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Enhancing Oil Recovery through Wettability Alteration of Sand Aggregates using a Surfactant derived from Bitter leaf Sap

Igoru U.A[*1], Ogbue M[1], Agbabi P.O[1], Eboibi B.E[2], Oghenejoboh K.M[2]

[1]Department of Petroleum Engineering, Faculty of Engineering, Delta State University, Nigeria.
[2]Department of Chemical Engineering, Faculty of Engineering, Delta State University, Nigeria.

*Corresponding Author: ufuomaigoru@delsu.edu.ng

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ABSTRACT

Wettability alteration of the reservoir rocks using surfactant flooding is one of the mechanisms for enhanced oil recovery (EOR). However, due to issues with the cost and environmental factors of conventional chemical surfactants, research has led to the development of biobased surfactants. The performance of 100%, 50% and 25% concentrations of bitter leaf sap(BLS) surfactant in oil recovery was utilized in this research paper through the use of core displacement tests as well as qualitative and quantitative analysis. Experiments included water flooding, oil flooding, and tertiary recovery using 100%, 50% and 25% concentrations of surfactant derived from BLS. The study was carried out using a peristaltic pump for fluid injection, samples were examined using SEM, FTIR, XRD, and XRF analytical techniques in accordance with ASTM guidelines. The findings demonstrated that employing 100%, 50%, and 25% concentrations of BLS for tertiary recovery produced cumulative recoveries of 84%, 78%, and 87% respectively. The bitter leaf sap proved to be a highly effective EOR agent, achieving recovery factors of 71%, 77% and 60% at concentrations of 100%, 50% and 25%, respectively. The displacement efficiencies of 42%, 39%, and 43%, of bitter leaf sap show promise in optimizing overall oil recovery processes. The findings suggest that bitter leaf sap has strong potential for oil mobilization and recovery, particularly in reducing interfacial tension and improving oil displacement.

Keywords: Bitter leaf sap; Enhanced oil recovery; Sand aggregates; Wettability; Wettability alteration.

1. Introduction

The ability of one fluid to spread across or stick to a solid surface over another immiscible fluid is referred to as "wettability". Numerous scientific fields are very interested in this phenomenon, including the oil and gas industry, dentistry, textiles, corrosion control, and, most importantly, oil and gas production from natural hydrocarbon reservoirs (Noruziet al. 2024).Three phases, comprising any combination of two immiscible liquids and a gas, two immiscible liquids and a solid, or three immiscible liquids and a gas, are typically associated with wettability (Nicholas et al. 2017). Wettability alteration could be described as the process of injecting external fluids into the reservoir to restore its original wettability, which is assumed to be water-wet. The goal of this restoration treatment is to recover the unrecoverable oil through convectional water flooding (Mohammed et al.2015).

Currently, wettability is adjusted through the use of surfactants, nanoparticles, and polymers. Since these are synthetic substances, they do not biodegrade easily and may react with formation minerals (Wang et al.2023) which will cause damage to reservoirs, pollute groundwater and destroy the ecological environment of reservoirs. In addition to their harsh environmental impact, these inorganic solvents are also very expensive and not readily available (Yayoo et al. 2021). In recent years, there has been a growing interest in using natural substances to modify wettability. This research shift is being driven by the need for environmentally friendly and economically viable solutions in the petroleum industry. Smith et al. (2019) investigated the wettability alteration properties of a bio-based surfactant derived from plant extracts, focusing on its ability to modify the surface characteristics of oil-wet sandstone cores. The study reported that the surfactant which is a saponin extracted from the Quillaja saponaria plant, commonly known as the soapbark tree reduced the contact angle from 135° (oil-wet) to 45° (water-wet), indicating a significant shift in wettability. The surfactant was tested in core flooding experiments, where it achieved a 25% increase in oil recovery after secondary water flooding, compared to a 15% increase observed with a conventional chemical surfactant under similar conditions. The bio-based surfactant also reduced the interfacial tension between oil and water from 30 mN/m to 5 mN/m, facilitating better oil displacement and oil recovery was improved. Mandel et al.(2011) examined the suitability of a naturally occurring surfactant extracted from soap nut shells for enhanced oil recovery. Their study revealed that as the concentration of soap nut powder increased, the surface tension of the surfactant solutions decreased significantly, both in hot and cold-water extractions. In hot water extractions, the surface tension decreased from 72 mN/m at a 0.5% concentration to 32 mN/m at a 2.5% concentration. Similarly, in cold water extractions, the surface tension dropped from 75 mN/m at a 0.5% concentration to 35 mN/m at a 2.5% concentration Shadizadeh et al. (2012) investigated the interfacial tension (IFT) between an oil solution and a natural surfactant derived from Seidlitzia rosmarinus. Their study demonstrated that as the concentration of the Seidlitzia rosmarinus surfactant increased, the oil-water interfacial tension decreased significantly. Specifically, at a low concentration of 0.05 wt%, the IFT was recorded at 15.8 mN/m. As the concentration increased to 0.1 wt%, the IFT dropped to 8.9 mN/m. Further increasing the concentration to 0.5 wt% resulted in an even more substantial reduction, bringing the IFT down to 2.1 mN/m. Ahmadi et al. (2015) investigated the effectiveness of a

natural surfactant derived from the roots of Glycyrrhiza glabra for enhanced oil recovery. They assessed the wettability alteration of oil-wet surfaces using both qualitative and quantitative methods. The results showed that the natural surfactant was able to reduce the oil-wetness of the surfaces but was not sufficient to completely change the wettability to a water-wet state. Quantitatively, the contact angle measurements indicated a reduction from 150° (strongly oil-wet) to around 90° (neutral-wet), demonstrating that while the surfactant reduced oil-wetness, it could not achieve a full transition to water-wet conditions. Mehdi et al. (2015) conducted an in-depth study on the impact of natural surfactants derived from Mulberry and Henna plants on interfacial tension (IFT) reduction and wettability alteration, their research demonstrated that both Mulberry- and Henna-derived surfactants effectively reduce IFT between kerosene and distilled water, which can facilitate the mobilization of trapped oil in reservoirs. Their results show that as the concentration of Mulberry surfactant increased, the IFT between kerosene and water decreased significantly, dropping from an initial value of 43.9 mN/m to 4.01 mN/m at a concentration of 10 wt%. Khorram et al. (2015) studied the feasibility of three types of plants based on natural cationic surfactants, named Olive, Spistan, and Prosopis. They investigated the effect of these natural surfactants on the interfacial tension of oil and water systems and their results showed increasing natural surfactant concentration reduces the interfacial tension between Kerosene (Oil phase) and distillated water. Ahmadi et al. (2024) examined the impact of a natural surfactant extracted from the Vitex agnusplanton the wettability alteration of both carbonate and sandstone rocks. Their results indicated that the application of the Vitex gnus surfactant resulted in a substantial change in contact angle measurements, decreasing from approximately 150° (oil-wet) to 45° (water-wet) in carbonate rock and for sandstone rock, the contact angle shifted from 110° (moderately oil-wet) to 30° (strongly water-wet) after treatment with the Vitex agnus surfactant.

