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PREPARATION AND CHARACTERIZATION OF DIFFERENT ECO-FRIENDLY DEMULSIFIERS FROM CALABASH SEED FOR EMULSION MANAGEMENT

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Abstract

The process of crude oil demulsification is still confronted with numerous challenges within the petroleum industry. Consequently, it is pertinent to develop innovative means or materials to accomplish the efficient separation of oil–water emulsions. In this work, three different Eco-friendly demulsifier: oil-based, ethanol-based and Nano-based demulsifiers were prepared via a simple one-step hydrothermal route using Lagenaria siceraria (calabash) seed as raw materials. The eco-friendly demulsifiers were evaluated by Fourier transform infrared spectroscopy (FT-IR) and Gas chromatographic-mass spectroscopic (GC-MS) and their chemical content and Physico-chemical properties compared with a commercial demulsifier (Phase treat). The results obtained showed that the seed have an oil content of 31%. The phytochemical screening of the extracted oil reveals the presence of most compounds found in chemical demulsifiers such as phenols, flavonoids, tannins, saponins, steroids, terpenoids etc. The FT-IR spectra of the chemical demulsifier was found to be similar to that of the oil and most of the functional groups present in the ethanol and oil-bases demulsifiers whereas that of Nano-based was observed to differ. The GC-MS analysis reveals the presence of both lipophilic and hydrophilic compound needed for demulsifiers preparation. In the bottle test analysis carried out to determine the efficacy of the eco-friendly demulsifiers, it was observed that the nano-based demulsifier performed better than the commercial demulsifier in the following trend: Nano-based > commercial > ethanol-based > oil-based. This current study not only encourage the effectual application of agricultural waste (Calabash seed), but also creates an understanding into the search of new demulsifying materials that would offer excellent performance. Finally, future investigations should focus on assessing the efficacy, stability, and potential industrial applications of these bio-demulsifiers and Nano-based demulsifiers.

1.0 INTRODUCTION

Crude oil extraction and exploration have persisted in maintaining the status quo of a non-stagnant and constantly expanding sector. However, this procedure generates a significant amount of produced water (PW), which is contaminated with heavy metals and hydrocarbons (organic matter) [1] According to [2], the PW can react with crude oil in two different ways: as an emulsion that spreads as droplets in the oil phase, or as free water that slowly settles in the sedimentation tanks. When there is a water-emulsion in crude oil, some issues arise. Some examples include an increase in the viscosity of the produced fluids, which affects its transportation by increasing the cost of transportation and also increased the cost of equipment, as well as technical problems like pipeline

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corrosion and dripping. Emulsions are created when immiscible liquid phases from two or more systems are combined.

The chemical demulsification (CD) process has been used in a number of demulsification processes, with biological, electrical, thermal, chemical, and mechanical techniques all utilized for the purification process [3][4]. However, additional techniques or technologies that have reportedly been employed include extraction, adsorption, flocculation, membranes, and precipitation [5]. Numerous chemical demulsifiers, such as polysiloxane, hyperbranched polymers, copolymers, dendrimers, and ionic liquids, have been developed in recent years; however, their practical application is constrained by the growing concern for environmental protection [6]. Additionally, the majority of these techniques generated dangerous substances and had results that were comparable to PW. The usage of nanoparticles (NPs) is a recent demulsifying technique that has been discovered [6;7].

Similarly, to extract water from crude oil emulsions, many demulsification methods, including mechanical, thermal, electrical, and chemical ones, are used. Chemical demulsification is more popular among researchers than other procedures for demulsifying crude oil emulsions due to its higher and quicker efficiency [8][9]. Additionally, the chemical used in the demulsification operations can be created using various nonionic surfactant mixes. These demulsifiers have a two-part chemical structure: a hydrophobic portion made up of amide, alkyl fatty esters, polyoxypropylene, and alkyl phenol formaldehyde ethers, and a hydrophilic portion made up of polyoxyethylene. For the surfactant to replace the asphaltene coatings and occupy the water/oil interface, it must be able to absorb water or oil droplets. Because the currently utilized chemicals have various drawbacks, such as being expensive and polluting, it is necessary to build new demulsifiers that are both affordable and environmentally benign [10].

