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Research Article

Test on Bitter Leaf Sap as a Surfactant for Wettability Alterations in Enhanced Oil Recovery from Sand Aggregates

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Abstract

Alteration of reservoir-wettability is very important during Enhanced Oil Recovery (EOR) process since it helps to mobilize hydrocarbon and thus increase its recovery from the reservoirs. However, conventional wettability alteration agents used in the industry are inorganic chemicals which are expensive, constitute and have been found to be harmful to the environment. Hence, there was need for cheaper and environmentally-friendly alternative. Also, there was need to find more use for abundant local materials which have are under-utilized. In this article, bitter leaf sap (BLS) was studied to ascertain its possibilities as bio-surfactant for wettability alteration. In order to establish its phytochemical composition, BLS was analyzed using SEM, FT-IR, XRD, and XRF in accordance with ASTM standards. Wettability alteration capacity of three different concentrations of BLS solution on three sand aggregates was investigated. Active compounds which qualified BLS as bio-surfactant were identified from phytochemical analyses. Phytochemical analyses of BLS do not reveal any compounds that could be dangerous to the environment. The results from wettability tests obtained showed that core Sample A, (grain-size 0.118 cm) gave highest degree of wettability alteration with wettability index change from - 0.3030 to - 0.2020. Degree of wettability alteration increased as grain size of sand increased. It was also found that the degree of wettability alteration increased as concentration of BLS increased. Although, BLS could cause wettability alteration, its degree of alteration was lower than the degree of alteration of industrial wettability alteration agent.

Keywords

Wettability Alteration, Amott Test, Bitter Leaf Sap, Sand Aggregates, Enhanced Oil Recovery

1. Introduction

Wettability of porous medium depends on the surface roughness, the pore size, layer of the adsorbed liquid and the adsorptive properties of minerals [1]. The distribution and the flow of fluids in the reservoir are strongly affected by the wettability of the reservoir. The wettability of reservoir rocks contributes to effectiveness of enhanced oil recovery. During enhanced oil recovery process, dispersed oil droplets coalesce, create a zone saturated with oil then migrate to the production

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well [2]. Hydrophilic rocks allow easy migration of oil for production. For this purpose, different methods are used in modifying wettability in favour of hydrophilic condition - chemical and thermal [3]. Wettability alteration enables change of the reservoir from hydrophobic to hydrophilic condition. Wettability alteration agents used in the industry are inorganic chemicals that can either produce higher pore-scale displacement efficiency or increase the sweep efficiency in the reservoir [4, 5]. These conventional chemicals have been found to damage reservoirs, pollute groundwater resources, and destroy the ecological environment of reservoirs. They are synthetic substances and not easy to biodegrade [6]. The ability of a bio-based surfactant to alter wettability has been tested [4, 7-9]. In this study, sap from bitter leaf shrub (*Vernonia amygdalina*) was tested as a bio-based surfactant for its potential to alter the wettability of sand aggregates. Biologically active compounds of *Vernonia amygdalina* are saponins, alkaloids, terpenes, steroids, coumarins, flavonoids, phenolic acids, lignans, xanthones and anthraquinones [10]. Bitter leaf contains, along other nutrients, phosphorus, ascorbic acid, iron, -carotene, calcium, water, and fibre, essential oils, iso-acids, and a-acids found in it [11]. People in Nigeria's South-Southern and South-Eastern Region consume the most of it. [12].

Bitter leaf (Vernonia amygdalina) has been used medicinally as antioxidant [13]; treatment for malaria [14, 15]. treatment for parasitic infestations [16]; many other uses [10, 17-20]. In spite of the many benefits of bitter leaf sap only very small quantity is used to meet these benefits. The quantity utilized is very minimal compared with the quantity wasted. The phytochemistry analysis in literature shows that Bitter leaf is made up of the following key chemical compounds: Flavonoids, Deoxy andrographolide, 14-deoxy-n, andrographolide 12-didehydroandrographolide, Homandrographolide, Ketones, Alkane, Aldehydes, Potassium, Sodium, Calcium, Acid grit and Resin [21]. All these chemical components of bitter leaf sap suggest the possibility of altering wettability. Bitter leaf sap is biodegradable, like some plants used as substitute for inorganic chemicals in oil industry [22].

2. Materials and Methods

2.1. Materials and Preparation

The materials used in this study are bitter leaf, crude oil, conventional chemicals for wettability alteration and sharp sand. The bitter leaf was obtained from Oleh, crude oil sample was obtained from a field in the Niger Delta area of Nigeria. The sharp sand was obtained at Delta State University, Oleh Campus. Bitter leaf sap (BLS) was crushed into a fine paste using a mortar and pestle. The ground bitter leaf paste was pressed to recover the sap. The sharp sand was washed under running water for 30 minutes to remove all debris. Then, the sharp sand was sun-dried for 21 days until constant moisture content. Then filtered to remove big particles and sieved into various grain sizes (0.025cm^3, 0.06cm^3 and 0.118cm^3).

