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Investigation into the Use of *Thevetia Peruviana* seed oil for Surfactant Flooding

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Abstract

Surfactant is a surface-active agent that aids to improve oil recovery via changing the rock properties from oil-wet to water-wet. Synthetic surfactant is mostly used chemical enhanced oil recovery method but its vulnerability to high temperature and salinity reservoir pose a challenge to its application. In this study, Thevetia Peruviana oil was used as a precursor for surfactant formulation via saponification reaction. Soxhlet extraction technique was used to extract the oil from the seeds. Physicochemical properties of the extracted oil were investigated. Characterization using Fourier transform infrared spectrometer (FTIR) and X-ray fluorescence was carried out on the formulated surfactant to determine the functional groups and elemental composition. The results of this study showed that the Thevetia Peruviana seed have percentage of oil yield (61.3%), saponification value (218.79mg/100g), acid value (28.05mg/g), free fatty acid (14.03 mg/L), iodine value (9.39mg/L), specific gravity (0.90 g/cm3) and pH (4.04). The FTIR test results on the formulated surfactant showed the presence of the hydroxyl (OH) and carboxyl (COOH) functional groups. The XRF test showed major elements such as silicon, magesium, chlorine, iron and copper. This indicate that the surfactant is anionic and have hydrophilic behavior which will be effective for use in enhanced oil recovery in sandstone reservoir.

Introduction

Surfactant flooding is one of the various methods used in the oil and gas industry to improve oil recovery from the reservoir. It involves the injection of surfactants which are chemicals to displace residual oil within the reservoir by decreasing the interfacial tension between the displacing and displaced fluids thereby maximizing oil production [15]. Surfactant is a surface acting agent, which can adsorb at a surface of the oil/water interface and alter the rock wettability, via reducing the interfacial tension and surface chemistry of the rock properties [13,12]. In addition, surfactant exhibits molecular structures with hydrophilic group [7]. The hydrophilic group have a strong attraction force to the solvent while the hydrophobic group have a small attraction force to the solvent [8]. Surfactant can be grouped according to the behavior of the hydrophilic part such as non-anionic, anionic, cationic and zwitterionic [10]. According to [16], surfactant are organic compounds which consist of the hydrophilic head and hydrophobic tail. The hydrophilic head consist of the anionic surfactant which have a negativ charges while the non-anionic have no charge. However, cationic have a positive charge and surfactant are organic compounds which consist of the hydrophilic head and hydrophobic tail [20]. The hydrophilic head consist of the anionic surfactant which have a negative charge while the non-anionic have no charge [19]. However, cationic have a positive charge and zwitterionic have both positive and negative charge [5]. The hydrophobic tail has a chain structure as a surfactant and mostly formed a short polymer chain and long hydrocarbon chain [16]. In addition, the head group, consists of the alcohols, carboxylates, sulfates, sulfonates and polyoxyethylene chains. These groups showed the presence of amphiphilic nature of the surfactant [6]. Figure 1 shows the types of surfactant and the groups.

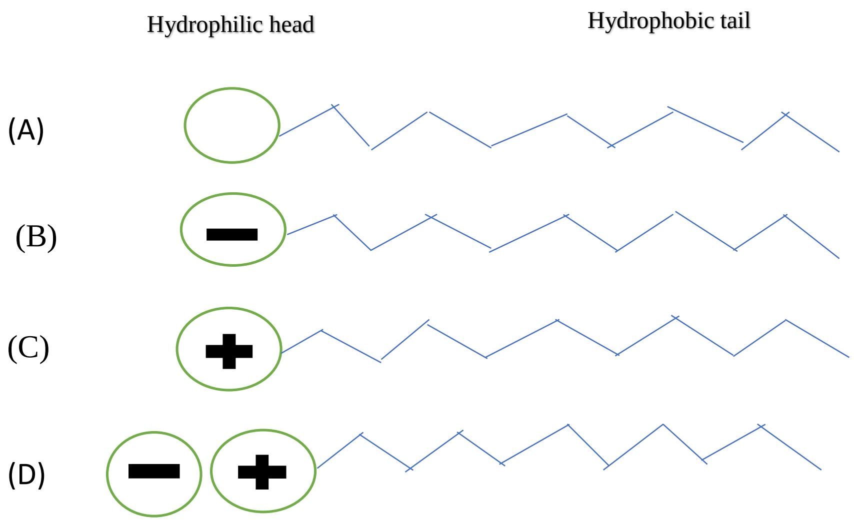

Figure 1 *Surfactants with charge headgroup: (a) Non-ionic (b) Anionic (c) Cationic (d) Zwitterionic surfactants [11].*

