

A Novel Demulsifier Used to Separate Water from the Emulsion

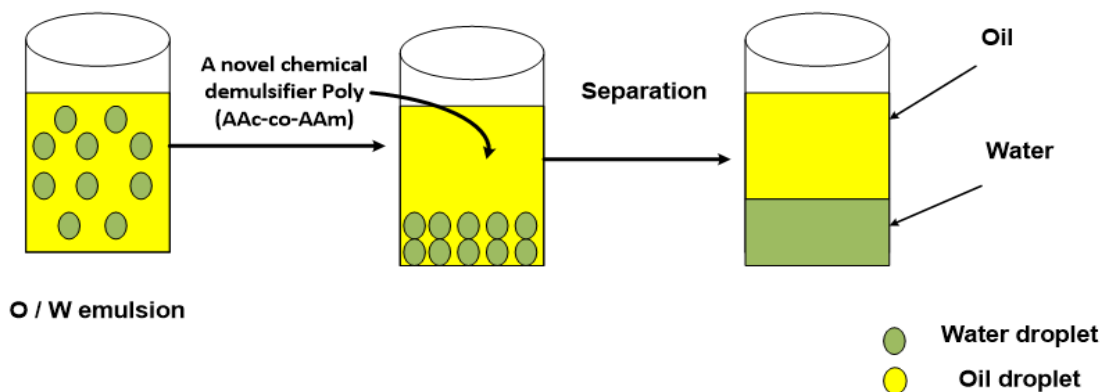
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ABSTRACT: Recently, there has been interest in using chemical demulsifiers to separate the water phase from crude oil emulsion. Separating the water from the emulsion is crucial before transportation and refining to avoid complications from the water phase. This research introduces a novel chemical demulsifier, Poly (AAc-co-AAm) hydrogel, synthesised at Sebha University. Its characteristics were examined using the Fourier Transform Infrared Spectroscopy test (FTIR). Its efficiency was tested against commercial demulsifiers (Emulsotron and Dmo-66813) used in some Libyan oil fields. The chosen concentrations for Poly (AAc-co-AAm) were 0.5%, 1%, and 2%, while commercial demulsifiers were tested based on the standard method in the oil field. The results revealed that Poly (AAc-co-AAm) outperformed the commercial demulsifiers in terms of separation time, volume, and quality. Notably, the 0.5% concentration of Poly (AAc-co-AAm) provided the best separation results.

المخلص: إزداد مؤخراً الإهتمام باستخدام المَفْصَلات الكِيمِيائِيَّة لِفَصْلِ مَرْحَلَةِ المَاءِ مِنَ الزَّيْتِ الخَامِّ المُسْتَحْلَبِ. يُعَدُّ فَصْلُ المَاءِ عَنِ المُسْتَحْلَبِ أَمْرًا حَاسِمًا قَبْلَ النَّقْلِ وَالتَّكْرِيرِ لِتَجَنُّبِ المُشْكَلَاتِ النَاجِمَةِ عَنِ مَرْحَلَةِ المَاءِ. تُقَدِّمُ هَذِهِ الدِّرَاسَةُ مَفْصَلًا كِيمِيائِيًّا جَدِيدًا، هِيدْرُوجِيل Poly (AAc-co-AAm)، تَمَّ تَحْضِيرُهُ فِي جَامِعَةِ سَبْهَاءِ. تَمَّ فَحْصُ خَصَائِصِهِ بِاسْتِخْدَامِ إِخْتِبَارِ التَّحْلِيلِ بِالطَّيْفِ الأَشْعَاءِ تَحْتَ الحَمْرَاءِ بِاسْتِخْدَامِ تَقْنِيَّةِ تَحْوِيلِ فُورِيَّةِ (FTIR). تَمَّ إِخْتِبَارُ فَعَالِيَّتِهِ مُقَابِلَ المَفْصَلَاتِ التِّجَارِيَّةِ (Emulsotron وَ Dmo-66813) المُسْتَحْدَمَةِ فِي بَعْضِ حُقُولِ النِّفْطِ اللَّيْبِيَّةِ. تَمَّ إِخْتِبَارُ تَرَكِيزَاتِ Poly (AAc-co-AAm) بِمَقَادِيرِ 0.5%، وَ 1%، وَ 2%، فِي حِينِ تَمَّ إِخْتِبَارُ المَفْصَلَاتِ التِّجَارِيَّةِ اسْتِنَادًا إِلَى الطَّرِيقَةِ المِغْيَارِيَّةِ فِي حَقْلِ النِّفْطِ. أَظْهَرَتِ النَتَائِجُ أَنَّ Poly (AAc-co-AAm) أَفْضَلُ مِنَ المَفْصَلَاتِ التِّجَارِيَّةِ مِنْ حَيْثُ وَقْتِ الفَصْلِ، وَالحَجْمِ، وَالجُودَةِ. يُبَارِ إِلى أَنَّ تَرَكِيزَ 0.5% مِنَ Poly (AAc-co-AAm) قَدَّمَ أَفْضَلَ نَتَائِجَ فَضْلًا.