2.2. Phytochemical Analysis on Bitter Leaf Sap, Analysis on Sand Samples and Analyses on Crude Oil

The bitter leaf was subjected to phytochemical analysis using UV-Visspectrophotometry (Shimadzu UV-1800). FTIR analysis (PerkinElmer Spectrum 2) was used to recognize functional groups in the bitter leaf. XRD analysis (Bruker D8 Advance) and XRF (PANalytical Epsilon 3) were used to determine mineral composition and elemental contents of sharp sand respectively. Crude oil properties were measured using a Brookfield DV-II+ Pro viscometer, and sulfur content was determined using ASTM D4294. The contents were determined in agreement with the process described in literature: tannin [23] amino acids [24, 25]; carbohydrate content [26] and phenolic [27].

2.3. Experimental Procedure

Three sand aggregates were tested with three different concentrations of bitter leaf sap solution. Eight core samples were prepared from each of the sand aggregate. One of such core samples was prepared to be water-wet. The other seven of such core samples were prepared to be oil-wet. Bitter leaf sap was prepared to be 100%, 50% and 25% concentrations. The wettability index of the water-wet core sample of each of the sand aggregate was determined. The wettability index of one of the oil-wet sample from each of the sand aggregate was also determined. In order to alter their wettability, three of the oil-wet samples were treated with 100%, 50% and 25% concentrations of bitter leaf sap respectively. Subsequently, the wettability indexes of the three samples treated with BLS were determined. The wettability alterations of the samples were ascertained by the results. The remaining three of the oil-wet samples were treated with 70% concentrations of three different conventional wettability alteration agents respectively. Subsequently, the wettability indexes of the three samples treated with BLS were determined. Also, the wettability indexes of the three samples treated with conventional wettability alteration agents were determined. The wettability tests were determined by Amott test and Amott-Harvey Criterion was used to determine the wettability indexes.

The process for testing wettability of each core samples began at the residual oil saturation. Each core sample to be tested was initially saturated with water and crude oil. The fluids in each core sample tested are reduced to S_{or} (residual oil saturation) by forced displacement of the oil. The core sample was immersed in crude oil for 20 hours, and the amount of water displaced by the spontaneous imbibition of oil was measured. The water was displaced to the residual water saturation (S_{iw}) by oil, and the total amount of water displaced (by the imbibition of oil and by forced displacement) was measured. Also, the core sample was immersed in brine for 20 hours, and the volume of oil displaced by spontaneous imbibition of water was measured. The oil remaining in the core was displaced by water to S_{or} and the total amount of oil displaced (by the imbibition of water and by forced displacement) was measured. The Amott-Harvy index for water and oil was determined from the following formulas [1, 28].

$$I_o = \frac{\Delta S_{os}}{1-S_{wi}-S_{or}} \quad (1)$$

$$I_w = \frac{\Delta S_{us}}{1-S_{wi}-S_{or}} \quad (2)$$

$$WI_{Amott-Harvey} = I_w - I_o \quad (3)$$

Where:

$WI_{Amott-Harvey}$ is Amott-Harvey wettability index,

I_o is the displacement-by-oil ratio

I_w is the displacement-by-water ratio

ΔS_{os} is the volume of water displaced by the spontaneous imbibition of oil

ΔS_{us} is the volume of oil displaced by the spontaneous imbibition of water

S_{wi} is the irreducible water saturation

S_{or} is the residual oil saturation

According to studies of wettability index, the rock is hydrophilic when $I_w = \leq 0.3 \leq 1.0$; neutral rock wettability, respectively ($-0.3 \leq I_w = \leq 0.3$) and hydrophobic rock, where $-1 \leq I_w = \leq -0.3$ [29]. Amott-Harvey wettability criterion is as shown in Table 1.

Table 1. *Wettability criterion based on Amott-Harvey index.*

Wettability	$WI_{(Amott-Harvey)}$
Water Wet	0.3 to 1
Intermediate	-0.3 to 0.3
Oil wet	-1 to-0.3

3. Results and Discussion

3.1. Qualitative and Quantitative Analysis of Samples

The results obtained from the qualitative phytochemicals analysis of bitter leaf sap (this study) are presented in Table 2. Results from other articles were presented alongside for easy comparison [30-32]. As shown in the Table 2, the Steroids, phenols, xanthoproteic compounds, and flavonoids were consistently detected. while Carbohydrates were consistently present also. Terpenoids showed variability, being absent in some reports [32], suggesting potential geographic or methodological differences. While Phytosteroids were detected in other studies but absent in this study. Stain (Fix fat and oil) and Phlobatannins were not always present, they are not major components. These findings emphasize that environmental conditions, extraction methods, and preparation techniques influence the phytochemical detected in the results.