In addition, [17] noted that surfactant can be formulated through plant such as *Jatropha curcas* plant that produces seed oil (*Jatropha* oil) via saponification reaction. The synthesized anionic surfactant has the ability to alter the rock properties which can aid in enhanced oil recovery method. In the work of [14] used *neem* oil from (Castor oil) to prepare surfactant for used in enhance oil recovery process. They reported that the produced surfactant can reduced the interfacial tension of the oil because of its hydrophilic nature. In addition, [18] reported that characterization of surfactant for enhanced oil recovery method is important in order to determine the behavior of the surfactant based on its hydrophilic or hydrophobic nature. [9] noted that, before surfactant could be applied into the reservoir, it is necessary to character and determine the effectiveness of the surfactant in term of the hydrophilic head groups (anionic, non-anionic, cationic, zwitterionic). The focus of this study is to extract oil from the *Yellow oleander* through Soxhlet extraction method, formulate and characterized the surfactant.

Azadirachta indica plant was used to produce a surfactant. The results suggested that the new surfactant has the capacity to alter the rock surface chemistry via reduction of the interfacial tension of the oil. [3] used the seed oil from *Ricinus communis* plant for surfactant formulation.

Thevetia peruviana plants

Thevetia peruviana plants is a plant that grows as hedges and have attractive flowers, and mostly found in the Northern part of Nigeria [1]. The plant can produce about 400–1000 fruits in a year depending on the favorable weather conditions of the plant. The fruits are mainly green in appearance and black on matured stage [15]. [2] noted that *Thevetia peruviana* seed contain oil of high quantity (about 60-65%). *Thevetia peruviana* seed have high oil content of (45-67%) as reported by [4]. Figure 2 and 3, is the *Thevetia peruviana plant* and the matured stage of the seeds.

Figure 2 Thevetia Peruviana plant

Figure 3 Thevetia peruviana seed (matured stage)

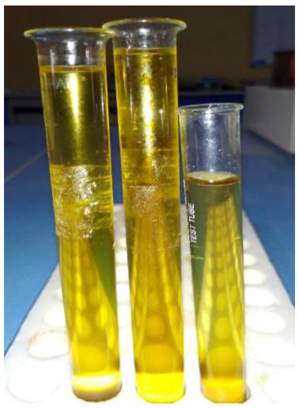

Figure 4 Extracted oil from the Thevetia Peruviana seed oil

Twenty kilograms (20 kg) of *Thevetia peruviana* seeds (Fig. 3) were hand–picked in Abubakar Tafawa Balewa University environment. It was sundried and packed in bag. *Thevetia peruviana* seeds were washed and cleaned in order to remove any bacterial attack and stored in a dried place to avoid sample decay. *Thevetia peruviana* seeds was cracked into pieces using mortal and later sieved for uniformity of the sample using mesh size particle of 90 micros.

Extraction of oil

The sieved *Thevetia peruviana* was wrapped with a filter paper. 50 mils of n-hexane were measured using measuring cylinder and poured into a conical flask. The *Thevetia peruviana* oil extraction were carried out using Soxhlet extractor where n-hexane was used as the solvent. A heating mantle was attached to the solvent at 60 ˚C for 2 hours. The Soxhlet extractor is made of the reflux which aids to circulates the solvent, the filter paper laved the solids while the siphon empties the filter paper. The condenser cools the solvent vapor, that drips back into the chamber where the material was housed. When the chamber was full, it was emptied by the siphon and the solvent returned to the distillation flask. The oil being extracted remained in the conical flask while the filter paper that housed the material was been discarded. Figure 4 is the extracted oil from the *Thevetia peruviana* seed.