Keywords: : Demulsifier; Poly (AAc-co-AAm); Emulsion; Bottle test; Water separation.

الكلمات المفتاحية: مفصل؛ بولي (AAc-co-AAm)؛ مستحلب؛ اختبار الزجاجاة؛ فصل الماء.

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INTRODUCTION

Demulsification is the separation of emulsion into water and oil phases (Fan et al., 2018; Liu et al., 2010; Orijji & Appah, 2012; Yi et al., 2017). The formation of emulsion is often linked to shear forces and pressure (Abdulredha et al., 2020). Up to the present, there are many challenges to obtaining material (demulsifier) that can make the pressure and shear forces low to allow the water droplets to separate easily (Daniel-David et al., 2008; Razi et al., 2011). So, the demulsifier works as a surface-active agent, which reduces the shear forces and pressure between the water-oil interface and causes a merge of the water droplets (Mhatre et al., 2018). Generally, before the formations are separated, the separation process passes through different steps (processes), which are creaming, sedimentation, flocculation, Ostwald ripening, and coalescence (Saad et al., 2019; Yi et al., 2017). Through the development of studies, most studies were not looking only for effective separation side but also for the optimum chemical materials that can give special characterisations such as better separation, appropriate amount of chemical material, and enough retention time in the separators to let the water phase settle down, and adequate mixing of the chemical material in the crude oil (emulsion) (Razi et al., 2011; Yi et al., 2017).

The challenges started in 1997 when McLean and Kilpatrick discovered that the high concentration of salts in emulsion could result in corrosion problems or catalyst poisoning (McLean & Kilpatrick, 1997). Thus, adding demulsifiers into the emulsion had become necessary to avoid many problems. Among the most prominent of these studies was in 2018 by Ahmad A. Adewunmi and Kamal. This work presented a novel demulsifier (coal fly ash CFA) for W/O emulsions; the results proved that the increase of CFA causes an increase in the separation process (Adewunmi & Kamal, 2018). Also, in 2020, Piromchart reported on carbonate-based ionic liquid (CBIL) as a demulsifier for W/O emulsions. The CBIL has a better demulsifier compared with conventional demulsifiers, and it has shown the ability to separate the water within 15 min at 600 °C (Arayachukiat & Piromchart, 2020). Currently, the nanoparticle NPs materials also have proven their ability to assist in the separation process of the water from the emulsion. In 2020, the SiO₂ NPs were used for the dehydration of the crude oil, and the SiO₂ was synthesised with graphene oxide (GO). The results showed that GO-SiO₂ gave the best performance compared with other materials (oleic acid and sodium dodecyl benzene sulfonate) (Javadian & Sadrpoor, 2020). Based

on the above literature review, many materials have not been investigated yet in this area. A novel material has been decided to include it in this study and investigate its ability to separate the water phase.

METHODOLOGY

Poly (AAc-co-AAm) demulsifier was synthesised at Sebha University (College of Science). Different molar ratios of monomers with Poly (Acrylic-Acid-Acrylamide) co-polymers were synthesised based on specific procedures as follows: the solid material of Acrylamide was put in 50 ml of distilled water and mixed in three flasks, then gradually heated to 40 °C by using a water bath under nitrogen protection. Thereafter, the gained solution was subjected to mixing for 20 min and then added 2.5 ml of acrylic acid into the gained solution. Additionally, 0.05 gm of Methylene Bis-Acrylamide (MBA) was added into the flask as a cross-linking agent and mixed for 20 min under nitrogen. A 0.01 gm of initiator dissolved (KPS) was mixed in 10 ml of distilled water and then gradually added into the flask to start the polymerisation process. Afterwards, the gained solution was mixed for 2 hrs at 80 °C. Finally, the obtained solution is a cross-linked poly (AAc-co-AAm) super absorbent polymer (SAP) (Figure 1). The water in the gained SAP was removed by using the ethanol solution. The solution was also put into a petri dish and dried by using an oven at 80 °C for 24 hrs in order to obtain the pure chemical equation of the cross-linked synthesis (Figure 2). Finally, the material that has been synthesised was subjected to the FTIR test in order to obtain the function group of the synthesis material.