Table 2. *Qualitative Phytochemicals Analysis for Bitter leaf sap.*

Parameters	This study	References		
		Ruth et al. (2021)	Ojeaga et al. (2021)	Ogunlade et al. (2022)
Terpenoid	+	+	-	+
Alkaloid	+	++	+	+
Phlobatannins	-	-	+	+
Steroid	+	+	+	+
Saponin	+	++	+	+
Phyto-steroid	-	+	+	+
Phenol	+	+	+	+
Triterpenoid	++	++	+	+
Fehling's (Flavonoids)	+	+	+	+
Xanthoproteic	+	+	+	+
Keller Killanis (Glycoside)	++	+	+	+
Alkaline Reagent	++	+	+	+
Iodine (Carbohydrates)	+	+	+	+

Parameters	This study	References		
		Ruth et al. (2021)	Ojeaga et al. (2021)	Ogunlade et al. (2022)
Benedict's (Carbohydrate)	+	+	+	+
Stain (Fix fat and oil)	-	+	-	+
Gelatine (Tannin)	-	+	+	+

KEY = ++ abundantly present, + present, - absent

Table 3. Quantitative Phytochemicals Analysis for Bitter leaf sap.

Parameters	This study	References	
		Ruth et al.(2021)	Ojeaga et al. (2021)
Tannim(mg/tannin)	0.4633	12.33±0.01	-
Phenolic Content (mEq/GAE)	11.235	44.763±0.02	-
Flavonoid(mEq/QE)	7.706	-	18.00±0.02
Reducing Power (mg/glucose)	14.589	3.43±0.01	-
Total Carbohydrate (mg/glucose)	10.899	-	10.00±0.02
Saponin	5.823	-	6.00±0.05
Total alkaloids	8.305	5.6±0.01	-
Lipids	3.230	-	2.72
Steroids	0.42	0.30±0.01	-
Proteins (mg/100g)	9.563	-	5.20±0.02

Results from quantitative phytochemical analysis of the bitter leaves sap (this study) are presented in Table 3. Results from other articles were presented alongside for easy comparison [30, 31]. Tannin content was 0.4633 mg/tannin in this study but higher values (12.33±0.01) were reported by Ruth et al. (2021). Flavonoids concentrated was 7.706 mEq/QE but Ojeaga et al. (2021) recorded 18.00±0.02 mEq/QE. Phenolics was 11.235 mEq/GAE) while Ojeaga et al. (2021) reported 44.76±0.02 mEq/GAE. Carbohydrates have a greater concentration in this study (10.899 mg/glucose) compared to 10.00±0.02 mg/glucose reported by Ojeaga et al. (2021). Alkaloids are higher (8.305) compared to 5.6±0.01 reported by Ruth et al. (2021). Saponins are less abundant in this study (5.823) but higher (6.00±0.05) report of Ojeaga et al. (2021). Lipids are slightly higher in this study (3.230) than report of Ojeaga et al. (2021) recorded as 2.72. Proteins are higher in this study (9.563 mg/100 g) than in report of Ojeaga et al. (2021) which recorded 5.20±0.02. Steroids recorded in this study was 0.420 but 0.30±0.01 was recorded by Ruth et al. (2021).

3.2. The Fourier-Transform-Infrared Spectroscopy (FT-IR) Analysis of Dry Bitter Leaf

The Fourier-Transform-Infrared Spectroscopy (FT-IR) of dry bitter leaf is shown in Figure 1.

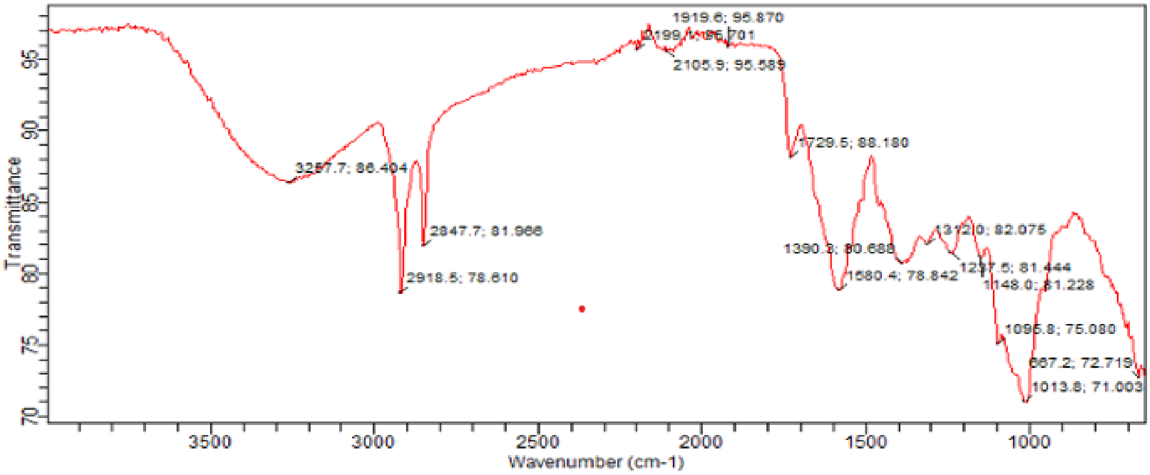

Figure 1. FT-IR analysis of dry bitter leaf.