Physicochemical Properties of the extracted oil (*Thevetia Peruviana Seeds)*

The saponification value, acid value, and iodine value, free fatty acid of the oil was obtained via titration. One and half grams (1.5g) of the oil was poured into a 150 mils conical flask. Potassium hydroxide of 0.5 N was measured and added into the mixture and stirred continuously. The reaction mixture was refluxed using water condenser on a water bath for one hour. The solution result was then cooled. It was titrated with 0.5 N hydrochloric acid (HCL) solution adding 1mil of phenolphthalein (indicator). The initial and final readings of the titration reactions were recorded. Other properties of the oil such as pH was obtained using a pH meter while the density and specific gravity of the oil were obtained by knowing the specific gravity of the oil plus the gravity of the bottle dividing it with the bottle plus water. More so, the density of the oil was obtained by 1000 $\frac{kg}{m^3}$ × Specific gravity. The oil yield was calculated by knowing the initial mass of the sample before extraction and the yield of the oil after extraction.

Formulation of new surfactant

Thevetia peruviana oil of three hundred (300) mils was poured into a conical flask. Potassium hydroxide (KOH) of three grams was added as an alkali and stirred continuously. The formulation of the surfactant was done via saponification reaction of an oil with a base to form glycerol and soap (surfactant). The mixture was heated for about 15 minutes and stirred vigorously. A viscous creamy liquid was observed and was noticed to form soap which was soluble in water. The formulated anionic surfactant (in form of detergent) was noted to be slippery when formulated. The reaction of the process is shown in Figure 5.

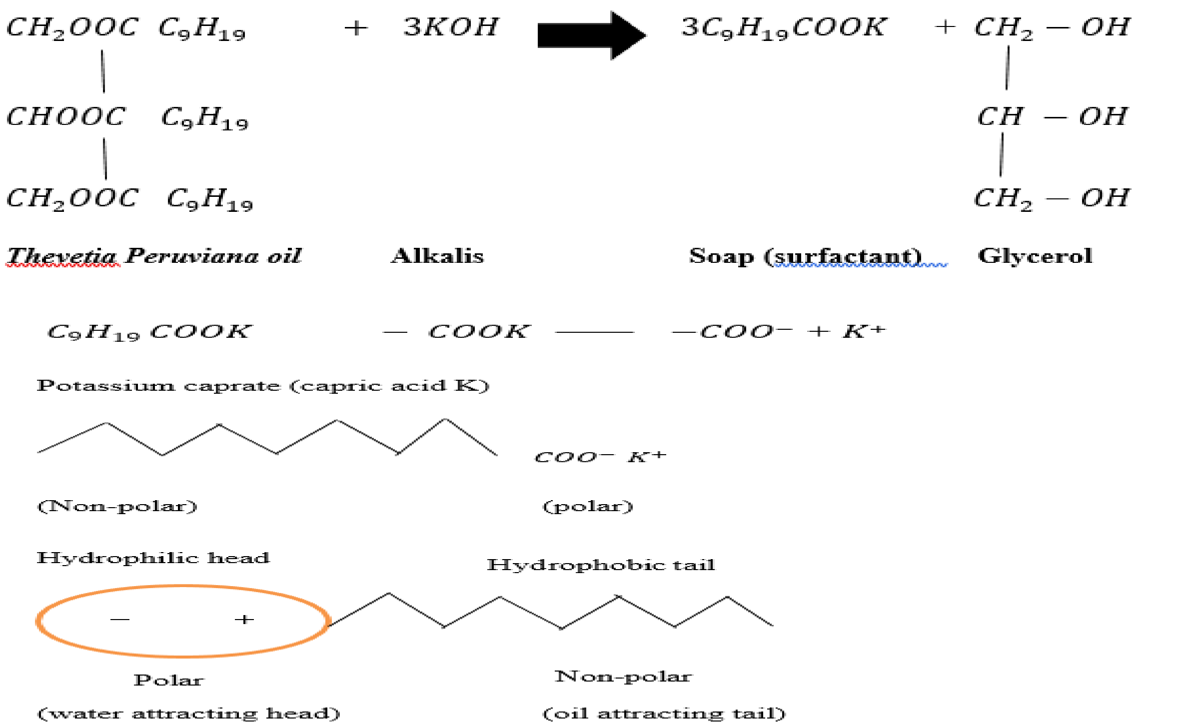

Figure 5 Saponification Reaction (Formulation of New Surfactant)

Characterization of New surfactant

Fourier Transform Infrared Spectroscopy Test

FTIR test was carried out on the formulated surfactant to determine its functional group. FTIR machine was warmed

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for fifteen minutes. It was dried of water so that the potassium chloride (KCl) plates will not be affected. The plate was thoroughly cleaned with acetone. Using a syringe pipette, a drop of the surfactant was placed in the potassium chloride (KCl) plate. The chloride plate was attached to a Fourier Transform Infrared Spectrometer coupled to a computer. The surfactant in the plate was irradiated by infrared lamp source at one end of the spectrometer and the sample was analyzed between the ranges of 600cm^{-1}- 4000cm^{-1}.