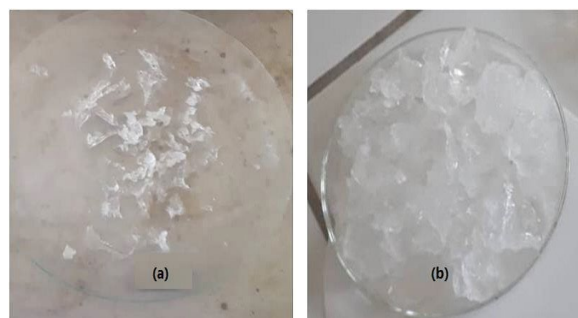


Figure 1. a) Poly (AAc-co-AAm) when it formed as foam. b) Poly (AAc-co-AAm) when it becomes dry.

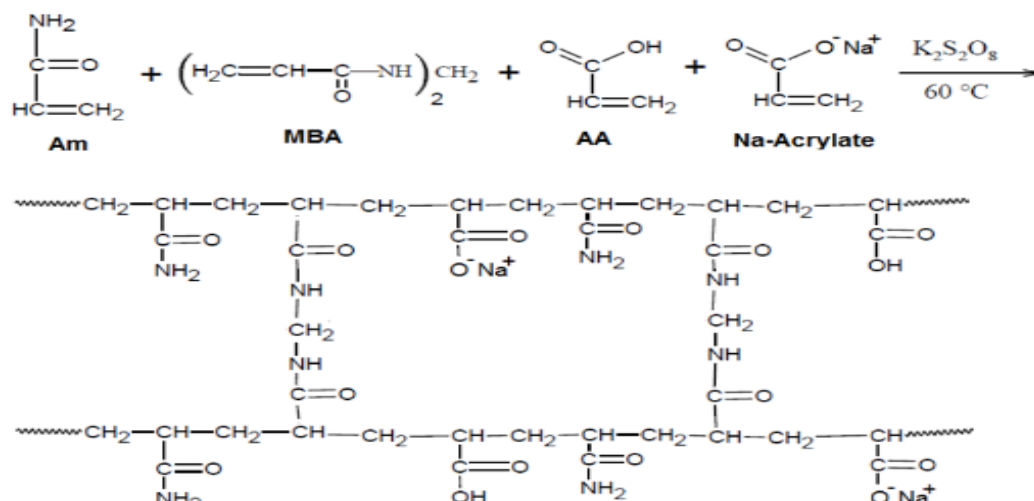


Figure 2. Chemical equation showing the synthesis of cross-linked poly (AAc-co-AAm).

EXPERIMENT PROCEDURES

In the experiment procedures, different concentrations of Poly (AAc-co-AAm) were selected based on solution liquidity because the high concentrations made the solution difficult to pour into the bottle samples. Different weights of the Poly (AAc-co-AAm) were prepared in order to prepare different solutions with different concentrations (Table 1). Each weight was dissolved in 50 ml of distilled water (Figure 3). Three concentrations, 0.5%, 1%, and 2%, were prepared in the form of the liquid phase in order to add them into the emulsion based on volume per cent.

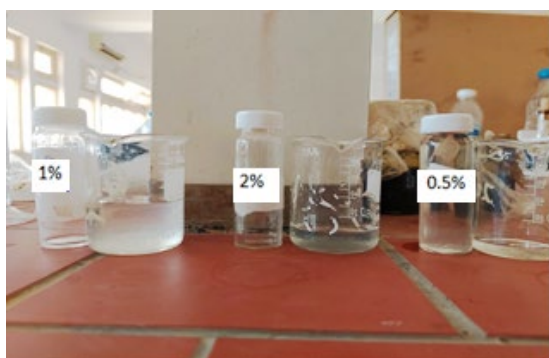


Figure 3. Concentrations of Poly (AAc-co-AAm) demulsifier.