However, while all the aforementioned research has demonstrated the effectiveness of various natural surfactants in altering wettability and reducing interfacial tension (IFT) in different reservoir types, the transition to a fully water-wet state was not always achieved, indicating a need for further investigation into more effective natural surfactants. Also, the application of Bitter leaf sap (BLS) as a surfactant has not been extensively studied in these contexts, in terms of its performance across various concentrations and its impact on different reservoir types, such as sand aggregates. Therefore, further research is necessary to evaluate the efficiency of bitter leaf sap in altering wettability, and enhancing oil recovery in sand aggregate reservoirs, potentially comparing its performance with other plant-based surfactants to determine its suitability as an effective alternative in EOR processes. Therefore, this study aims to obtain data on the potential of BLS and its impact on oil recovery in sharp sand reservoirs. The study would verify if BLS can effectively alter the wettability of sharp sand samples; elucidate the relationship between the concentration of BLS and the volume of the original oil in place recovered; and Quantify recovery efficiency from wettability altered grain sand using BLS as the wettability alteration agent.

2. Materials and Methods

2.1 Samples Preparation

The materials used in this study include bitter leaf, crude oil, and sharp sand. The bitter leaf sample (Vernonia amygdalina) was collected from Abraka, Nigeria. The collected bitter leaves were washed to remove dirt and were pounded into a fine paste using a mortar and pestle. The obtained fine paste was squeezed via a fine cloth to extract the sap, referred to as BLS. The obtained BLS was used immediately for laboratory studies. The dried sample of the bitter leaf was dried to constant weight and kept in an airtight container before analysis. The sharp sand sample was collected from Oleh, Nigeria, and washed under running distilled water for 10 minutes to remove contaminants. Following washing, the sand was sun-dried for 14 days. Drying the sand was essential to remove all moisture content, which could affect its properties and performance in laboratory experiments. Dried sharp sand samples were filtered to remove heavy particles thereby improving the quality of the sand and facilitating the sieving process. The filtered sand samples were sieved into two grain sizes of 1.118 cm and 0.06 cm to ensure that the sand particles were in uniform size. The crude oil was obtained from an oil well X in Olomoro, Delta State, Nigeria.

2.2 Experimental procedure

The experimental study was conducted under procedures described by Lake et al. (2023). Briefly, the experimental setup for fluid injection and collection involved a securely fixed peristaltic pump, which operates by squeezing a flexible tube to create a vacuum, drawing fluid through the tube. A hose was connected at one end to the core via a pipe, allowing fluid from the core to flow into the hose. The other end of the hose was placed inside a conical flask, which served as the collection vessel for the extracted fluid. The core was clamped horizontally in place using a retort stand to ensure stability and prevent any disruptions during the fluid extraction process. A schematic view of the experimental set-up for water flooding, secondary recovery, and tertiary recovery is shown in Figure. 1

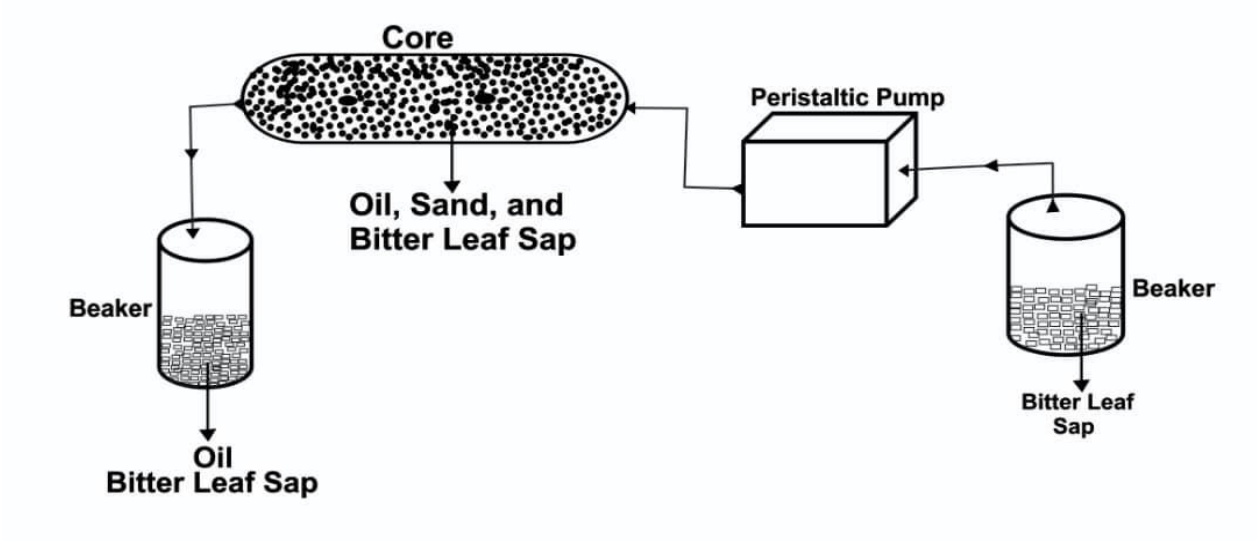


Figure 1: Schematic view of experimental set-up. (Field source)

Water Flooding

Core Preparation: Core Sample A, made of water-wet sharp sand with a 0.118 cm grain size, was compacted to eliminate void spaces and ensure uniform flow, after which 150 cm^3 of water was measured and injected into the core using a peristaltic pump at 10 rpm. The pump was stopped when the first drop of water emerged, with 100 cm^3 remaining in the beaker, indicating 50 cm^3 injected.

Oil flooding

The core sample A was saturated with a precise volume of 100cm^3 of crude oil. The peristaltic pump was stopped when the first drop of oil was detected, similar to water flooding. The remaining crude oil volume in the beaker was recorded as 50cm^3.

Secondary Recovery (Water flooding)

Oil Displacement: An additional 150 cm^3 of water was pumped into the core to displace the crude oil. The volume of recovered oil was recorded as 25 cm^3 at the first water breakthrough.

Tertiary Recovery

Oil displacement with BLS: 100% concentration BLS was introduced to displace and recover the remaining oil. The pump was stopped upon the first BLS breakthrough, recording 10 cm^3 of displaced oil. This step was repeated with 50 % and 25 % BLS concentrations, and the volumes of recovered oil were measured. The entire sequence, including all steps and concentrations of BLS, was repeated for other core samples. The volume of oil recovered from each core was recorded for comparative analysis.

The bulk volume (V_1) of the core was estimated using Equation 1.

$$V_1 = \frac{\pi d^2}{4} \times L \quad (1)$$

where d represents the diameter of the core and L is the length of the core. The volume (V_2) of water pumped into the core was calculated using Equation 2.

$$V_2 = V_i - V_f \quad (2)$$

where V_i and V_f represent the initial volume before saturation and the final volume after saturation respectively. The porosity (ϕ) of the sharp sand in the core was calculated using Equation 3.

$$\phi = \frac{V_p}{V_1} \quad (3)$$

where V_p represents pore volume and V_1 is the bulk volume of the core. The original saturation of water (S_{wo}) was estimated using Equation 4.

$$S_{wo} = \frac{V_2}{V_p} \quad (4)$$

where V_p represents pore volume and V_2 is the volume of water pumped into the core. The volume (V_3) of oil used in flooding the core was estimated using Equation 5.

$$V_3 = V_{oi} - V_{of} \quad (5)$$

where V_{oi} and V_{of} represent the initial volume and final volume of oil respectively. The initial saturation of oil in the core sample (S_{oi2}) was estimated using Equation 6

$$S_{oi} = \frac{V_3}{V_p} \quad (6)$$

The initial volume of water in the core sample V_{wi} is equal to $V_2 - V_3 = V_4$,

V_5 is the volume of of water pumped into core sample, V_6 the volume of oil recovered from the core sample, V_7 is the volume of water displaced from the core sample. V_{or} is equal to V_3- $V_6 = V_8$ which is the residual volume of oil in the core sample. The residual saturation oil in the core sample was determined using $S_{or} = \frac{V_8}{V_p}$, while the residual volume of water in the core sample was estimated as $V_{wr} = V_9 = V_4 + V_5 - V_7$.

