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ANALYTICAL EVALUATION OF OIL AND WATER OBTAINED FROM DEMULSIFICATION OF CRUDE OIL USING CASHEW (*ANACARDIUM OCCIDENTALE)* NUTSHELL LIQUID

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ABSTRACT

The physiochemical characteristics of oil and water obtained from the demusifier treatment of crude oil using equal concentrations of Cashew nutshell liquid (CSNL) and a commercial grade demulsifier (DX077) were evaluated. Results obtained shows that basic sediment and water (BSW) of the crude after treatment with CSNL and DXO77 were 17.5 and 17.9 % respectively which was 0.4% apart. The total oil and grease (TOG) and total petroleum hydrocarbon (TPH) of the produced water after treatment with CSNL were 24.4 and 21.7 mg/l respectively while results after treatment with DXO77 were 23.7 and 20.5 mg/l respectively. The TOG and TPH of the produced water after demulsifier treatment with CSNL and DX077 were within acceptable limit of < 30.0 mg/l as specified by Department of Petroleum Resources (DPR). Analyses of the same crude oil before demulsifier treatment gave a lower BSW of 9.50 % as well as an emulsion band of 16.2 % indicating improper oil/water separation. The TOG and TPH of the produced water before demulsifier treatment were 42.5 and 38.7 mg/l respectively which were above DPR specification. Disposal of produced water with high TOG and TPH into the environment can lead to the release of volatile organic compounds (VOCs) into the ecosystem resulting in environmental pollution as well as other health hazards. Results obtained also show that the water density, pH, electrical conductivity, salinity and chloride of the produced water after demulsifier treatment with CSNL and DX077 were within DPR specification. Reinjecting produced water with high salinity, chloride and conductivity into the reservoir can reduce oil recovery especially from sandstone and carbonate reservoirs. CSNL proved to be an effective demulsifier and is preferrable to the synthetic demulsifier (DX077) because it is more environmentally friendly owing to its green nature.

Keywords: Demulsifier, produce water, environment, reservoir, emulsion.

INTRODUCTION

Crude oil production from oil reservoirs is often accompanied with water and gas. Refined hydrocarbon gas from crude oil is very necessary and can be put to several use such as powering of various engines, source of energy for cooking and other industrial purposes (Gafonova, 2001), on the other hand water produced from crude oil constitutes a nuisance and impurity during oil exploration (Chikwe and Iwuoha, 2024). Water in crude oil has been a major challenge in the oil and gas industry both in upstream oil production as well as downstream refining, distribution, and transmission. Most Oil/Gas exploration industries produce an average of three barrels of water for each barrel of oil especially from old, depleting reservoirs, the older an oil reservoir the higher its propensity to produce water (Chikwe and Okwa, 2016). Water shows a higher solubility in crude oil at elevated temperatures, about 0.4 % water dissolves in crude at approximately 150 ^{0}C, part of the dissolved water in crude forms emulsion therefore can be separated by demulsification while a minute quantity of water is entrapped in the crude as residual water which cannot be separated (Chikwe and Iwuoha, 2024). The residual water in crude oil do not pose a challenge as regards the quality of the crude whereas the water-in-oil emulsion is usually a cause for concern (Chikwe and Ogwumike, 2018). Emulsions in oil/gas installations could occur as water-in-oil, oil-in-water or water and oil-in-water multiple emulsion systems, however the water-in-oil emulsion is the most encountered in oil field operations. Demulsification is the separation of crude oil emulsion into oil and water phases. The stability of the emulsion formed by oil and water is dependent on the stability of their interfacial films which is influenced by the water pH. The strength of the interfacial film between the oil and water decreases as the water pH increases hence, they are converted to mobile films at high pH (Opawale, 2009; Ikpea et al., 2018). Water-in-oil emulsion is produced within an acidic range while oil-in-water emulsion is formed within an alkaline pH. There are several methods employed in the treatment of crude oil emulsions such as chemical, thermal, mechanical, and electrical methods, however the most common method of emulsion treatment is the chemical method (Adeyanju and Oyekunle, 2017; Chikwe and Osuji, 2023).