Several functional groups that can influence wettability alteration were observed in the FT-IR analysis of dry bitter leaf. Wettability alteration influence better oil recovery [33]. The functional groups recognized (hydroxyl, carbonyl, ether/ester) encourage alteration from oil-wetness to water-wetness and improve oil displacement efficiency [6, 33-36]. Carbonyl compounds such as ketones and aldehydes with C=O stretching (1739.5 cm^{-1}) was observed. Carbonyl compounds enhance surface polarity thus support water-wet conditions. C=C stretching (1648.0 cm^{-1}) is linked with alkenes or aromatic compounds, though they are non-polar, they can effect wettability alteration [37]. C-H bending (1452.0 cm^{-1}, 1373.8 cm^{-1}) indicating alkanes and methyl groups was found. C-O stretching (1247.5 cm^{-1}, 1095.8-1013.8 cm^{-1}) indicates alcohols, ethers, or esters. These groups have the capacity to increase hydrophilicity and expedite water-wetness [38]. C-H stretching (2918.5 cm^{-1}, 2847.7 cm^{-1}) indicates aliphatic hydrocarbons. O-H stretching (3257.7 cm^{-1}) indicates alcohols, phenols, or carboxylic acids, which aid hydrophilicity [39]. C≡C stretching (2105.9 cm^{-1}, 1919.6 cm^{-1}) indicate alkynes or combination bands.

3.3. X-Ray Diffraction (XRD) Analysis of Bitter Leaf

The X-ray diffraction analysis spectrum for bitter leaf is shown in Figure 2, reveals intensity peaks at different angles (2θ), each conforming to different crystalline phases in the sample. The identified phases include Periclase (MgO) which enhances water-wetness in reservoirs, improving fluid injection efficiency and boosting oil recovery [40]. Zinc Aluminium Phosphate and Sulfates - Hanksite (Na K(SO) (CO)2Cl), Minoruzaite, Woodhouseite (CaAl (PO)(SO)(OH) transform the surface chemistry of reservoir rocks, encouraging water-wet conditions that facilitate improved oil displacement [41]. Haggstattite (syn) and Hicksite are also present, contributing to the overall mineral profile of bitter leaf. 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. Zinc Aluminium Phosphate, is hydrophilic and can increase water-wettness. Sodium and potassium salt present in Hanksite may influence ion exchange processes that affect wettability [39]. Hydroxyl groups in Woodhouseite can interact with water, encouraging water-wetness.

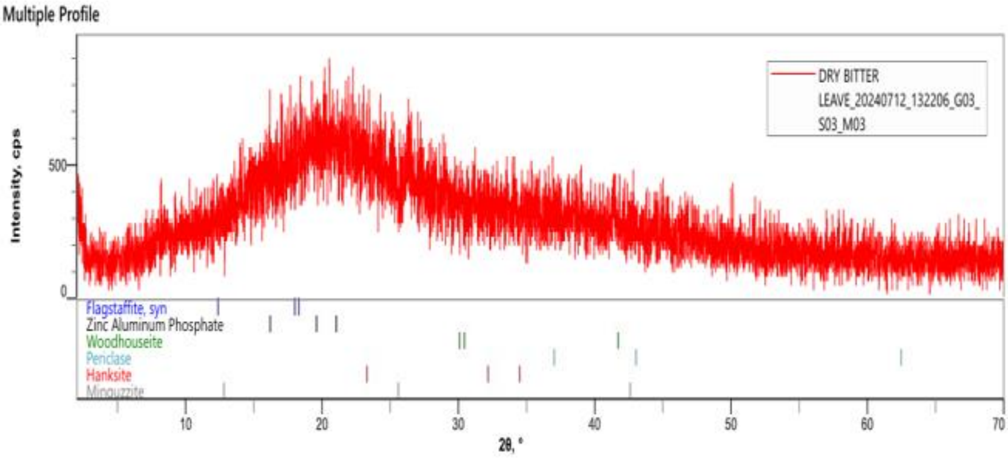

Figure 2. *X-ray diffraction analysis spectrum for Bitter leaf.*

The phase data view from X-ray diffraction (XRD) analysis on dry bitter leaves is shown in Figure 3. Phases identified are Flagstaffite, syn (Blue colour), Periclase (Aqua), Zinc Aluminium Phosphate (Black), Woodhouseite (Green), 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. These minerals possess distinct chemical and structural properties that can influence the wettability of reservoir rocks. Hanksite and Woodhouseite contains sulphur salts which influences ion exchange processes, thus affecting wettability [39]. Woodhouseite containing hydroxyl groups, could interact preferentially with water, promoting water-wetness.