The residual saturation of water was estimated as $S_{wr} = \frac{V_9}{V_p}$

The volume of bitter leaf sap (BSL) pumped into the core is V_{11} while the volume of oil recovered was estimated as $V_{12} = V_B - V_{11}$. The irreducible oil saturation was estimated as $S_{oir} = \frac{V_{12}}{V_p}$ while the irreducible water saturation was estimated as $S_{wir} = 1 - S_{oir}$

The recovery factor (RF) was estimated using Equation 7.

$$Rf = \frac{V_{11}}{V_{or}} \quad (7)$$

Equation 8 was used to estimate the mobilization sweep efficiency, while Equation 9 was used to estimate the overall displacement efficiency.

Mobilization sweep efficiency $E_m = \frac{S_{or} - S_{oir}}{S_{or}}$ (8)

Overall displacement efficiency $E_v = \frac{V_a + V_{11}}{V_p}$

Phytochemical analysis of the dry bitter and its sap was conducted using UV-Visspectrophotometry (Shimadzu UV-1800) to investigate the presence of tannin, terpenoid, glycoside, phenols, flavonoids, steroids, saponin, alkaloid, carbohydrates, proteins, amino acids, phlorotannin, and cardiac glycosides. FTIR analysis (PerkinElmer Spectrum 2) was used on dry bitter to identify functional groups relevant to wettability alteration. XRD analysis (Bruker D8 Advance) was performed on sharp sand to determine mineral composition, while XRF (PANalytical Epsilon 3) quantified elemental contents. Crude oil properties such as the API, specific gravity, density, pour point, asphaltene content, and carbon residue viscosity were measured using a Brookfield DV-II+ Pro viscometer, and sulfur content was determined using ASTM D4294 with an XRF analyzer. Core flooding experiments employed a peristaltic pump (Watson-Marlow 120S/DV) to investigate oil recovery using bitter leaf sap at varying concentrations, with oil displacement and recovery quantified by gravimetric analysis. Scanning electron microscopy (SEM) was performed to examine the structural morphology of the dry bitter leaf using an SEM model Phenom ProX by Phenom-World, Eindhoven.

3. Results and Discussion

3.1 Results of the Qualitative and Quantitative Analysis

The qualitative phytochemical analysis of dry bitter leaf and its sap as presented in Table 1. Compounds across studies include steroids, phenols, xanthoproteic compounds, flavonoids, alkaloids, triterpenoids, glycosides, and saponins, highlighting their stability in both dry and sap forms. Terpenoids showed variability, being absent in some reports (e.g., Okeke *et al.*(2015); Ogunlade *et al. (*2022). While Phyto steroids were absent in this study and Ruth *et al.* (2021), they were detected in other studies, suggesting potential geographic or methodological differences. Phlobatannins and fats were mostly absent, indicating they are not major components, while carbohydrates showed mixed results, being absent in this study but variably present in others. This result aligns with previous studies by Ruth *et al*. (2021), Ojeaga *et al*. (2021), Okeke *et al.* (2015).These findings emphasize that environmental conditions, extraction methods, and preparation techniques influence the detected phytochemical profiles.

Table 1: Qualitative Phytochemicals Analysis for Dry Bitter Leaf and Sap

Parameters	Dry leaf	Sap	References						
	Present study		Ruth et al. (2021)	Ojeaga et al. (2021)	Okeke et al.(2015)	Ogunlade et al. (2022)	Owolabi et al. (2022)	Oyeyemiet al. (2014)	Clement et al. (2022)
Steroid	+	+	+	+	+	+	+	+	+
Alkaloid	+ +	+	++	+	+	+	+	+	+
Terpenoid	+	+	+	-	-	+	+	-	+
Saponin	+	+	++	+	+	+	+	+	+
Triterpenoid	++	++	++	+	+	+	+	+	+
Phytosteroid	-	-	+	+	+	+	+	+	+
Phlobatannins	-	-	-	+	-	-	-	-	
Iodine (Carbohydrates)	-	+	+	+	-	+	+	-	-
Phenol	+	+	+	+	+	+	+	+	+
Xanthoproteic	+	+	+	+	+	+	+	+	+
Benedict's (Carbohydrate)	-	+	+	+	+	+	+	+	+
Fehling's (Flavonoids)	+	+	+	+	+	+	+	+	+
Alkaline Reagent	++	++	+	+	+	+	+	+	+
Stain (Fix fat and oil)	-	-	+	-	+	+	-	-	+
Gelatine (Tannin)	+	-	+	+	+	+	+	+	+
Keller Killanis (Glycoside)	++	++	+	+	+	+	+	+	+

++: abundantly present, +present, -:absent

Table 2 provides a comparative analysis of the quantitative phytochemical content in dry bitter leaves and sap. The variations observed in phytochemical content between dry bitter leaf and its sap, as well as comparisons with other studies, show that tannins are higher in the sap (0.463 mg/tannin) compared to the dry leaf (0.329 mg/tannin), though Ojeaga *et al.* (2021) reported a much higher value (12.33±0.01 mg/tannin). Flavonoids concentrated more in the sap (7.706 mEq/QE) than in the dry leaf (5.323 mEq/QE). Ojeaga *et al.* (2021) recorded 18.00±0.02 mEq/QE. Phenolics are higher in the sap (11.235 mEq/GAE) than in the dry leaf (7.72 mEq/GAE), with Ojeaga et al. (2021) reporting 44.76±0.02 mEq/GAE. Carbohydrates have a greater concentration in the sap (10.899 mg/glucose) compared to the dry leaf (8.122 mg/glucose), aligning with Okeke et al. (2015). Alkaloids are higher in the dry leaf (10.604) compared to the sap (8.305). Saponins are more abundant in the sap (5.823) than in the dry leaf (3.837). Lipids are slightly higher in the sap (3.230) than in the dry leaf (2.880).Proteins are higher in the sap (9.563 mg/100 g) than in the dry leaf (7.649 mg/100 g).Steroids were consistent across samples, with slightly higher content in the sap (0.420) than in the dry leaf (0.363).

Table 2: Quantitative Phytochemicals Analysis for Dry Bitter Leaf and Sap

Parameters	Dry leaf	Sap	References		
	Present study		Ruth*et al* (2021)	Ojeaga*et al* (2021)	Okeke*et al* (2015)
Tannim(mg/tannin)	0.329	0.463	12.33±0.01	-	-
Flavonoid(mEq/QE)	5.323	7.706		18.00±0.02	-
Phenolic Content (mEq/GAE)	7.72	11.235	44.76±0.02	-	-
Total Carbohydrate (mg/glucose)	8.122	10.899	-	10.00±0.02	-
Reducing Power (mg/glucose)	4.907	14.589	3.43±0.01	-	-
Total alkaloids	10.604	8.305	5.76±0.01	-	-
Saponin	3.837	5.823	-	6.00±0.05	-
Lipids	2.880	3.230	-	-	2.72+0.00
Protein (mg/100 g)	7.649	9.563	-	5.20±0.02	-
Steroids	0.363	0.420	0.30±0.01	-	-