X-ray Fluorescence (XRF) Test

XRF was carried out on the formulated surfactant to determine the elemental composition of the material. The composition of the material will help to know the type of reservoir the sample could be suiltable for use in surfactant flooding.

Results and Discussion

Table 1 Physicochemical properties of the *Thevetia Peruviana* Oil

Property	Values	American Society for Testing and Materials (ASTM)
Saponification value (mg KOH/g of oil)	218.79 mg/100g	> 150 mg/100g
Acid value	28.05 mg/g	2mg/g-35mg/g
Iodine value	9.39 mg/L	5mg/L-30mg/L
Free Fatty Acid (F.F.A)	14.03 mg/L	>2.5 mg/L
Specific gravity	0.90 g/cm^3	> 0.5 g/cm^3
Colour	Golden yellow	-
pH	4.04	> 2
Viscosity at room temperature (˚C)	31 Cp	> 20 Cp
Odour	Unpleasant	-
Density	0.88406 g/cm^3	> 0.35 g/cm^3
Oil yield	61.3 %	> 30%

Table 1 showed the result of the characterization of the *Thevetia Peruviana* oil. The results showed that the saponification value was 218.79 mg/100g and meet the standard as prescribed by the American Society for Testing and Materials (ASTM). Saponification analysis is the key parameter to consider for formulation of surfactant. The result of the saponification value showed that the formulated surfactant will exhibit a good surface acting agent to break the surface tension between two molecules (water and oil) in surfactant flooding process. The saponification result showed that the higher the value, the more effective the ability of the surfactant to reduce the interfacial tension between two fluids (oil and water) which can help to break the capillary forces and help the trapped oil that remained in the reservoir to be mobile to flow into the production well, hence improved oil recovery. In addition, the pH. of the oil was 4.04 (that is acidic) while the acid value was calculated to be 28.05 mg/g. The result of the acid value showed that the sample (*Thevetia Peruviana)* have high acid content with free fatty acid as 14.03 mg/g. The acid value fall within the range of American Society for Testing and Materials (ASTM) standard. The iodine value was noted to be 9.39 mg/L while the viscosity at room temperature was observed to be 31 ˚C which showed that the surfactant is less viscous and can flow in the porous media (core-flooding process). More so, the oil yield was calculated to be 61.3% which showed good percentage of oil extraction recovery.

Results of the formulated surfactant

Figure 6 showed the sample of the formulated surfactant. The formed surfactant has the ability of reducing the surface tension between two fluids (water and oil) because of the hydroxyl group (OH) present in it based on the FTIR test. The OH group shows the hydrophilic properties of the material (that is, the oxygen atom has higher electronegativity to the hydrogen atom creating a negative charge (anionic), which suggests that the formulated surfactant has the capacity of altering the rock wettability from oil-wet to water-wet which is the main mechanism for surfactant flooding process. The formulated surfactant (in form of detergent) was observed to be soluble in water. The formation of micelles (cloudy soapy water) was also observed. The new surfactant was observed to be slippery and foamed when mixed with water.

