, 4-5 drops of hydrogen peroxide were added to it (so that toxic H_2S gas was released). Then, it was boiled under the hood for 5min. After cooling, 1mL of aqueous phase was removed from it; using Mohr titration method, the quantity of salt in crude oil in terms of pounds per thousand barrels (ptb) was reported. Mohr's method determines the chloride ion concentration in a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitation of silver chloride forms. The end point of the titration is reached when the chloride ions are precipitated. Then, additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate. Each of the following methods was evaluated by measuring the difference between the amounts of absorption that took place in control test and salt absorption test by nano-adsorbent.

To understand the impact of nano-adsorbents on crude oil, initially, the impact of salt absorption in crude oil was investigated using dispersion in solution method; then, nano-adsorbents that offered the best results were selected and accuracy of the results of dispersion in solution was determined by filtration method.

2.4. Dispersion in solution method

Initially, 50mL of crude oil was heated up to a temperature of 70 °C to reduce the viscosity; then, all of the carbon adsorbents (carbon single-walled nanotubes, multi-walled carbon nanotubes, 1-3 layers of Graphene, and functionalized carbon nanotubes) at weights of 0.25 and 0.5g were added to 50mL of crude oil. The oil containing nano-adsorbent was stirred at a temperature of 60 °C for 30min. In this way, separation of salt from crude oil was performed. In order to specify the amount of salt absorption by nano-adsorbent, the IP-77 test was used. The amount of salt absorbed by nano-adsorbent was also estimated by Mohr titration.

2.5. Filtration method

A filter layer was placed at the bottom of a hopper located on a flask to prevent the passage of nanoparticles. Then, the carbon nano-adsorbent that had the best absorption among other carbon adsorbents was placed with the weights of 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5g at the bottom of the hopper. Next, 50mL of crude oil was combined with 50mL of xylene and allowed to be stirred with the temperature of 70 °C until the mixture became completely homogeneous such that crude oil became quite smooth and there were no problems in terms of its viscosity. The crude oil was poured onto the nano-adsorbent. The passage of oil over the adsorbent lasted for one hour. Finally, the IP-77 test was performed. The amount of salt absorbed by the adsorbent was determined by Mohr titration.

At the end, to regenerate nano-adsorbents, the nano-adsorbent that demonstrated the best result was selected and the amount of regeneration was investigated through filtration method.

2.6. Nanocarbon regeneration method

Initially, nano-adsorbents used in the primary steps were collected and poured onto a sieve and rinsed with some xylene so that the oil dipped onto the surface of nano-adsorbents was completely removed. The rinsed nano-adsorbent was dried completely inside the oven at 80 °C for 12h. The substance in the beaker was mixed completely for 3min. Then, beaker content was poured on a membrane and some hot deionized water was poured over it for 30min to ensure it was completely rinsed off. The rinsed nano-adsorbent was dried completely in an oven for 12h. Then, regeneration testing was performed by filtration method on dried nano-adsorbent at the weights of 0.1 and 0.25g.

3. Results and Discussion

The results of removal of salt from crude oil by carbon nanotubes using dispersion in solution method have been shown in Figs. 1 and 2. With regard to these figures and absorption percentage in Table 2, it can be concluded that carbon adsorbents are effective in removal of salt from crude oil. The SWCNT and MWCNT carbon nano-adsorbents have the highest absorption because the surface areas of SWCNT and MWCNT carbon nano-adsorbents are higher than those of other carbon nano-adsorbents. As indicated in Fig. 1, an increase in the nano-adsorbent increases the amount of salt absorption.

After performing experiments of the first step, by choosing SWCNT and MWCNT carbon nano-adsorbents, which had the highest absorption, crude oil desalination test was performed in different weights by filtration method. The results of this experiment have been presented in Figs. 3 and 4. As can be seen in these figures, the nano-adsorbent up to the weight of 0.5g is effective for 50mL of crude oil. In weights higher than this amount, since the ratio of nano-adsorbent volume to oil volume grows, the amount of absorption decreases and the nano-adsorbent returns the salt that has been absorbed to the solution.

Table 2. The percentage of salt absorbent via 0.5g of nano-absorbent.

Nano-adsorbent	Initial salt content (ptb)	Salt content after absorbent (ptb)	The absorbed salt (ptb)	Absorbent percentage (%)
MWCNT	40405	20222	20183	50
SWCNT	38926	21820	17106	44
1-3 Geraphene	40860	35456	5404	13
Functionalized nano(MWCNT+COOH)	35882	32882	2978	9

After the experiment, multi-walled carbon nano-adsorbent, which had the highest absorption, was selected using filtration method and its recycling rate was studied on 50mL of crude oil at different weights using filtration method.