3.2 Results of the FTIR Analysis of Dry Bitter Leaf

The FT-IR analysis of dry bitter leaf identifies several functional groups that can influence wettability as shown in Figure 2. O-H stretching (3257.7 cm^{-1}) indicates alcohols, phenols, or carboxylic acids, contributing to hydrophilicity (Zhao *et al.* 2020). C-H stretching (2918.5 cm^{-1}, 2847.7 cm^{-1}) reflects aliphatic hydrocarbons, suggesting the presence of alkanes. C≡C stretching (2105.9 cm^{-1}, 1919.6 cm^{-1}) represents alkynes or combination bands. C=O stretching (1739.5 cm^{-1}) is found in carbonyl compounds (e.g., aldehydes, ketones), enhancing surface polarity and promoting water-wet conditions for better oil recovery (Zhang *et al*. 2021).C=C stretching (1648.0 cm^{-1}) is associated with alkenes or aromatic compounds, which can contribute to wettability alteration despite being non-polar (Guo *et al*. 2018). C-H bending (1452.0 cm^{-1}, 1373.8 cm^{-1}) is found in alkanes and methyl groups. C-O stretching (1247.5 cm^{-1}, 1095.8–1013.8 cm^{-1}) indicates alcohols, ethers, or esters, increasing hydrophilicity and facilitating water-wet conditions (Liang *et al*. 2019). The functional groups identified (hydroxyl, carbonyl, ether/ester) enhance surface hydrophilicity, promote water interaction, and shift the system from oil-wet to water-wet, facilitating enhanced oil recovery (EOR). Recent studies confirm the role of these groups in modifying surface properties, improving oil displacement efficiency (Zhang *et al.,* 2021; Zhou *et al*., 2022; Liu *et al*., 2020; Wang *et al*., 2023; Singh *et al.,* 2021).

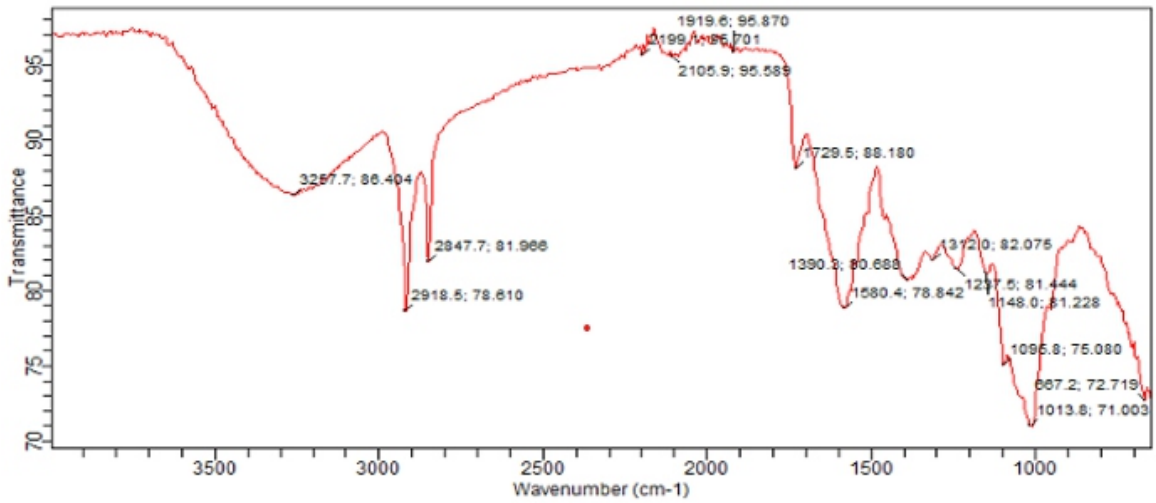


Figure 2: FTIR analysis of bitter leaf

3.3 Result of the XRD Analysis of Bitter Leaf

The X-ray diffraction (XRD) analysis of bitter leaf presented in Figure 3 reveals several crystalline phases, each identified by intensity peaks at specific angles (2θ). These phases include Periclase (MgO) which enhances water-wetness in reservoirs, improving fluid injection efficiency and boosting oil recovery (Xu *et al*. 2020). Zinc Aluminium Phosphate and Sulfates (Hanksite, Minoruzaite, Woodhouseite) modify the surface chemistry of reservoir rocks, promoting water-wet conditions that facilitate better oil displacement (Ju *et al.* 2020). Haggstattite (syn) and Hicksite are also present, contributing to the overall mineral profile of the sample. The presence of these minerals indicates the potential for wettability alteration, shifting the reservoir surface from oil-wet to water-wet, which is critical for improving the efficiency of enhanced oil recovery (EOR) processes.

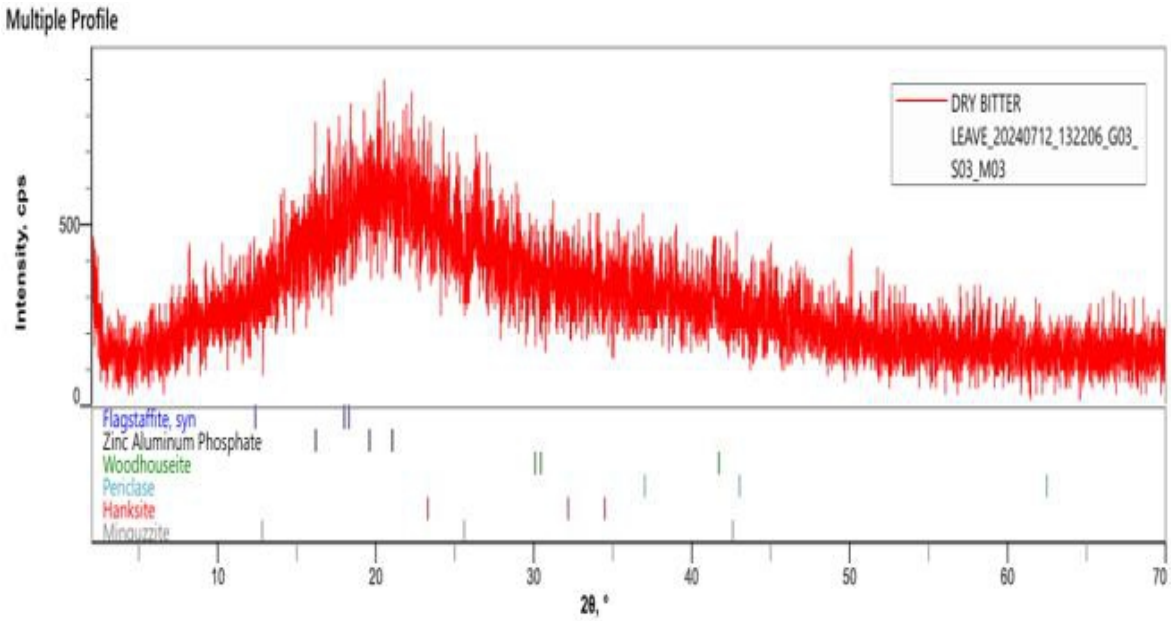


Figure 3: X-ray diffraction quantitative analysis spectrum for Bitter leaf

Figure 4 represents the phase data view from X-ray diffraction (XRD) analysis on dry bitter leaves. The x-axis represents the 2θ angle (degrees), and the y-axis represents the intensity (counts per second, cps). Different phases identified in the sample are marked with their respective peak positions. XRD Pattern: The red line represents the diffraction pattern of the sample, indicating the presence of various crystalline phases. The intensity peaks correspond to specific d-spacing values that can be used to identify the mineralogical phases present in the sample. Identified Phases: Flagstaffite (syn): Blue, Zinc Aluminium Phosphate: Green, Woodhouseite: Aqua, Periclase: Black, Hanksite: Red, Minguzzite: Cyan. The colour-coded markers at the bottom show the peak positions for each identified phase, which correspond to the peaks in the red diffraction pattern.