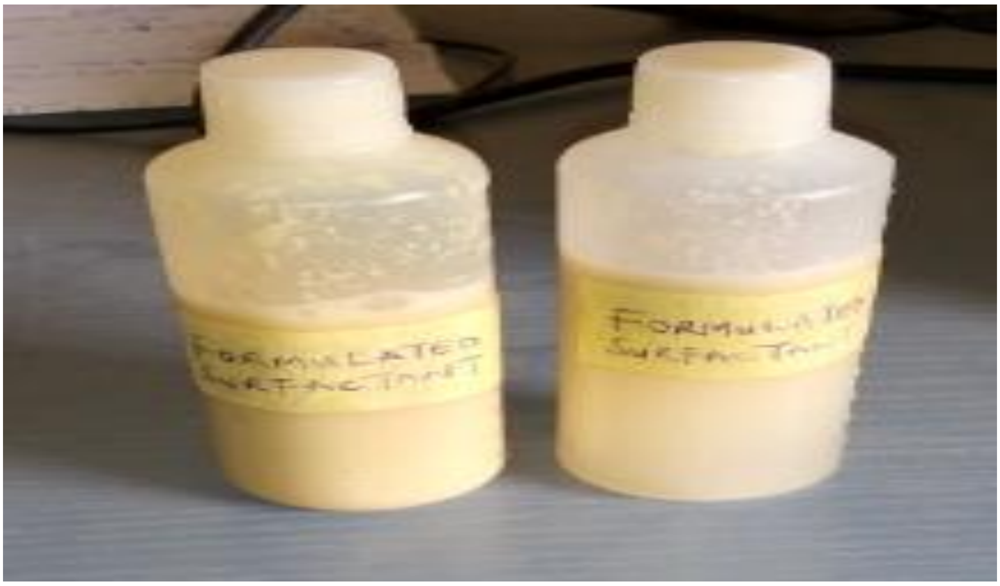

Figure 6 Formulated surfactant

Fourier Transform Infrared Spectroscopy (FTIR) Test Result

Table 2 Functional Groups and modes of vibration in the spectra (formulated surfactant)

S/no	Frequency (cm^{-1})	Vibrational mode	Functional group assignment
1	2950.5	Stretching	C-H
2	2900.3	Stretching	OH
3	2850.1	Stretching	O-CH
4	1700.6	Stretching	COOH
5	1500.3	Stretching	COOH
6	1400.0	Stretching	OH
7	700.2	Bending (out-of-plane)	CIS-C-H