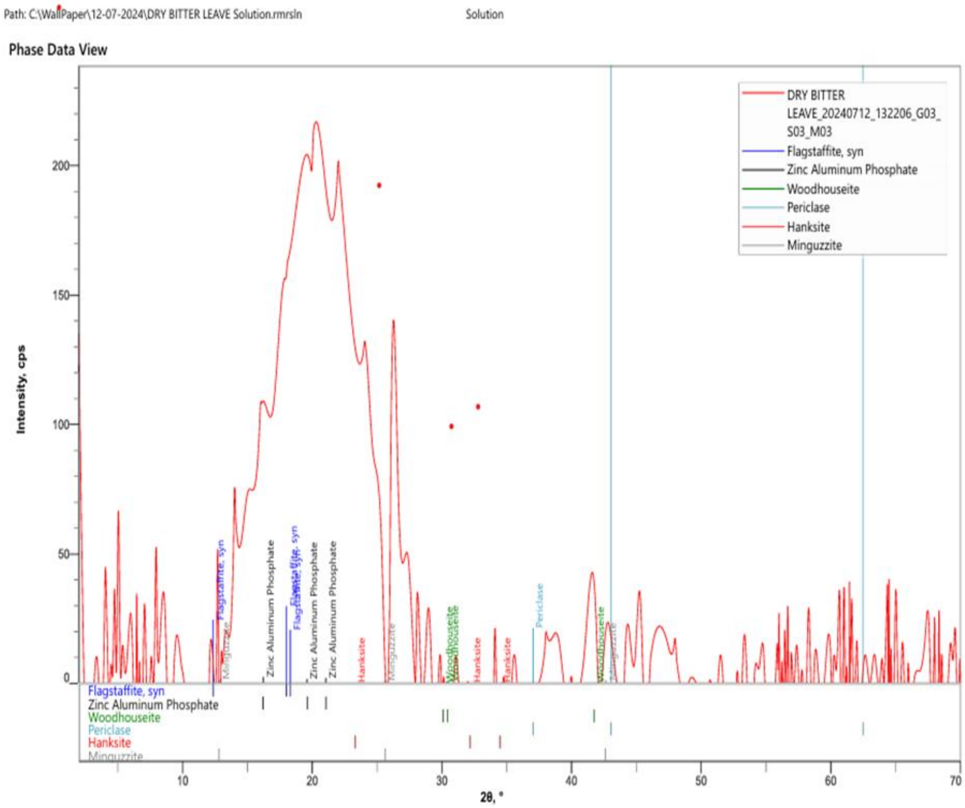

Figure 3. *Phase Data view from X-ray diffraction (XRD) analysis on dry Bitter leaf.*

3.4. X-Ray Fluorescence (XRF) Analysis of Sharp Sand

The X-ray fluorescence (XRF) analysis on sharp sand is shown in Table 4. As shown in the table, Silicon dioxide (SiO_2) is the major constituent (95.2%) of the sand as such Quartz is the mineral. Aluminium Oxide (Al_2O_3) makes up 1.9% of the sand. Iron (III) Oxide (Fe_2O) makes up 0.5% of the sand. The composition of Calcium Oxide (CaO) is 1.2%. The composition of Magnesium Oxide (MgO) is 0.1%. The composition of Potassium Oxide (K_2O) is 0.3%. The content of Silt is 0.2%. The content of organic impurities is 0.5%.

Table 4. X-ray Fluorescence Analysis on the Sharp Sand.

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Silt Content	Moisture Content	Organic Impurities
Composition, %	95.2	1.9	0.5	1.2	0.1	0.3	0.2	0.15	0.5

3.5. Petroleum Crude Oil Analysis

The result from analysis of petroleum crude oil is presented in Table 5. The table shows that the Sulphur content was 0.5%, classifying the crude as sweet [42]. The specific gravity is 0.95 confirms the heavy nature of this crude oil. The asphaltene content is 0.9% The carbon residue, at 8.0%, is high and indicates that crude oil has a significant number of heavy components. The viscosity of the crude oil was 72.0 Pa.s, which is relatively high, indicating that the oil is quite thick and resistant to flow, typical of heavy crudes. The crude oil is heavy crude (API gravity of 17.8). This classification is further supported by its density of 0.95g/cm³.

Table 5. Data obtained from Petroleum Crude Oil Analysis.

Parameters	API Gravity	Specific Gravity	Density	Sulphur Content	Viscosity	Asphaltene Content	Carbon Residue
Composition	$17{\cdot}8^0$	0.95	0.9g/cm³	0.6%	72.0pa.s	0.9%	8.0%