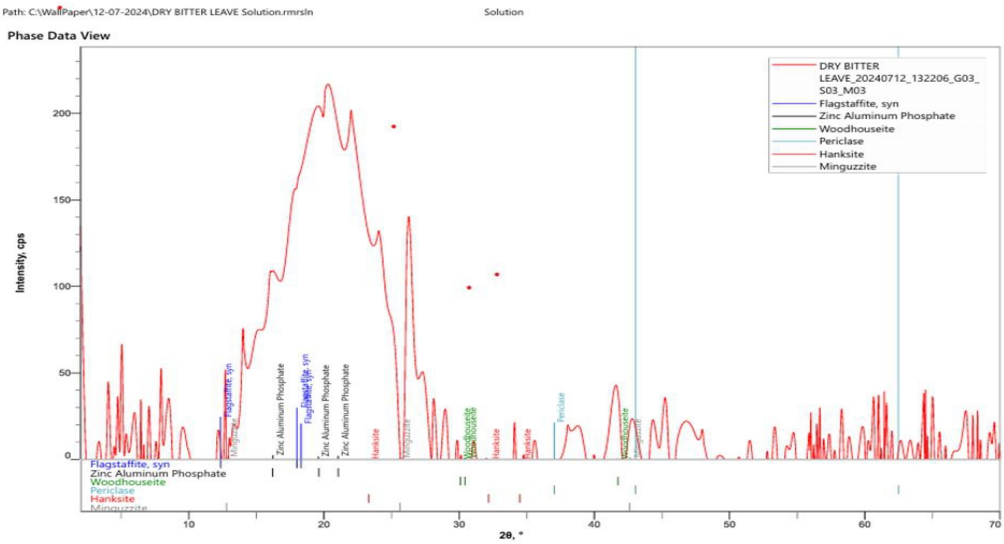
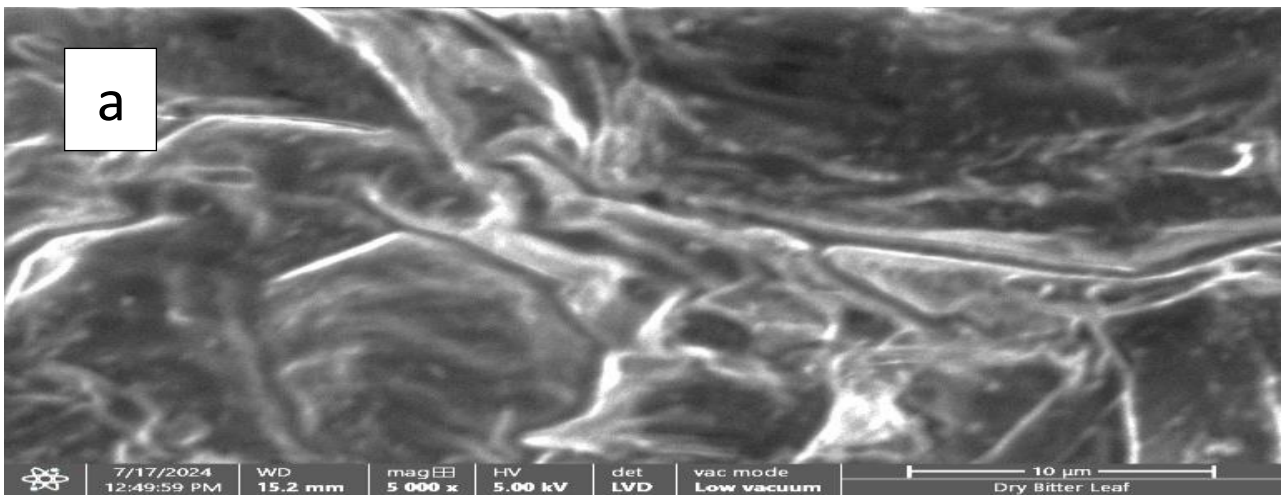


Figure 4: Phase Data view from X-ray diffraction (XRD) analysis on dry Bitter leaf

The identified phases of the XRD analysis include Woodhouseite ($CaAl_3(PO_4)(SO_4)(OH)_6$), Periclase (MgO), Hanksite ($Na_{22}K(SO_4)_9(CO_3)2Cl$), and Zinc Aluminium Phosphate. These minerals possess distinct chemical and structural properties that can influence the wettability of reservoir rocks. Zinc Aluminium Phosphate, when present, is noted for being hydrophilic, which can potentially increase water wettability (Lashkarbolooki et al. 2013). Periclase (MgO), a reactive mineral, interacts with water and may enhance water-wet conditions. Hanksite, due to its sodium and potassium salt content, may influence ion exchange processes that affect wettability (Zhao et al. 2019). The structure of Woodhouseite, with its hydroxyl groups, can interact favorably with water, promoting water-wet conditions.

3.4 Results of SEM Analysis of Dry Bitter Leaves

Figure 5 (a to c) shows the SEM (Scanning Electron Microscope) micrographs of dry bitter leaves at varying magnifications (5000x, 1500x, 1000x, 250x, and 100x). This structure, with interconnected fibers and irregular surfaces, enhances the surface area, promoting interactions between bitter leaf extract and fluids to alter wettability from oil-wet to water-wet, crucial for EOR processes (Al-Mahdawi *et al.* 2023); Zhou *et al.* 2022); Yousef *et al*. 2023). The presence of functional groups like hydroxyl and phenolics supports adsorption onto rock surfaces, facilitating oil displacement (Zhang *et al.* 2022). The morphology suggests that BLS can act as an effective, natural surfactant, ensuring consistent wettability alteration across reservoir rocks, aligning with recent trends favouring eco-friendly bio-surfactants Wang *et al*., 2023; Moghadasi *et al*. (2022).