Nanotechnology, which focuses on atomic, molecular, and supramolecular molecules in order to build nanostructures with improved functions, is a field of study that deals with particulate matter that ranges in size from 1 to 100 nm [7;11]. NPs can range in dimension from 0 to 3 depending on their overall shape [12]. NPs consists of three different layers: the surface, shell, and core because they are not simple molecules in and of themselves. The core is essentially the central region of the NP and is typically used to refer to the NP itself [12]. There are many different small molecules, meal ions, surfactants, and polymers that can be used to functionalize the surface layer. NPs are divided into two major categories: organic and inorganic nanoparticles. According to [14] , inorganic NPs are magnetic, noble (gold and silver), and semiconductor (titanium oxide and zinc oxide) NPs while organic NPs are Carbon NPs (fullerenes). The development of antimicrobials, diagnostics, microelectronics, catalysis, and sensing devices are just a few of the several applications of NPs that have proven effective [7; 11;14]. Physical and chemical approaches are used to create NPs, however they result in toxic NPs and have significant energy inputs and expensive downstream processing [11; 12]. These factors have led to a limited increase in the use of these two approaches to create NPs. Green synthesis (GS) is a current technique that is being used to produce NPs more frequently. According to [11], GS is the process of synthesizing NPs using environmentally benign and suitable resources like plants, bacteria, and fungi. The GS method was superior to the physical and chemical approaches because it addressed some of their shortcomings. In this study, calabash seed will be employed as a plant-based source of GS to create silver nanoparticles. The calabash plant provided the source. Accordingly, this tree is valued as a crop in a number of nations, including Nigeria.

Therefore, this study focused on the preparation and characterization of different Eco-Friendly demulsifiers from Calabash Seed for Emulsion Management which may be more efficient, cost effective and readily available demulsifier for the management of emulsion oil.

2.0 MATERIALS AND METHODS

2.1 Materials

Materials utilized in this research are as follows: Hexane, Soxhlet Apparatus, Rotary Evaporator, Filter Paper, Weighing Balance, Heating Mantle, and Centrifuge.

2.1.1 Plant source

The plant *Lagenaria siceraria* (Calabash) Seed used for this study was collected within Tarauni Local Government Area, Kano state, Nigeria.

2.1.2 Chemicals

Crude oil samples were sourced from Nigerian Oil field in Rivers State, Port Harcourt, Nigeria. The commercial demulsifier (Phase treat: 42172) used as reference is obtained from Chemistry department laboratory, University of Port Harcourt. Other chemicals used are of analytical grade and obtained from Chemistry laboratory, Nile University, Abuja.

silver nitrate, Sulfuric acid, sodium hydroxide, ferric chloride, hexane, sodium chloride, chloroform, potassium hydroxide, copper 11 sulphate, hydrochloric acid, ethanol and distilled water.

2.2 Methodology

2.2.1 Extraction of *Lagenaria siceraria* (Calabash) seed oil

Oil from the calabash seed was extracted using the Soxhlet method with hexane as solvent according to the method of [15]. The seeds were kept in the sun until they are completely dried. When dried, the seeds were pounded in a mortar before it was transferred into a Soxhlet extractor. 50g of the pulverized seed was used with 1litre of hexane in a round bottom flask of the Soxhlet apparatus. Extraction was carried out at 70°C until a clear solution of the extracting solvent was obtained. The oil was obtained after distilling the extracting solvent. The percentage of oil recovered was calculated as follows:

$$\% \, Yield = \frac{Weight\ of\ oil\ (g)}{Initial\ weight\ of\ sample\ (g)} \times 100\,[16] \qquad (1)$$

2.2.2 Solvent/Hexane recovery

Mixture of the extract and solvent in a round bottom flask was connected to the rotary evaporator. The mixture was put to boil at a temperature of 50°C while extract recovery takes place. After about 2 hours, separation was complete. Extract was left for 24 hours for final evaporation.