3.6. Results of Wettability Experiment

In Table 6, results from wettability test of the different core samples were presented. The grain size of Sample A is 0.118cm³, Sample B has grain size of 0.06cm³, while the grain size of Sample C is 0.025cm³. As shown in Table 6, wettability indices of the water-wet samples of grain size 0.118cm³, A_w and oil-wet samples of grain size 0.118cm³, A_o, are 0.3030 and -0.30303 respectively. These indices agree with the criteria shown in Table 1. The wettability index of the oil-wet samples A, treated with 100% BLS, X_{o100}, was -0.2020. A significant difference between wettability indices of A_o and A_{o100} was therefore obtained. as presented in Table 6, wettability index of A_{o100} is within the range of intermediate-wetness, indicating that treatment with 100% BLS has brought about a significant alteration of wettability. The wettability index of the oil-wet Sample A, treated with 50% BLS, A_{o50}, was -0.2222, thus, showing a significant difference between wettability indices of A_o and A_{o50}. Wettability index of A_{o50} is within the range of intermediate-wetness, indicating that treatment with 50% BLS has caused a substantial change in wettability. It was also observed that there was marked difference between wettability indices A_{o50} and A_{o100} which suggests that concentration of BLS affect degree of wettability alteration. The wettability index of the oil-wet Sample A, treated with 25% PSS, A_{o25}, was shown to be -0.2424. As observed, there was notable difference between wettability indices of A_o and A_{o25}. Wettability index of A_{o25} was within the range of intermediate-wetness, indicating that treatment with 25% BLS has caused a significant alteration of wettability. Also, there was comparable difference between wettability indices A_{o25}, A_{o50} and A_{o100} suggesting that concentration of BLS has effect on degree of wettability alteration. As concentration of BLS increased, the wettability index tends more towards water-wetness. BLS of 100% concentration produced the highest degree of wettability alteration. In addition, it was observed that 100% concentration of BLS could not fully convert oil-wet sample to become water-wet. There was noticeable difference between A_w and A_{o100}. However, since BLS has the capacity to alter wettability, it can improve microscopic efficiency of EOR process. The increase in the microscopic sweep recovery corresponds with increase in the recovery factor [43, 44].

Table 6. *Experimental Data obtained with Core Samples for Wettability Alteration.*

Core Samples	Sand Grain Size (cm)	Wettability Before Test	Concentration of PSS Tested with (%)	Comments	Symbol	Wettability Index	Wettability After Test
		Water-wet	No test	Control sample	A_w	0.3030	Water-wet
		Oil-wet	No test	Control sample	A_O	-0.3030	Oil-wet
A	0.118	Oil-wet	25	Test sample	A_{O25}	-0.2424	Intermediate
		Oil-wet	50	Test sample	A_{O50}	-0.2222	Intermediate
		Oil-wet	100	Test sample	A_{O100}	-0.2020	Intermediate
		Water-wet	No test	Control sample	B_w	0.3131	Water-wet
		Oil-wet	No test	Control sample	B_O	-0.3132	Oil-wet
B	0.06	Oil-wet	25	Test sample	B_{O25}	-0.2727	Intermediate
		Oil-wet	50	Test sample	B_{O50}	-0.2525	Intermediate
		Oil-wet	100	Test sample	B_{O100}	-0.2323	Intermediate
		Water-wet	No test	Control sample	C_w	0.3333	Water-wet
		Oil-wet	No test	Control sample	C_O	-0.3030	Oil-wet
C	0.025	Oil-wet	25	Test sample	C_{O25}	-0.2929	Intermediate
		Oil-wet	50	Test sample	C_{O50}	-0.2727	Intermediate
		Oil-wet	100	Test sample	C_{O100}	-0.2525	Intermediate

As shown in Table 6, wettability index of the water-wet samples of grain size 0.06cm^3, B_w, and index of the oil-wet samples of grain size 0.06cm^3, B_o, were shown to be 0.313131 and 0.31313 respectively. The wettability index of the oil-wet samples of grain size 0.06cm^3, treated with 100% BLS, B_{o100}, was -0.2323 Wettability index of B_{o100} was within the range of intermediate-wetness, demonstrating that treatment with 100% BLS has brought about a change in wettability. Significant difference was observed between wettability indices of B_o and B_{o100}. The wettability index of the oil-wet samples of grain size 0.06cm^3, treated with 50% BLS, B_{o50}, was -0.2525. Wettability index of B_{o50} was within the range of intermediate-wetness, showing that treatment with 50% concentration of BLS has brought about a significant adjustment of wettability. There was obvious difference between wettability indices of B_o and B_{o50}. Also, observed, there was obvious difference between wettability indices B_{o50} and B_{o100} suggesting that concentration of BLS has effect on degree of wettability alteration. The wettability index of the oil-wet samples of grain size 0.06cm^3, treated with 25% BLS, Y_{o25}, was shown to be -0.2727 (intermediate-wetness). Observable difference between wettability indices of B_o and B_{o25} was noticed. Comparative differences between wettability indices B_{o25}, B_{o50} and B_{o100} were observed, signifying that concentration of PSS has effect on degree of wettability alteration. As concentration of BLS increased, the wettability index tends more towards water-wetness with 100% concentration of BLS producing the highest degree of wettability alteration. However, it was observed that there was noticeable difference between B_w and B_{o100} because 100% PSS could not fully convert sample to water-wet. The tests conducted also indicated that higher oil production can be obtained by treating reservoir with BLS. These trends observed conform with results in existing literature [45].