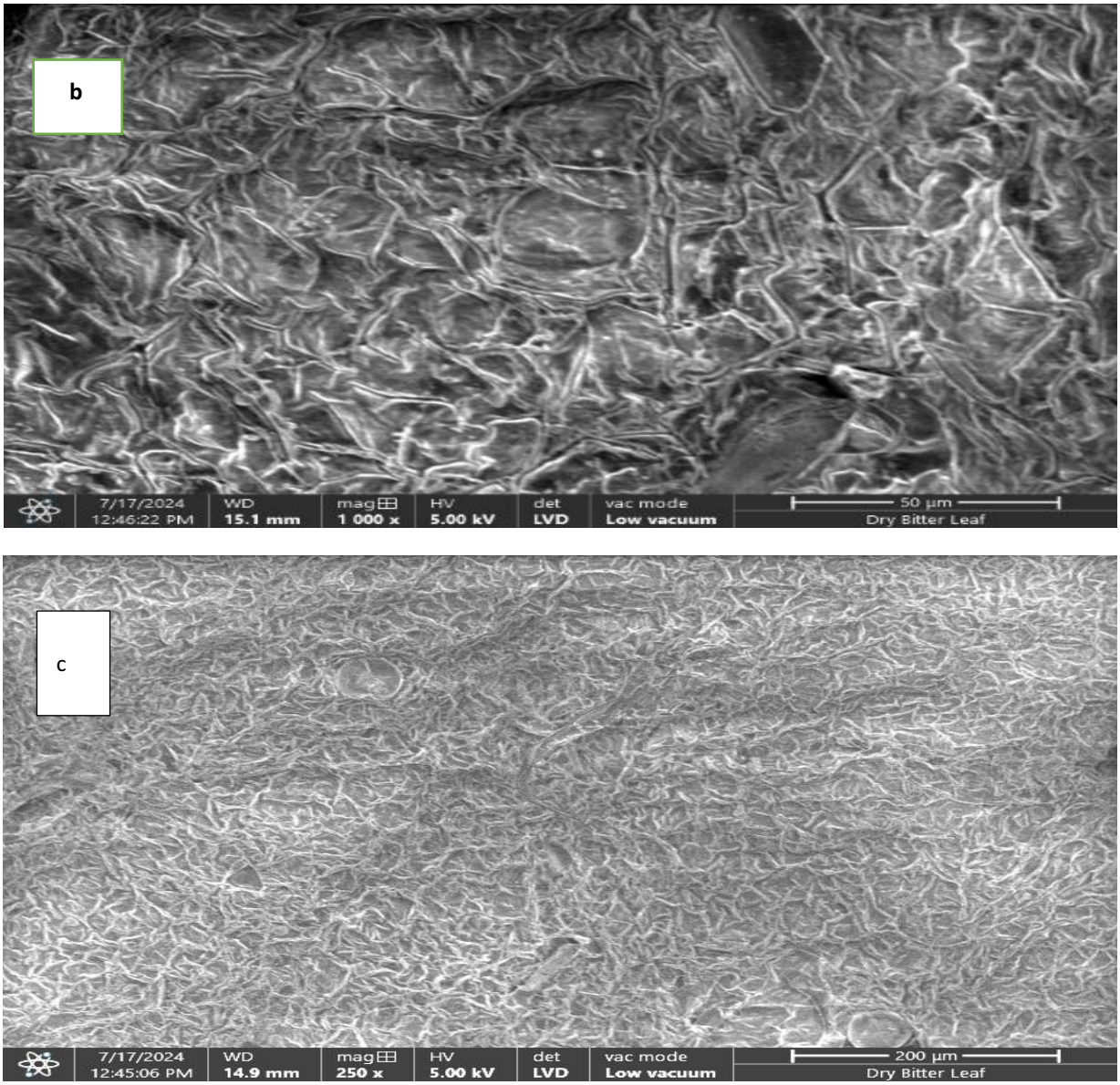


Figure 5: SEM Micrograph of dry bitter leaf at different magnifications (a: 10 m. b: 50 µm. c: 200 µm)

3.5 Result of XRF Analysis

Table 4 presents detailed results of the X-ray fluorescence (XRF) analysis of sharp sand, focusing on the composition of various components. As shown, SiO_2 is the dominant component, comprising 95.19% of the sand. This high percentage indicates that the sand is predominantly composed of quartz. Al_2O_3 accounts for 1.93%, while Fe_2O_3 is present at 0.52%, suggesting a minor presence of iron-bearing minerals. The CaO content at 1.16% indicates the presence of calcareous minerals, such as limestone fragments. MgO, with a 0.12% composition, likely reflects minor contributions from magnesium-bearing minerals. K_2O at 0.25% suggests the presence of feldspar or mica minerals. The silt content, at 0.18%, represents a very small fraction of fine-grained particles, indicating that the sand is quite clean and free from fine impurities, which is beneficial for construction and filtration purposes. Organic impurities make up 0.5%, indicating the presence of some organic material within the sand. The moisture content, at 0.15%, reflects the amount of water present in the sand.

Table 3: X-ray fluorescence Analysis on the sharp sand

S/N	Properties	Composition, %
1	SiO_2	95.19
2	Al_2O_3	1.93
3	Fe_2O_3	0.52
4	CaO	1.16
5	MgO	0.12
6	K_2O	0.25
7	Silt Content	0.18
8	Organic Impurities	0.5
9	Moisture Content	0.15

3.6 Physicochemical Analysis of Crude Oil

The data obtained from the physicochemical analysis of the crude oil is presented in Table 4. The table shows crude oil has an API Gravity of 17.80, indicating that it is a heavy crude. This classification is further supported by its specific gravity of 0.95 and density of 0.9 g/cm^3.

Table 4: Results of Physicochemical Analysis on the Crude Oil

S/N	Parameters	Composition
1	API Gravity	$17{\cdot}8^{o}$
2	Specific Gravity	0.95
3	Density	0.9g/cm^3
4	Sulphur Content	0.5%
5	Pour Point	12^{o}
6	Water Content	0.3%
7	Asphaltene Content	0.9%
8	Carbon Residue	8.0%
9	Viscosity	84.0pa.s

The Sulphur content was 0.5%, classifying the crude as sweet (Jones *et al. 2017*). The specific gravity of 0.95 confirms the heavy nature of this crude oil (Smith & Brown, *2018*), while the pour point of 12°C suggests that the oil has a high temperature below which it ceases to flow (Johnson & Lee, *2020)*. The water content is low at 0.3%, indicating minimal water contamination and good quality in this regard (Wang *et al.2019*). The asphaltene content is 0.9% (Garcia et al. 2016). The carbon residue, at 8.0%, is high and indicates that crude oil has a significant number of heavy components (Miller & Davis*, 2021).* The viscosity of the crude oil was 84.0 Pa.s, which is relatively high, indicating that the oil is quite thick and resistant to flow. This high viscosity is typical for heavy crudes (Chen & Zhao, *2022)*.

3.7 Performance Evaluation of Tertiary Recovery Using Bitter Leaf Sap (BLS)

The tertiary recovery using 100%, 50%, and 25% concentrations of BLS on Sample A (water-wet sharp sand) is presented in Table 5. The cumulative recovery (C.R) percentages, which represent the total amount of oil recovered as a percentage of the original oil in place (OOIP), are 84%, 78%, and 87% for bitter leaf sap at 100%, 50%, and 25% concentrations, respectively. These results outperform those obtained using Mulberry extract, which ranges from 57% to 63% as reported by Ravi et al. (2015), due to its unique combination of phytochemicals, including alkaloids, flavonoids, and saponins, which are more effective in altering the surface energy of the rock. This leads to a stronger shift from oil-wet to water-wet conditions. The natural surfactants in bitter leaf sap also exhibit higher surface activity, resulting in better reduction of interfacial tension and more effective displacement of oil from the rock surface. Additionally, bitter leaf sap contains a higher concentration of active components, such as saponins, that contribute to more efficient wettability modification. Its interaction with crude oil components may also be more favourable, leading to enhanced oil desorption from the rock surface. Furthermore, the viscosity of bitter leaf sap might allow it to penetrate more effectively into porous rock structures, improving wettability alteration. These values also outperform traditional enhanced oil recovery (EOR) methods such as polymer and surfactant flooding, which achieve cumulative recoveries of 50-70% of OOIP (Billa *et al*. 2019, Levitt *et al*. 2011). The significant cumulative recovery using BLS indicates its effectiveness as an EOR agent. Traditional EOR methods generally exhibit recovery factors ranging from 30-60%(Sheng, 2015).In comparison, the recovery factors of 71%, 77%, and 60% for BLS concentrations of 100%, 50%, and 25% respectively, suggest the potential for oil mobilization and recovery compared to many established methods. For example, polymer and surfactant flooding typically achieves mobilization sweep efficiencies between 50-70% (Levitt *et al*. 2011).The RF of 78%, 59.3%, and 76% using BLS of 100%, 50%, and 25% concentrations indicate higher efficiency, suggesting high effectiveness in reducing interfacial tension and improving oil displacement. The overall displacement efficiency for conventional methods typically ranges between 30-50%(Song *et al*. 2021). 42%, 39%, and 43% for BLS at 100%, 50%, and 25% concentrations place it within this range, indicating good performance in mobilization and recovery, with potential for optimization in the overall displacement process.