Cashew tree (*Anacardium Occidentale*) is a nut-bearing multipurpose tropical plant cultivated for its fruit, nut and wood from which other products are obtained. Cashew nutshell liquid (CNSL) is a viscose dark brown liquid obtained from cashew nutshell which is regarded as a cheap agricultural by product (Hammed et al., 2008). Studies show that CNSL contains four major components which are anacardic acid, cardanol, cardol and 2-methyl cardol, these components are made up of various functional groups such as hydroxyl, carboxylic, phenyl, aromatic, C_{15} alkyl side chain etc which increases the possibility of several reaction sequence at the various functional groups hence making CNSL a precursor for the manufacture of several industrial and commercial products (Idah et al., 2014;Ike et al., 2021). CNSL modified through the process of esterification and decarboxylation are essential assets in oil field operations, the carboxylate functional groups make them very good surfactants that facilitates the recovery of residual oil by reducing the interfacial tension between oil and water thereby making them good demulsifiers suitable for separating water from emulsions (Hammed et al., 2008). The physiochemical characteristics of oil obtained from a water-in-oil emulsion determines the quality of the oil in terms of its market value, suitability as a source of energy and in the manufacture of other products. The quality of the water obtained after demulsification is also of interest in terms of proper disposal to the environment to protect the ecosystem from pollution and subsequent degradation (Gafonova, 2001). The quality of the water separated from crude oil also determines its suitability as reinjected water into the reservoir for enhanced oil recovery (Chikwe and Iwuoha, 2024). The aim of this study therefore is to evaluate the physiochemical characteristics of oil and water obtained from the demulsification of crude oil using CNSL as a demulsifier compared to a commercial grade synthetic demulsifier tagged DX077

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MATERIALS AND METHODS

Sample Collection and Preparation

Cashew nuts from cashew (*Anacardium Occidentale)* were obtained from a village in Okene local government area of Kogi state Nigeria. CNSL were extracted from the cashew nuts by solvent extraction using a Soxhlet extractor with acetone as the solvent. The extracted CNSL was treated with calcium hydroxide to isolate anacardic acid which is the active ingredients in the liquid. Anacardic acid (AA) from CNSL was modified by esterification reaction to obtain the carboxylate form of the acid. The same quantity of CNSL and a synthetic demulsifier (DXO77) were used respectively in the treatment of a crude oil emulsion from bonny light crude obtained with a 1-liter glass sampling bottle from an oil well in the Niger Delta to separate the oil from the water. The physiochemical characteristics of the oil and water separated by CNSL were determined and compared with the characteristics of the oil and water separated by the synthetic demulsifier (Victor-Oji et al., 2019).

Determination of Basic Sediment and Water (BSW) of Crude Emulsion

The BSW of the crude emulsion was determined using Rotanta 460R Petroleum centrifuge. The crude emulsion contained in the 1-liter glass bottle was properly agitated to ensure homogeneity and 50 ml was quickly poured into two of each 100 ml centrifuge bottle, each of the bottles was filled to the 100 ml mark with xylene and 2 drops of the demulsifier was added into the samples. The centrifuge bottles were shaken again and then introduced into the trunnion cups on opposite sides of the petroleum centrifuge to maintain balanced condition. The centrifuge bath was set at 60 ^{0}C with a minimum relative centrifugal force of 1500 rpm and started to spin for 15 minutes. The volumes of sediment, water and oil in each tube were read and recorded to the nearest 0.05 ml. (ASTM D4007, 2011). The BSW was calculated using equation 1:

$$BSW\ (\%) = \frac{S}{V} \times 100 \ldots\ldots\ldots\ldots..(1),$$

$$Where:\ S = Volume\ of\ Sediment;\ V = Volume\ of\ crude\ emulsion$$

Determination of Specific Gravity of Crude Oil

A 400ml graduated cylinder was filled with the sample to be analysed and a hydrometer with calibrations of 0.70 or 0.75 was submerged into it. Readings were taken as the hydrometer floats on the sample and a thermometer was then inserted into the graduated cylinder for 10 s and the temperature recorded. Specific gravity values corresponding to the temperature in ^{0}C were read as values for the corrected specific gravity (ASTM D1298, 2002).