As shown in Table 6, wettability indices of the water-wet samples of grain size 0.025cm^3, C_w, and the oil-wet samples of grain size 0.025cm^3, C_o, was was shown to be 0.3333 and -0.3030 respectively. These values were in agreement with the criteria shown in Table 1. The wettability index of the oil-wet Sample C, treated with 100% BLS, C_{o100}, was shown to be -0.2525 (intermediate-wetness) indicating significant alteration of wettability by treatment with 100% concentration of BLS. As observed, there was marked difference between wettability indices of C_o and C_{o100}. The wettability index of the oil-wet samples of grain size 0.025cm^3, treated with 50% BLS, C_{o50}, was shown to be -0.2727(intermediate-wetness). It showed that significant alteration of wettability by treatment with 50% concentration of BLS. The wettability index of the oil-wet samples of grain size 0.025cm^3, treated with 25% BLS, C_{o25}, was shown to be -0.2929 (intermediate -wetness), indicating that treatment with 25% BLS has brought about a significant alteration of wettability. Also, observed, there was marked difference between wettability indices C_{o25}, C_{o50} and C_{o100} suggesting that concentration of BLS has effect on degree of wettability change. As concentration of BLS increased, the wettability index tends more towards water-wetness. 100% BLS produced the highest degree of alteration. From earlier study it has been shown that oil production increased as the wettability changed in the direction of the water-wetness [46].

3.7. Comparison of Wettability Indices of Specified Aggregates of Sand Samples

As shown in Figure 4, there is marked difference between wettability indices of A_w, A_w and A_w. it shows that grain size of core has effect on wettability of sand sample. It could be observed that as grain size increased, the wettability index tend towards oil-wetness. Similar trend was observed between A_o, B_o and B_o in one hand; A_{o100}, B_{o100} and C_{o100} in another. The trend also extended to A_{o50}, B_{o50} and C_{o50} then A_{o25}, B_{o25} and C_{o25}.

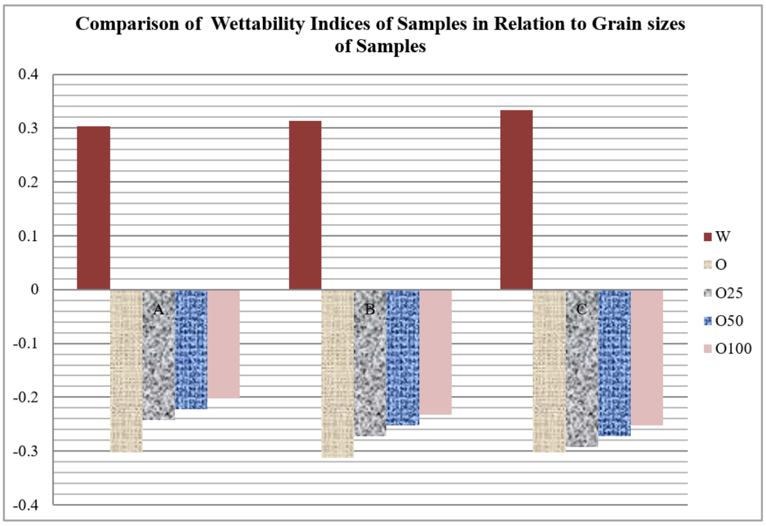

Figure 4. Comparison of Wettability Indices of Samples in Relation to Specified Grain Sizes of Samples.

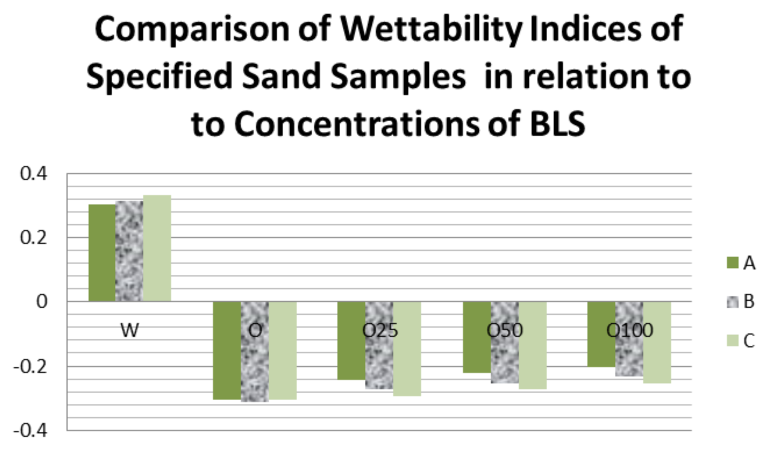

Figure 5. Comparison of Wettability Indices of in Relation to Specified Sand Samples Concentrations of BLS.