2.2.3 Ash and acidification of the calabash seed residue

The ash procedure of the calabash seed residue was carried out following the procedure of [17] with slight modification. The residue of the calabash seed was collected after constant weight was obtained by drying at 80°C in an oven. The dried residue (23 g) was placed in a porcelain crucible and combusted to ash for 6 hours at 500°C in a furnace (muffle). Thereafter, the ashes were soaked in 100ml 2 % H_2SO_4 and stirred for 1hr. After acidification, the mixture was washed four times to acquire a neutral pH. The calabash seed ash extract was kept in a container in the Laboratory at 5°C for further formulation of demulsifiers.

2.2.4 Preparation of silver nanoparticle ash

The silver nanoparticles ash was achieved by adopting the method of [18] by mixing 15 g of the calabash ash extract with 150 mL H_2O and of 10.0 mM $AgNO_3$. The mixture was stirred in the dark for 90 mins at 200 rpm and room temperature. The reaction condition was attuned to an optimal pH of 10.0 from the initial pH of 4 using 0.2M NaOH solutions. Afterwards, the AgNPs were attained by repetitive centrifugation at 12, 000 rpm for 20 mins to eliminate the water-soluble biomolecules. Furthermore, the pellet was spread in distilled water, the procedure was carried out in triplicate. The decontaminated pellets were consequently dried on Petri plates at 60ºC under vacuum condition for 24 hours. Hence, the dried AgNPs were stored for further study.

2.2.5 Preparation of eco-friendly demulsifiers

2.2.5.1 Preparation of the demulsifiers using calabash seed oil, and acidified ash

The method of [17] was adopted for this procedure. 3 g of the calabash stalk ash residue was added to 4 g of the calabash seed oil and the blends were positioned on the magnetic stirrer- heater to dissolve at a controlled temperature of 40°C. The mixture was homogeneously mixed for 5 mins to form the demulsifier and further cooled to room temperature.

2.2.5.2 Preparation of the demulsifiers using ethanol and acidified calabash seed ash

The method of [19] was used to formulate the ethanol based demulsifier. 5g of the calabash seed ash was transferred into a beaker containing 5 ml of absolute ethanol and the mixture was homogenously stirred in a magnetic shaker for 10 mins. The demulsifier formed was kept back in the refrigerator for more analysis.

2.2.5.3 Preparation of the silver nanoparticle demulsifiers

Silver nanoparticle demulsifier was prepared using a modified method of [19] 5g of the synthesized silver nanoparticle ash was added to 5ml of ethanol and the mixture was stirred for 10 mins using a shaker. After the formulation of the demulsifier, it was stored in a refrigerator for further analysis.

2.2.6 Crude oil emulsion preparation

The method of [19] was adopted in the preparation of water in oil emulsions. Distilled water (400ml) and crude oil (140ml) were mixed thoroughly in a 800 mL beaker, and the blend were heated at 70ºC for 20 mins. The blend was then homogenized for 20 mins at a rotation of 11000 rpm with a magnetic shaker. The stirring progression was carried out twice to attain a stable oil–water emulsion. To complete the aging procedure, the emulsion was kept stable for seven days at ambient temperature.

2.2.7 Bottle test demulsifier screening

The crude oil emulsion breaking capacity of the developed biodemulsifier was assessed using the bottle test method, and performance against chemical demulsifier was compared. The different bottles received equal amounts of both demulsifiers. To guarantee that, the crude oil emulsions and demulsifiers were thoroughly mixed, the bottles were placed to observe the separation at 5 mins interval.

$$Water\ separation\ EFF\ (\%) = \frac{Volume\ of\ water\ separated}{Original\ volumn\ of\ water\ in\ the\ crude\ oil\ emulsion} \times 100 \qquad (2)$$

2.2.8 Phytochemical analysis

The phytochemical screening of *Lagenaria siceraria* seed oil was determined by adopting the methods of [30]. The phytochemicals screened are Flavonoids, Alkaloids, Tannins, Oil spot, Phenols, Terpenoids, Glycosides, Saponins, Steroids, Carbohydrates and Proteins.

2.2.9 Chemical characterization procedures

2.2.9.1 FT-IR analysis

The FT-IR analysis was carried out with Nicolet iS10 FT-IR Spectrophotometer. The spectral frequency was in the range of 4000-350 cm^{-1} with a spectral resolution of 4 cm^{-1}. The spectra were examined with spectroscopic software (Win-IR Pro Version) at a peak sensitivity of 2 cm^{-1}.