Determination of Density and Kinematic Viscosity of Crude Oil

The cell of the Anton Paar DMA 4500M densitometer was thoroughly cleaned with acetone. Exactly 2 ml of the test sample was introduced into the equipment through the connector installed for filling samples into the measuring cells with the use of a suitable syringe after proper agitation of the test sample. The start button was pressed to initiate different series of measurement. Density, kinematic viscosity, dynamic viscosity readings were displayed, and the readings recorded (ASTM D4052, 2002).

Determination of Cloud Point of Crude Oil

The test sample was poured into the test jar to the level mark, the test jar was closed tightly by the cork carrying the test thermometer. The test jar was inserted in the jacket of the cooling bath maintained at a temperature of 0 +/- 1.5 ^{0}C. At each test thermometer reading that is a multiple of 1 ^{0}C the test jar was removed from the jacket quickly without disturbing the sample, cloud was inspected, and test jar replaced into jacket. The cloud point was reported to the nearest 1 ^{o}C (ASTM D5771, 2002).

Determination of Pour Point of Crude Oil

The test sample was poured into the test jar to the level mark. The test jar was closed with a cork carrying the high pour thermometer. The appearance of the test sample was examined when the temperature of the test sample was 9 ^{0}C above the expected pour point. The pour point is the temperature at which the sample ceases to flow. This was recorded for all the test samples (ASTM D97, 2012).

Determination of Total Oil and Grease (TOG) in Water from Crude Oil

Sample obtained was acidified with Hydrochloric acid. 25 ml of tetrachloroethylene

(TCE) was used to extract the organic portion of the sample. The extract was diluted to 50 ml with distilled water. 25 ml of the organic extract was analysed with a bulk 404 hydrocarbon analyzer to measure the amount of Oil and Grease.

Determination of Total Petroleum Hydrocarbon in Water from Crude Oil

Sample obtained was acidified with Hydrochloric acid. 25 ml of Tetrachloroethylene (TCE) was used to extract the organic portion of the sample. The extract was filtered through Florisil to remove polar components and then diluted to 50ml with distilled water. 25 ml of the organic extract was analysed with a bulk 404 hydrocarbon analyser to measure the total petroleum hydrocarbon (ASTM D3921, 2013).

pH Determination of Water from Crude Oil

The pH meter and associated electrodes were standardized using two reference buffer solutions within the range of the anticipated sample pH. The sample measurements were made under strict controlled conditions and prescribed techniques. The already calibrated electrodes were immersed into the sample. As soon as the electrode output stabilizes, the stability indicator appears displaying the pH and temperature (ASTM D1293, 2018).

Determination of Electrical Conductivity of Water from Crude Oil

The Conductivity meter was calibrated with the appropriate buffer solution. The probe from the already calibrated conductivity meter was immersed into the beaker containing the sample. Time was allowed for the conductivity meter to gain stability then conductivity recorded.

Determination of Salinity of Water from Crude Oil

One ml of the sample was made up to 20 ml using distilled water and 1 ml of potassium dichromate indicator was added. Titration was carried out with a silver nitrate solution until color changed to brick red. Titration was achieved using a combined ring silver coated electrode (Chikwe and Okwa, 2016).

Salinity was calculated using the equation:

$$Salinity\ (\frac{mg}{l}) = \frac{A \times N \times 58.5 \times 1000}{Vol.of\ Sample} \ldots\ldots\ldots\ldots \quad (2)$$

$Where:\ A = Volume\ of\ Siver\ Nitrate;\ N = Molarity\ of\ Silver\ Nitrate$

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RESULTS AND DISCUSSION

Results obtained in Table 1 shows the physicochemical characteristics of oil obtained from demulsification of crude oil emulsion using CNSL as a demulsifier.