Table 5: Data obtained for Tertiary Recovery using 100%, 50% & 25% concentration BLS on Sample A (Water wet Sharp Sand)

Parameter	BLS concentration, %		
	100	50	25
Cumulative Recovery (CR)	84.00	78.00	87.80
Recovery Factor (RF)	71.00	77.00	60.00
Mobilization sweep efficiency (E_m)	78.00	59.30	76.00
Overall Displacement efficiency (E_v)	42.00	39.00	43.00

The results obtained for tertiary recovery using 100%, 50% and 25% concentrations of BLS with Sample A (oil-wet sharp sand) are presented in Figure 6. The table shows the cumulative recovery (CR) for BLS ranges from 75.50% to 87.23%, which is significantly higher when compared to traditional enhanced oil recovery (EOR) methods. For instance, polymer and surfactant flooding typically achieve cumulative recoveries in the range of 50-70% of the original oil in place (OOIP) (Billa *et al*. (2019). The use of C. *myxa* leaf extract yields 27% of OOIP as reported by Jalali *et al*. (2019)**.** The high cumulative recovery observed with BLS indicates its superior efficiency in mobilizing and recovering oil. The recovery factor (RF) for BLS ranges from 71.43% to 77.00%. This is also higher than the recovery factors achieved with conventional methods, which typically between 30 and 60% (Sheng, 2015). This finding shows that recovery factors obtained from BLS suggest its potential as an effective EOR agent. Furthermore, the mobilization sweep efficiency for BLS varies between 60.00% and 76.93%. Yang *et al*. (2018) reported that traditional polymer and surfactant flooding methods usually achieve sweep efficiencies in the range of 50-70%, which is within the range of the present study. The higher mobilization sweep efficiency with BLS favours better oil displacement and reduced interfacial tension, which enhances oil recovery. The overall displacement efficiency for BLS was observed for 33.64 to 45.56%. This is comparable to the overall displacement efficiencies of conventional methods, which typically range between 30-50% (Song *et al*. 2021). Although BLS has shown good performance, further study is necessary in terms of optimization in the displacement process.

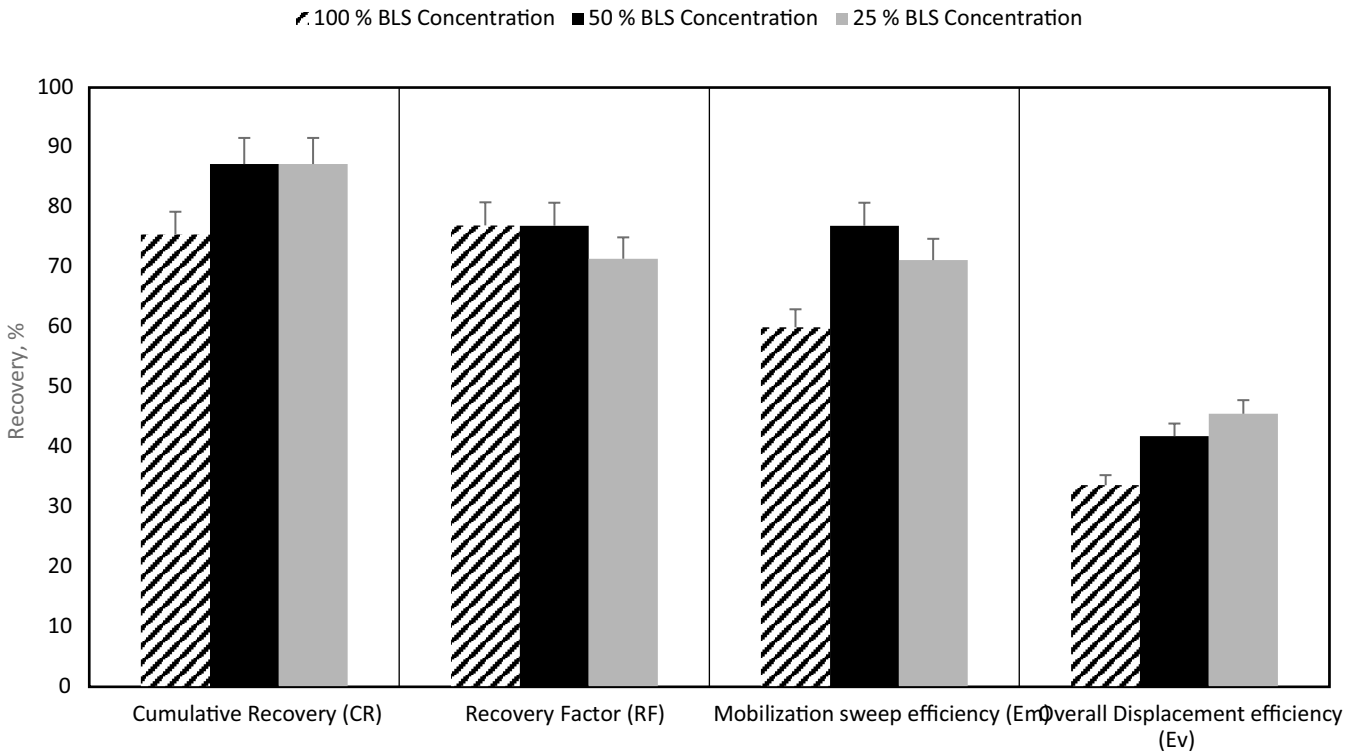


Figure 6: Data obtained for Tertiary Recovery using of 100%, 50%, and 25% concentration of BLS on Sample A (Oil wet Sharp Sand)

Figure 7 compares the cumulative recovery for Sample A at the end of tertiary recovery using 100%, 50%, and 25% concentrations of Bitter Leaf Sap in both water-wet and oil-wet conditions. From Figure7, it can be seen that 100% concentration of Bitter Leaf Sap yielded the highest cumulative recovery for both water-wet and oil-wet conditions, this is in line with the research by Liu et al. (2022) who demonstrated that higher concentrations of natural surfactants generally lead to improved oil displacement efficiency. The 50% concentration shows a noticeable drop in recovery compared to the 100% concentration, indicating that dilution significantly affects the effectiveness of Bitter Leaf Sap as a recovery agent. The 25% concentration, while still providing some recovery, is the least effective, further highlighting the concentration dependence of the Bitter Leaf Sap's efficacy. The recovery for both water-wet and oil-wet conditions follows a similar trend concerning concentration, though the exact recovery values differ. This suggests that while wettability influences the absolute recovery values, the relative performance of Bitter Leaf Sap concentrations remains consistent across different wettability conditions.