2.2.9.2 Gas chromatographic-mass spectroscopic (gc-ms) analysis

GC-MS study was assessed with Perkin Elmer Turbo mass spectrophotometer (Norwalk, CTO6859, USA) containing Parkin Elmer Auto Sampler (XLGC). An Elite -5 capillary column with capacity of 30m x 0.25mm and thickness of 0.25 mm containing Dimethyl polysiloxans was used for the study.

3.0 RESULTS AND DISCUSSION

3.1 Oil Yield

$$\%\,Yield = \frac{Weight\ of\ oil\ (g)}{Initial\ weight\ of\ sample\ (g)} \times 100 \qquad (3)$$

$$\%Yield = \frac{15.5}{50} \times 100 = 31\%$$

The concept of oil yield is a crucial parameter used in various fields, measuring the percentage of oil obtained from a sample and indicating its oil content. Calculation using the formulae above provides a standardized approach for assessing oil content. For example, if a sample weighing 50 grams yields 15.5 grams of oil, the oil yield is calculated as 31%. This calculation method enables efficient evaluation of oil extraction processes, optimization for higher yields, and informed decision-making in oil-dependent industries.

3.2 Phytochemical Analysis of Calabash Oil

The phytochemical results of *Lagenaria siceraria* seed oil showed the presence of the metabolites tested for which are also constituents of demulsifiers (Table 1). The emulsion breaking capacity of any demulsifier is a function of not only oil-emulsion stability but on the demulsifier's properties. The stability of crude oil emulsions depends on the physicochemical properties of the crude constituents, their interrelationships, and interactions with each other [17]. Phytochemical screening of the crude hexane extract (oil) of the calabash seed showed that the metabolites (tannins, terpenoids, alkaloids, saponins, carbohydrates, flavonoids, steroids, volatile oils and phenols are present while proteins are found to be absent (Table 1).

Table 1: Phytochemical Analysis of *Lagenaria siceraria* seed oil

S/N	METABOLITES	RESULT
1	Flavonoids	Present
2	Alkaloids	Present
3	Tannins	Present
4	Oil spot	Present
5	Phenol	Present
6	Carbohydrate	Present
7	Terpenoids	Present
8	Proteins	Absent
9	Steroid	Present
10	Glycosides	Present
11	Saponins	Present

This was done to determine the presence or absence of phytochemical, because polyphenols, ethers, esters, amides, polyoxypropylene that contain both hydrophobic and hydrophilic properties have been reported to as chief constituents of demulsifiers. The phytochemicals reported in this investigation such as flavonoids, saponins, tannins and phenols are known to possess the ability to breakdown the interfacial film created by asphaltenes, by this means, enhancing the coalescence of water/oil droplets thus, accomplishing the oil–water separation. Countless essential oils that belong to the terpenes group of compounds have been recognized to contain functional group derivatives of ketones, alcohols, aldehydes, esters, phenols and amines [21]. Notwithstanding their abundant and complex composition, oils are used in many industrial applications of which demulsification is one of them, they are also useful in cosmetics, food and perfumery domains. Thus, it is worthy to understand their chemistry, physicochemical properties, biological activity as well as their individual components as this would enhance their development into valuable products applicable in environment, agriculture and human health [23]

3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The result of the FTIR analysis carried out on the calabash seed oil are presented in Figure 1.