To perform regeneration testing, the nano-adsorbents used in the previous steps were collected and filtered and rinsed with some xylene so that the oil on the surface of the nano adsorbents was completely removed. Next, nano-adsorbent was completely dried inside the oven at 80 °C for 12h. Then, dried materials were poured in a beaker and some deionized water (with a temperature of 85 °C) was added to contents of the beaker. The content of beaker was completely located on a mixer for 30min. Then, beaker content was poured on a membrane-like sieve and some hot deionized water was passed over it for 30min to be completely rinsed. The rinsed nano-adsorbent was dried completely in an oven for 12h. Then, regeneration testing was performed by filtration method on different weights of dried nano-adsorbent.

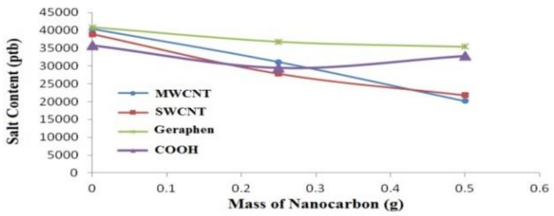

Figure 1. Influence of nanocarbon type on desalting results for different masses of nanocarbon by dispersion in solution method

Fig. 5 shows the regeneration process of multi-walled nanotubes at weights of 0.1 and 0.25g. As seen in this figure, the amount of regeneration in the second phase is less than that in the first phase, because some pores in nanotubes are not recoverable by this method. The curves concerned with regeneration are very close in the second and third phases and this shows that recycling for two times has the ability to absorb the salt. But, in the third phase, the possibility of restoration and reuse of multi-walled nanotubes does not exist. Therefore, by designing an appropriate system for recycling, these nano-adsorbents can be used for re-desalination operations.

4. Conclusion

Separating the salt water from crude oil is considered to be one of the most important processes in the oil industry. One of the new methods for separating brine from crude oil is the use of carbon nano-adsorbent, which, due to being simple and inexpensive, has commercialization capabilities. Considering experiments conducted in the first phase using dispersion in solution method, it was proved that the used nano-adsorbents had the ability to separate salt from crude oil and SWCNT and MWCNT nano-adsorbents had higher adsorption capabilities than other adsorbents. The second phase was performed by filtration method between two nano-adsorbents selected in the previous step; it was shown that MWCNT was the best adsorbent and had a capacity to adsorb more than 50% of the salt in crude oil. Given the increasing development of nanotechnology and recycling of these materials, it is hoped that by taking advantage of this method, the significantly high costs of other expensive industrial methods that are currently employed for crude oil desalination as well as the high costs of energy supply used for it could be avoided.

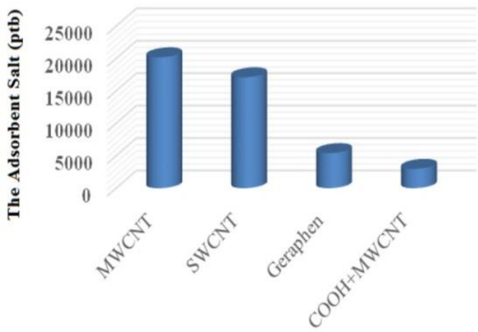

Figure 2. Comparison of adsorbed salt amounts with different nanocarbons

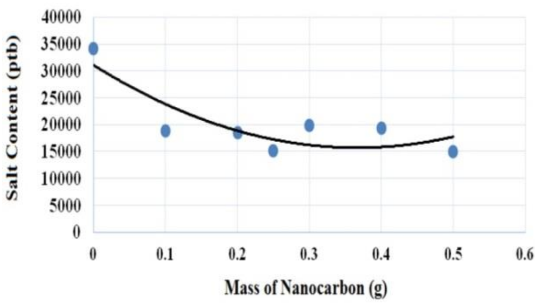

Figure 3. Influence of nanocarbon mass on desalting results with MWCNT

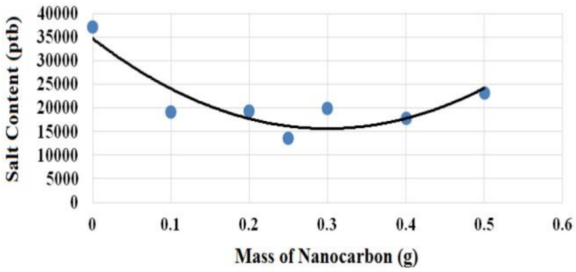

Figure 4. Influence of nanocarbon mass on desalting results with SWCNT

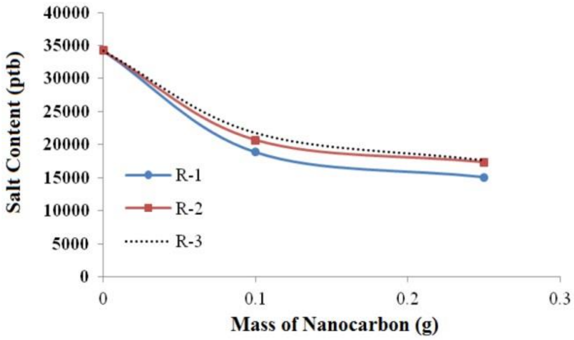

Figure 5. The effect of MWCNT recovery on desalting results

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