Table 1. Concentrations of demulsifier used in this study.

Poly (AAc-co-AAm)			
Concentrations	0.5%	1%	2%
Weight (gm)	0.25	0.5	1

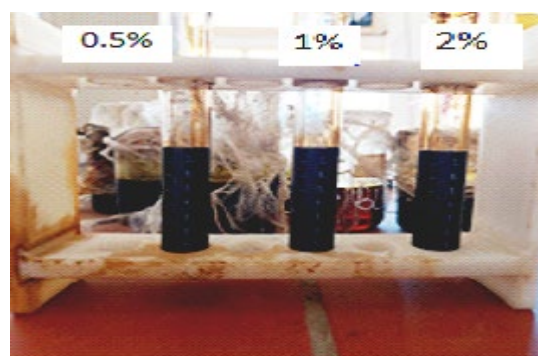


Figure 4. Graduated tubes containing crude oil and Poly (AAc-co-AAm) demulsifier.

After the solutions had been prepared, the graduated tubes were filled with (8ml) of crude oil (emulsion), and each graduated tube was mixed with (0.2 ml) of a different type of demulsifier, as shown in Figure 4.

After adding and mixing the mixture (crude oil and demulsifiers) in the graduated tubes, the performance of demulsifiers to separated water was recorded at $35\text{ }^\circ\text{C}$ and at $50\text{ }^\circ\text{C}$ by using a heating device. The tests were carried out for three hours, divided into 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 120 min and 180 min.

RESULTS

FTIR spectra analysis for Poly (AAc-co-AAc)

The FTIR test was done for Poly (AAc-co-AAm) between the ranges 400 to 4000 cm^{-1} (Figure 5). It noticed the appearance of the band peaks at $(1300\text{--}1400\text{ cm}^{-1})$ due to the existence of a (C-N) vibration, while the bands between $1600\text{--}1700\text{ cm}^{-1}$ are caused by (C=O). The peak at 2932 cm^{-1} is caused by the polymer's backbone being stretched in a (C-H) direction, while a band of absorption caused by (N-H) stretching is visible between 3200 to 3500 cm^{-1} (Mutar & Kmal, 2012; Stuart, 2004). The -OH from the carboxylic group was given an assignment to the absorption bands from 2960 to 3400 cm^{-1} (Li et al., 2002).

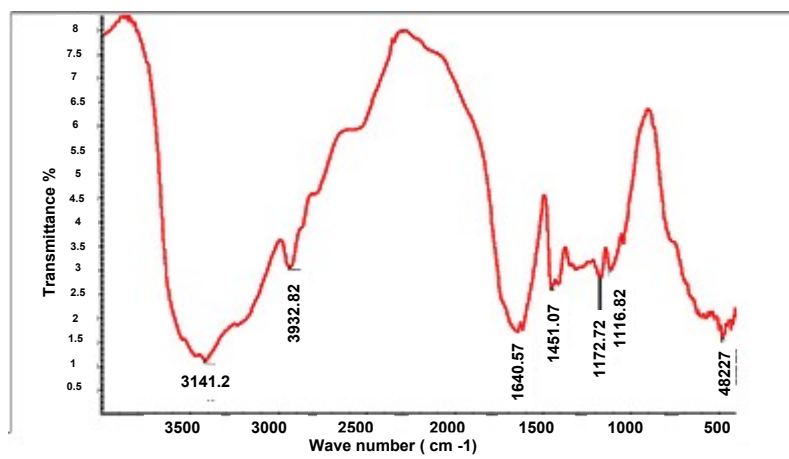


Figure 5. FTIR Test of Poly (AAc-co-AAm) in the range between 400 and 4000 cm^{-1} .

Intermolecular forces such as electrostatic interaction influence the vibration of functional groups on Poly (AAc-co-AAm) segments. This can be concluded from bands that showed between 3100 to 3500 cm^{-1} (O-H and N-H stretching) in Poly (AAc-co-AAm) hydrogen. Carbonyl stretching vibration C=O of the carboxyl group shows an absorption peak at 1742 cm^{-1} in Poly (AAc-co-AAm), while C=O of the anode group shows an absorption peak at 1670 cm^{-1} (Usov & Mezzenga, 2015). Symmetric and asymmetric stretching of COO⁻ have been noticed at 1448 cm^{-1} and 1580 cm^{-1} , respectively. This approves that the carboxylic groups of Poly AAc are separated into COO⁻ which complexes with the cationic group of Poly-AAm across electrostatic interactions to form the copolymer-hydrogel. These spectra also show a weak band at 2186 cm^{-1} , which is imputed to the presence of -C-N group of cross-linking agent and Acrylamide.