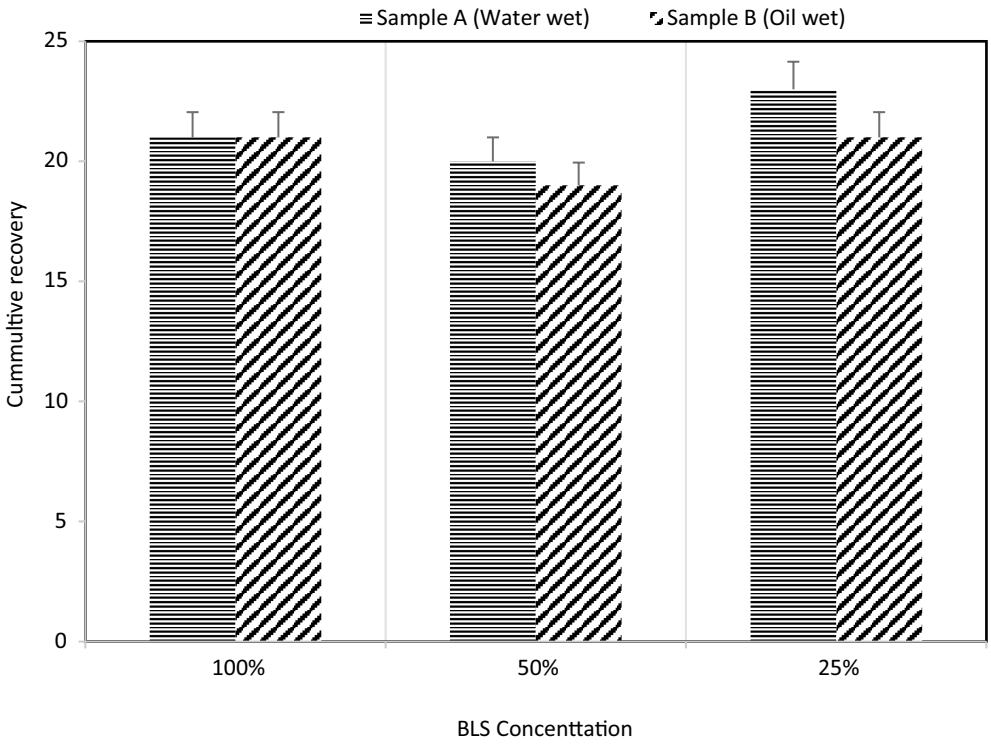


Figure 7: Comparison of cumulative recovery for sample A (Water wet and Oil wet) at the end of tertiary recovery from different BLS concentrations of 100% 50% and 25%.

Figure 8 compares the recovery factor for Sample A (both water-wet and oil-wet conditions) at different concentrations (100%, 50%, and 25%) of BLS. From the figure, it can be seen that 100% BLS concentration under water-wet conditions has a relatively high recovery factor. This finding suggests that a full concentration of BLS is effective in enhancing oil recovery in water-wet conditions. Also, under oil-wet conditions, the recovery factor is similarly high, though not slightly lower than in the water-wet condition. This suggests that while the sap is effective in both conditions, its efficiency might be marginally better in water-wet scenarios.50% BLS concentration. The water-wet conditioned to a noticeable drop in the recovery factor compared to the 100% concentration. This indicates a dilution effect, where the lower concentration of the sap is less effective in mobilizing the oil. The oil-wet condition is also similar to the water-wet condition, 13the recovery factor decreases, emphasizing that the concentration of the sap is crucial for optimal recovery. A 25% BLS concentration under water-wet conditions further decreases the recovery factor, showing that the 25% concentration has the least impact on oil recovery. This suggests that at very low concentrations, the sap's ability to alter wettability and reduce interfacial tension is significantly reduced. This trend was similar under oil-wet condition with a lower recovery factor, confirming that the lowest concentration is the least effective in enhancing oil recovery for both wetting conditions.

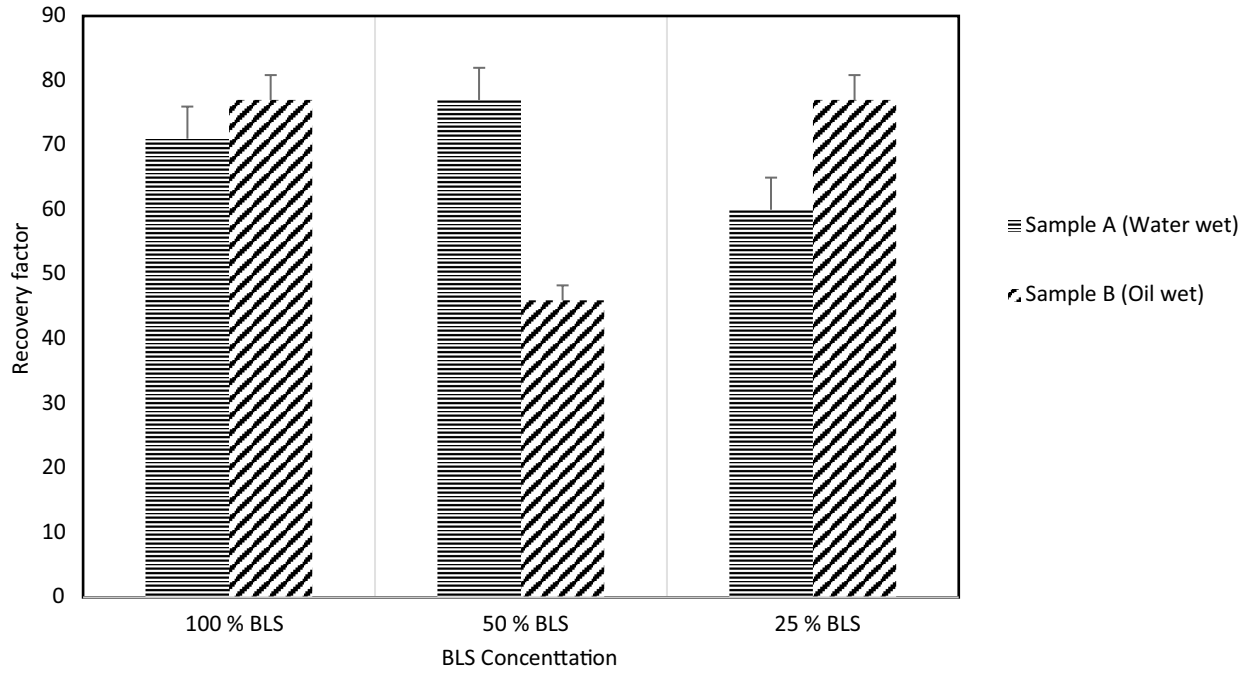


Figure8: Comparison of recovery factor for sample A (Water wet and Oil wet) at100% 50% and 25% concentrations of Sap.

4. Conclusion

This study investigated wettability alteration using bitter leaf sap on sand aggregates. The results of this study demonstrate the efficacy of bitter leaf sap as an enhanced oil recovery (EOR) agent, with significant differences in performance across different concentrations. For both water-wet and oil-wet sharp sand samples, the 100% concentration of bitter leaf sap consistently outperformed the 50% and 25% concentrations, yielding the highest cumulative recovery (CR) percentages. In water-wet conditions, cumulative recoveries of 84%, 78%, and 87% for the 100%, 50%, and 25% concentrations respectively were observed. These values not only surpass the performance of other natural extracts like Mulberry and C. *myxa* but also exceed the recovery rates typically achieved by conventional EOR methods, including polymer and surfactant flooding. The recovery factor (RF), mobilization sweep efficiency (), and overall displacement efficiency () for the bitter leaf sap also indicate its strong potential as a natural surfactant for EOR applications. The recovery factors observed in both water-wet and oil-wet conditions confirm that bitter leaf sap, particularly at higher concentrations, is highly effective in mobilizing and displacing oil. The data further suggest that while dilution reduces the sap's effectiveness, even the 50% and 25% concentrations demonstrate substantial recovery potential compared to traditional methods. In addition, the comparison between water-wet and oil-wet conditions revealed consistent trends in recovery performance across different concentrations, with slightly higher efficiency in water-wet scenarios. This consistency suggests that bitter leaf sap is versatile and effective in a range of wettability conditions, though optimization, particularly in displacement efficiency, may enhance its overall performance. Based on these findings, it is recommended that further research explore the optimization of bitter leaf sap concentrations and injection strategies to maximize displacement efficiency and recovery performance under diverse reservoir conditions.

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