Table 1: Physicochemical Characteristics of Oil Obtained from Demulsification with CNSL

Parameters	1st Reading	2nd Reading	Average	DPR Specification
BSW (%)	17.50	17.50	17.50	0 - 0.2
Specific Gravity	0.86	0.86	0.86	0.83 - 0.85
API Gravity (^{0})	33.90	33.90	33.90	34 -37
Oil Density @ 15.56 ^{0}C (g/cm^3)	0.86	0.86	0.86	0.83 - 8.85
Kinematic Vis. @ 40^{0}C (CSt)	13.65	13.65	13.65	11.5 - 13.5
Kinematic Vis. @ 100^{0}C (CSt)	3.33	3.33	3.33	3.0 - 3.5
Cloud Point (^{0}C)	10.00	10.00	10.00	10
Pour Point (^{0}C)	5.50	5.50	5.50	4.0 - 4.5

Results obtained in Table 2 shows the physicochemical characteristics of oil obtained from demulsification of crude oil emulsion using a synthetic demulsifier tagged DX077.

Table 2: Physicochemical Characteristics of Oil Obtained from Demulsification with Synthetic Demulsifier (DXO77)

Parameters	1st Reading	2nd Reading	Average	DPR Specification
BSW (%)	17.90	18.20	18.20	0 - 0.2
Specific Gravity	0.85	0.85	0.85	0.83 - 0.85
API Gravity (^{0})	34.42	34.44	34.43	34 -37
Oil Density @ 15.56 ^{0}C (g/cm^3)	0.85	0.85	0.85	0.83 - 8.85
Kinematic Vis. @ 40^{0}C (CSt)	13.44	13.44	13.44	11.5 - 13.5
Kinematic Vis. @ 100^{0}C (CSt)	3.28	3.28	3.28	3.0 - 3.5
Cloud Point (^{0}C)	10.00	10.00	10.00	10
Pour Point (^{0}C)	5.50	5.50	5.50	4.0 - 4.5

Results obtained in Table 3 shows the physicochemical characteristics of the same crude oil emulsion used in Tables 1 and 2 before any form of demulsifier treatment.

Table 3: Physiochemical Characteristics of Crude Emulsion

Parameters	1st Reading	2nd Reading	Avearge	DPR Specification
Water cut (%)	9.50	9.60	9.55	0 - 0.2
Emulsion band (%)	16.20	16.10	16.15	0 - 0.2
Water TOG (mg/l)	42.50	42.50	42.50	30.00
Water TPH (mg/l)	38.80	38.60	38.70	30.00
Specific Gravity	0.88	0.88	0.88	0.83 - 0.85
API Gravity (^{0})	29.90	29.88	29.89	34 -37
Oil Density @ 15.56 ^{0}C (g/cm^3)	0.88	0.88	0.88	0.83 - 8.85
Kinematic Vis. @ 40^{0}C (CSt)	16.58	16.58	16.58	11.5 - 13.5
Kinematic Vis. @ 100^{0}C (CSt)	5.10	5.10	5.10	3.0 - 3.5
Cloud Point (^{0}C)	30.00	30.00	30.00	10
Pour Point (^{0}C)	9.00	9.00	9.00	4.0 - 4.5

Results obtained in Table 4 shows the physicochemical characteristics of water obtained after demulsifier treatment with CNSL

Table 4: Physicochemical Characteristics of Water Obtained from Demulsification with CNSL

Parameters	1st Reading	2nd Reading	Average	DPR Specification
TOG (mg/l)	24.30	24.50	24.40	<30
TPH (mg/l)	21.70	21.80	21.75	<30
Water Density @ 15.56 ^{0}C (g/cm^3)	1.00	1.00	1.00	1.0000
pH	8.03	8.03	8.03	6.5 - 8.5
Electrical Conductivity (µs/cm)	2800.00	2800.00	2800.00	<20000
Salinity (mg/l)	1429.78	1429.78	1429.78	<15000
Chloride (mg/l)	794.32	794.32	794.32	<10000

Results obtained in Table 5 shows the physicochemical characteristics of water obtained after demulsifier treatment with a synthetic demulsifier tagged DX077

Table 5: Physiochemical Characteristics of Water Obtained from Demulsification with Synthetic Demulsifier (DXO77)

Parameters	1st Reading	2nd Reading	Average	DPR Specification
TOG (mg/l)	23.70	23.60	23.65	<30
TPH (mg/l)	20.50	20.50	20.50	<30
Water Density @ 15.56 ^{0}C (g/cm^3)	1.00	1.00	1.00	1.0000
pH	7.86	7.86	7.86	6.5 - 8.5
Electrical Conductivity (µs/cm)	2783.00	2785.00	2784.00	<20000
Salinity (mg/l)	1420.34	1421.45	1420.90	<15000
Chloride (mg/l)	789.08	789.70	794.32	<10000