Performance at 35 °C

The performance of laboratory demulsification tests was carried out using the bottle method for various demulsifiers concentrations (0.5%, 1%, and 2%). Firstly, it was noticed that the reference (blank) sample made a very stable emulsion in the absence of Poly (AAc-co-AAm) (Figure 6). Water separation was not noticed in the reference sample for 180 minutes. However, with the addition of different scenarios of Poly (AAc-co-AAm) into the emulsion samples, the separation of water from the emulsion began gradually directly proportional to retention time. Table 2 shows the results of the water separation efficiency of Poly (AAc-co-AAm) at 35 °C. At the concentration of 0.5%, the separation started from the first step, which is 5 min. The water phase of the sample stopped increasing continuously at 30 min. During this time, the Poly (AAc-co-AAm) has reached its ability to separate the water, whatever the time step has increased. While, at concentrations 1% and 2 %, the water phase of the samples increased with different time steps, the maximum volume of separated water was 0.4 and 0.42 ml, respectively. However, the performance of Poly

(AAc-co-AAm) at 35 °C with 0.5% has given the best performance compared with 1% and 2%.

In order to obtain the performance of the Novel material, the Poly (AAc-co-AAm) has been tested and compared with commercial materials. Table 3 shows the results of the water separation efficiency of Dmo-66813 and Emulsotron demulsifiers at 35 °C. Both demulsifiers have no effect on the separation at the first step. The effect of both demulsifiers started at 30 min. The maximum separation level was 0.6 ml for Emulsotron. While for Dmo-66813, the maximum separated level was 0.25 ml at 35 °C.

The clarity of the solution has been taken into account in this study. The results showed that the Poly (AAc-co-AAm) had given a clear solution for the water phase compared with the commercial demulsifiers (Figure 7). The Dmo-66813 has given a green solution, while the Emulsotron has given a brown solution. The clarity of the solution indicates the quality of the separated solution. The coloured solution indicates that few amounts of crude oil have dissolved in the water phase; thus, the poor performance of these two chemicals could be a result of the crude (Emulsion) density and the poor compatibility of the chemical with other production chemicals.

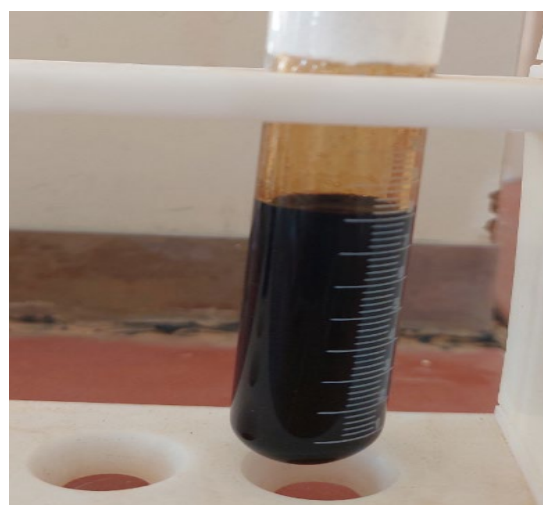


Figure 6. Reference (blank) sample.

Table 2. The water separation efficiency of Poly (AAc-co-AAm) at 30 °C.

Time (min)	Separated water				
	Poly (AAc-co-AAm)			Dmo-66813	Emulsotron
	0.5%	1%	2%		
5	0.3	0	0.2	0	0
10	0.38	0	0.3	0	0
15	0.38	0.2	0.3	0	0
30	0.8	0.2	0.3	0.25	0.6
45	0.8	0.2	0.36	0.25	0.6
60	0.8	0.2	0.36	0.25	0.6
120	0.8	0.2	0.42	0.25	0.6
180	0.8	0.4	0.42	0.25	0.6



Figure 7. Poly (AAc-co-AAm) demulsifier and conventional demulsifiers water separation.