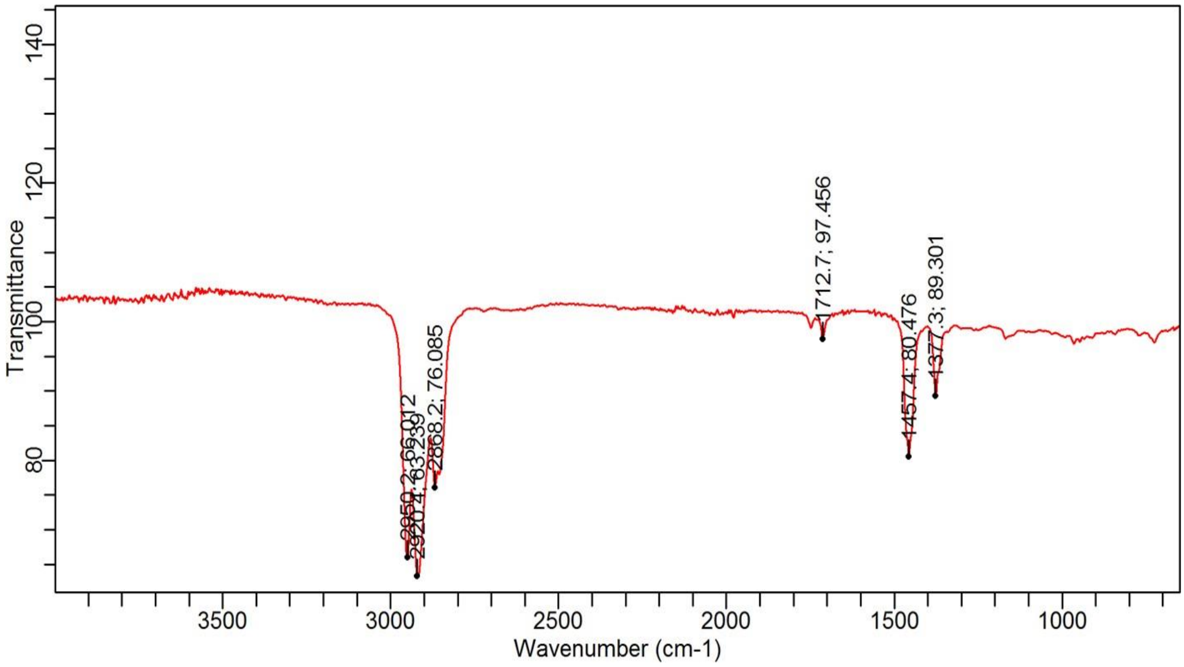

Figure 7 Functional group of the formulated surfactant

Figure 7 and Table 2 was the Fourier transforms infrared spectroscopy (FTIR) test result of the formulated surfactant. As observed in table 4.9, the band located at the spectrum region of 2950-2900 cm^{-1} is associated with the stretching vibration of OH and C-H (carboxylic group). At band location of 2850 cm^{-1}, is associated to stretching vibration of O-CH in ether group while the band around 1500-1700 cm^{-1} correspond to the stretching vibration of carboxylate (carboxylic acid salt) and hydroxyl group (COOH and OH). In addition, stretching vibration at 700.2 cm^{-1} in CIS-C-H was observed to be out of plane bending.

Results of the X-ray Fluorescence (XRF)

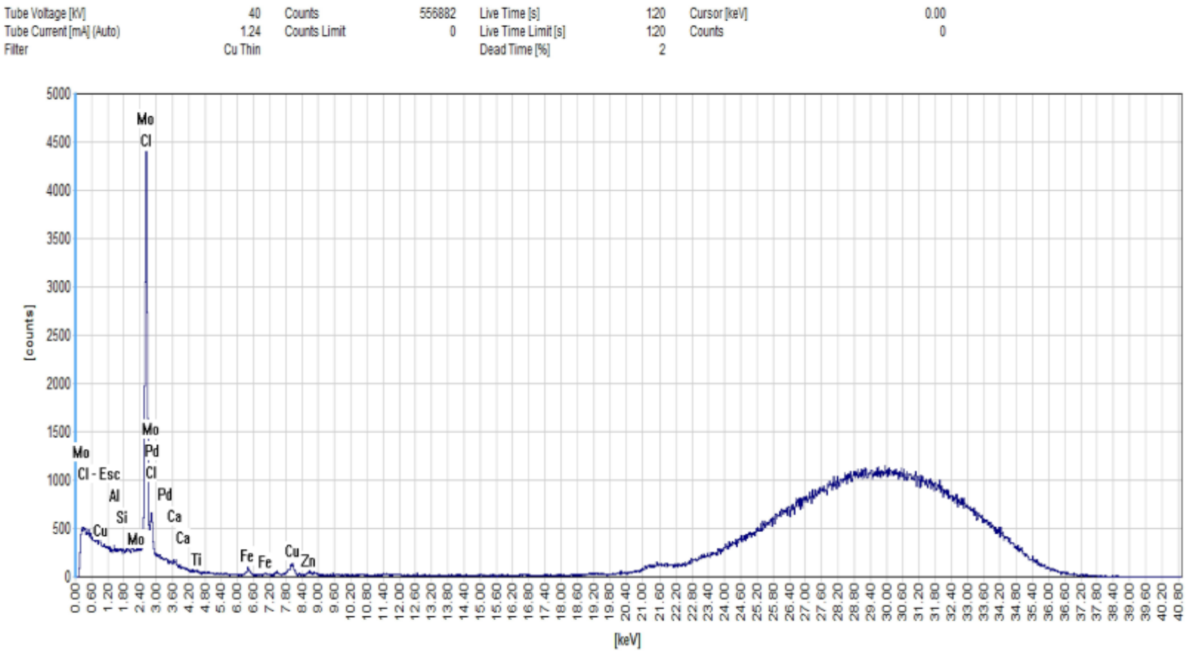

Figure 8 XRF of the Formulated Surfactant

The XRF result of the formation showed the presence of the chemical composition of silicon, chlorine, magnesium, iron, copper and zinc as the major element. This suggest that the surfactant will be effective in sandstone reservoir (Figure 8).

Conclusions

i. *Thevetia Peruviana* seeds showed high percentage of oil yield (61.3%).
ii. The extracted oil has high saponification value of (218.79 mg/100g) which showed potential of surfactant formulation.
iii. Characterization of the formulated surfactant showed the stretching vibration of OH (hydroxyl group) and COOH (carboxylic group) which suggest anionic surfactant with negative charge and hydrophilic head group.
iv. The results of the XRF showed that the formulated surfactant will be effective in sandstone formation.

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Conflicts of interest: There are no conflicts to declare.

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