Results obtained from Table 1 shows that the BSW which reflects the water and other non-hydrocarbon content of the crude separated from the crude by the demulsifier was > 17.0% of the entire crude which was quite high. Results obtained after separation of water and other non-hydrocarbon content shows that the specific gravity, API gravity, oil density, kinematic viscosity, cloud and pour point were within acceptable limits. The same crude emulsion was treated with a synthetic demulsifier (DXO77) at the same concentration and the results obtained are shown in Table 2. Results obtained from Table 2 revealed that the BSW of the same crude has gone slightly higher which indicates that it has a slightly better demulsification capacity than CNSL probably due to the presence of other additives, however the physiochemical characteristics of the oil in Table 2 were still within acceptable limit just like those in Table 1. In other to ascertain the impact of both demulsifiers (CNSL and DXO77) on the characteristics of the crude, the physiochemical characteristics of the crude emulsion were analysed without any form of demulsifier treatment and results were obtained in Table 3. Results obtained from Table 3 shows a water cut and an emulsion band which confirms an incomplete separation

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giving values above acceptable limits. The API gravity which reflects the market value and quality of the crude was drastically reduced below specification. The density and specific gravity affirm the presence of light and heavy petroleum fractions, this influences the crude kinematic viscosity (Chikwe and Iwuoha, 2024). The flow assurance parameters of petroleum were represented by their cloud and pour points. Results obtained from Table 3 shows that the crude was not able to flow through the expedition line without demulsifier treatment, thus affecting its availability for sales (export) as well as refinery operations with the kinematic viscosities at 40 ^{0}C and 100 ^{0}C as well as the cloud and pour points above acceptable limits. The results revealed wax formation at 30 ^{0}C and thus, stopping flow below 9 ^{0}C indicating a very dangerous parameter for crude oil drilling and exportation within a tropical region such as the Niger Delta.

The physicochemical characteristics of water obtained from the demulsification of crude emulsion using CNSL and DXO77 as demulsifiers were shown in Tables 4 and 5 respectively. Results obtained revealed that all the characteristics were within acceptable limit indicating proper and effective demulsifier treatment from both demulsifiers (CNSL and DX077 respectively). Lack of or improper demulsifier treatment gives rise to poor oil / water separation resulting in produced water with high TOG and TPH above acceptable limits which are hazardous when disposed to the environment (land or sea) or detrimental to the water injection wells when reinjected. Poor oil / water separation arising from ineffective demulsifier treatment also adversely offsets other produced water parameters such as pH, salinity, conductivity, TDS etc. Several research supported by field trial have suggested that oil recovery can be enhanced by ensuring that the salinity of injection water was not above acceptable limit. Produced water with high salinity, conductivity, TDS and chloride content can negatively affect oil recovery for both carbonate and sandstone reservoirs depending on the formation minerals and brine composition (Chikwe and Iwuoha, 2024).

CONCLUSION

Cashew nutshell liquid (CSNL) proved to be an effective demulsifier owing to its ability to separate oil and water in crude, with the separated oil and water having relatively similar characteristics with those obtained after treatment with a commercial grade demulsifier (DX077). Treatment of crude oil with weak demulsifiers produces oil with lower BSW than is present in the crude as well as water with high total oil and grease (TOG) and total petroleum hydrocarbon (TPH) which can cause a lot of harm when disposed to the environment or reinjected into the reservoir. The alteration of crude oil parameters such as pH, density, cloud point, pourpoint, viscosity, due to the presence of water in the crude makes the use of proper demulsfiers very critical. The salt content of the crude such as salinity, conductivity and chloride were unveiled from the produced water parameters of the crude and demulsifiers are responsible for adequate separation of water from crude oil. CSNL which is derived from cashew nut, a byproduct and non-edible part of the cashew plant is a better demulsifier than the commercial grade synthetic demulsifier tagged DX077 owing to its availability, cost implication and environmental friendliness.

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