Table 3: Demulsifier water separated quality and emulsion quantity

Demulsifier	Emulsion		Water quality	
	Top	Bottom		
Emulsotron	0.7	0.6	Brown	
DMO-66813	0	0	Green	
Concentrations				
Poly (AAc-co-AAm)	0.5%	0.9	0.8	Clear
	1%	0.5	0.4	Clear
	2%	0.5	0.42	Clear

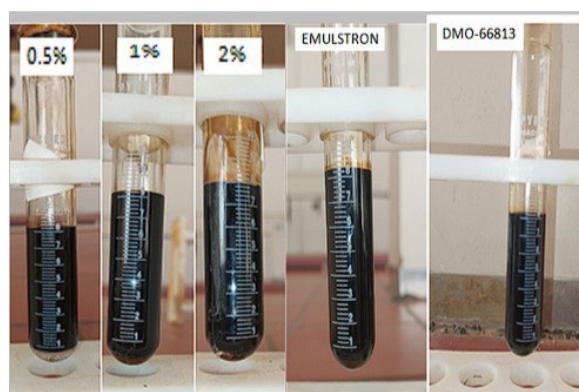


Figure 8. Poly (AAc-co-AAm) demulsifier water separation at temperature 50 °C.

Table 4. The water separation efficiency of Poly (AAc-co-AAm) demulsifiers at 50 °C.

Time (min)	Separated water				
	Poly (AAc-co-Am)			Dmo-66813	Emulsotron
	0.5%	1%	2%		
5	0.34	0	0.2	0	0
10	0.39	0	0.32	0	0
15	0.39	0.22	0.32	0	0
30	0.85	0.22	0.32	0.3	0.62
45	0.85	0.22	0.38	0.3	0.62
60	0.85	0.22	0.38	0.3	0.62
120	0.85	0.22	0.49	0.3	0.62
180	0.85	0.42	0.49	0.3	0.62

Table 5. Demulsifier water separated quality and emulsion quantity.

Demulsifier	Emulsion		Water quality	
	Top	Bottom		
Emulsotron	0.35	0.25	Brown	
DMO-66813	0.75	0.62	Green	
Poly (AAc-co-AAm)	0.5%	0.95	0.85	Clear
	1%	0.5	0.42	Clear
	2%	0.52	0.49	Clear

Performance at Temperature 50 °C.

Table 4 shows the results of the water separation efficiency of Poly (AAc-co-AAm) at a temperature of 50 °C. At a concentration of 0.5%, the separation started from the first step, even when the temperature had changed. The volume of separated water gradually increased until reaching the time step 30 min; after that, its volume stopped increasing. It has already reached its ability to separate the water, whatever the time step has increased. While, at concentrations 1% and 2 %, the water phase of the samples increased with different time steps, the maximum water volume of separated water was 0.42 and 0.49 ml, respectively. The increase in temperature has a slight effect on the separated water compared with 35 °C performance. Thus, the Poly (AAc-co-AAm) is able to separate the water from the emulsion at different temperatures. However, the performance of Poly (AAc-co-AAm) with 0.5% still gave the best performance compared with 1% and 2% even at the temperature of 50 °C.

Table 4 shows the results of the water separation efficiency of Dmo-66813 and Emulsotron demulsifiers at 50 °C. Both demulsifiers have no effect on the separation at the first step, similar to the first scenario. The effect of both demulsifiers started at 30 min. The maximum separation level was 0.62 ml. while for Dmo-66813, the maximum separation level was 0.3 ml.

Table 5 shows the results of the quality of the separation process at a temperature of 50 °C. Poly (AAc-co-AAm) has given a clear solution for the water phase against the commercial demulsifiers, whereas the Dmo-66813 has given a green solution, while the Emulstron has given a Brown solution.

CONCLUSIONS

The chemical Poly (AAc-co-AAm) demulsifier was used in this study to separate the water from the emulsion by using a bottle test and compared with two commercial demulsifiers that are currently used in Libyan oil fields. The results findings could be concluded as follows:

1. The chemical Poly (AAc-co-AAm) demulsifier has proved to be effective in separating the water phase from the emulsion compared with the commercial demulsifiers.
2. Based on the results, increasing the demulsifier concentration does not always cause an increase in the separation process, where the concentration at 0.5% gave the best treatment chemicals based on settling time, different temperatures, and quality of separation liquid compared with 1 and 2 %.
3. The chemical Poly (AAc-co-AAm) demulsifier gave a clear solution, which indicates its ability to separate the solution with high quality.
4. This work will provide a new window for petroleum engineering demulsification of crude oil.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding this article.

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