As shown in Figure 5, there is marked difference between wettability indices of A_w, A_o, A_{o100}, A_{o50} and C_{o25}. Especially, after treating samples with BLS. It was shown that as concentration of BLS increase, the degree of wettability alteration, sample tends ttowards water-wetness. Highest degree of alteration was observed with 100% concentration of BLS. The trend also extended to B_w, B_o, B_{o100}, B_{o50} and B_{o25}. and C_w, C_o, C_{o100}, C_{o50} and C_{o25}.

3.8. Comparison of Some Industrial Based Wettability Alteration Chemical Agent with Plantain Stem Sap.

Comparison between selected conventional wettability alteration chemicals and bitter leaf sap were made. The selected wettability alteration chemical agents are:

1. Petroleum sulfonates + alkyl ether sulphate (PSAES)
2. 1.25wt% Na_2CO^3 as alkali + 0.1wt% Petro step B-100 as surfactant (SCPSB)

The Results of wettability indices of sand samples treated with the specified wettability alteration agents are presented in Table 7.

Table 7. Comparison between Conventional Wettability Alteration Chemical Agent with BLS.

Core Samples	Sand Grain Size (cm)	Test Agent	Concentration of Agent Tested with (%)	Comments	Symbol	Wettability Index	Wettability After Test
A	0.118	PSAES	70	Test sample	A_{PSAES}	0.4444	Water-wet
		SCPSB	70	Test sample	A_{SCPSB}	0.4444	Water-wet
		No test	No test	Control sample	A_O	-0.3030	Oil-wet
		BLS	100	Test sample	A_{O100}	-0.2020	Intermediate
B	0.06	PSAES	70	Test sample	B_{POA}	0.4343	Water-wet
		SCPSB	70	Test sample	B_{SCP}	0.4242	Water-wet
		No test	No test	Control sample	B_O	-0.3131	Oil-wet
		BLS	100	Test sample	B_{O100}	-0.2323	Intermediate
C	0.025	PSAES	70	Test sample	C_{POA}	0.3939	Water-wet
		SCPSB	70	Test sample	C_{SCP}	0.3939	Water-wet
		No test	No test	Control sample	C_O	-0.3030	Oil-wet
		BLS	100	Test sample	C_{O100}	-0.2525	Intermediate

As shown in Table 7, Oil-wet Sample A treated with 70% concentration PSAES had wettability index of 0.4444 (water-wetness). Similarly oil-wet Sample A treated with 70% concentration SCPSB had wettability index of 0.4444 (water-wetness). Conversely, oil-wet Sample A treated with 100% concentration of bitter leaf sap had wettability index of -0.2020 (intermediate-wetness). Likewise, for Sample B, when 70% concentration of PSAES was used for wettability alteration, the wettability index of the sample change to 0.4343 (water-wetness), but with 100%, concentration bitter leaf sap changed wettability index of sample to -0.2323 (intermediate-wetness). Also, 70% concentration of SCPSB produced wettability index of 0.4242 (water-wetness). For oil-wet Sample C, when 70% concentration of PSAES was used wettability index changed to 0.3939 (water-wetness), but 100%, concentration of bitter leaf sap had -0.2525 (intermediate-wetness). However, 70% concentration of SCPSB produced wettability index of 0.3939 (water-wetness). Results show that BLS has the capacity to alter wettability of sand samples as shown in by other plant in literature [7]. However, it is not as effective as some of the industrial-based agent in altering wettability. Wettability alteration capacity is useful in enhancing oil recovery from reservoir.

4. Conclusion

Phytochemical analyses of bitter leaf sap have shown that BLS is non-toxic to the environment. Results from phytochemical analyses of BLS consistently suggest that BLS has potential wettability alteration compounds. In addition, since BLS is organic matter, it is bio-degradable. It has economic advantage because it is easily availability and affordability. The results of this study showed that regardless of size of sand grain, the wettability alteration was higher as concentration of bitter leaf sap increased. Core sample of smaller grain had comparatively lower degree of wettability alteration. Wettability indices of intermediate-wetness were achieved by BLS which was considerably lower in comparison to selected conventional wettability alteration chemicals. The wettability indices observed at various concentrations of BLS confirm that bitter leaf sap could effectively alter the wettability of reservoir, successfully mobilize entrapped oil and hence enhance oil recovery. Although, it was observed from this study that dilution reduces the effectiveness of BLS, nevertheless 25%

concentration of BLS revealed significant result. Thus BLS portrays oil-recovery potential and comparative result to conventional chemical agents. This research also demonstrated that BLS does not contain toxic components thus could be used as a wettability alterations agent without threat to environmental health.

Abbreviations

BLS	Bitter Leaf Sap
EOR	Enhanced Oil Recovery
WI	Wettability Index
FT-IR	Fourier-Transform-Infrared Spectroscopy
XRD	X-Ray Diffraction
XRF	X-ray Fluorescence
PSAES	Petroleum Sulfonates + Alkyl Ether Sulphate
SCPSB	1.25wt% Na2CO3 as Alkali + 0.1wt% Petro Step B-100 as Surfactant

Author Contributions

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Conflicts of Interest

The authors declare that there is no conflict of interest.

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