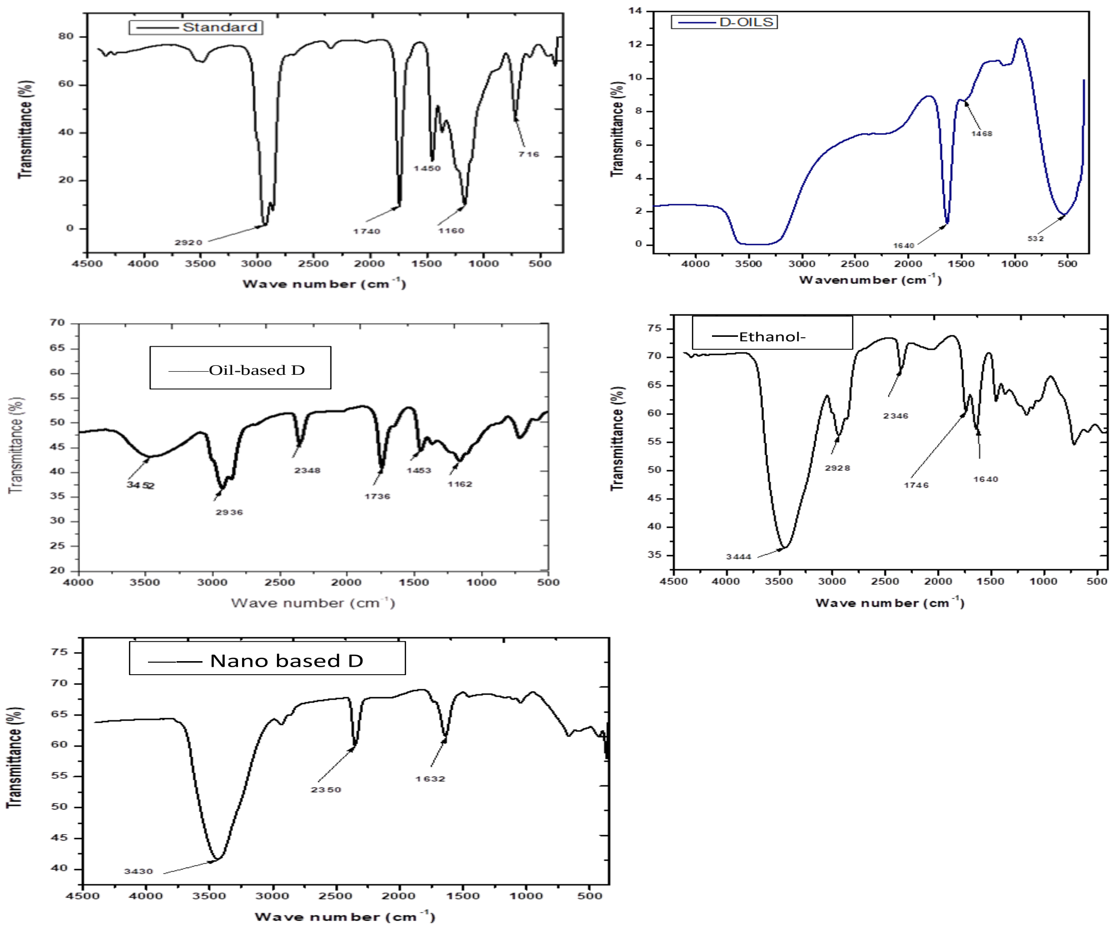

Figure 1: FT-IR Spectra of (a) chemical demulsifier (b) calabash seed oil (c) oil based demulsifier (d) ethanol-based demulsifier (e) Nano-based demulsifier

Infrared spectroscopy (FTIR) is a vital analytical tool that provide the possibility of measuring different functional groups or inter atomic bond vibrations at diverse frequencies present in a compound. The FT-IR analyses all samples contains fatty acids, alcohols, carbonyl containing compounds such as carboxylic acids and derivatives, terpenes/terpenoids, aliphatic and aromatic hydrocarbons, benzothiazole and aromatic acid esters which are evident in the characteristics stretching vibrations of C-H bonds, O-H bonds, C=C bonds, C=O bonds and C-O bonds [24]. The FT-IR spectrum (Figure 1a) of the chemical demulsifier (Phase treat) revealed the presence of various characteristic vibrational peaks when compared the spectra of the oil extract and those of eco-friendly demulsifiers. The spectrum reveals the presence of a low intensity peak at 3440 cm^{-1} which is distinctive of O-H stretching vibration of either alcohols or phenols. The low intensity demonstrated that the O-H group are less abundant in the chemical demulsifier. The presence of the peak at 2927.77 cm^{-1}, reveal the presence of C-H stretching vibrations which are present in all organic compounds. The peaks at 1743, 1453 and 1166 cm^{-1} confirmed the existence of C=O, C=C and C-O. stretching vibrations respectively. Their presence confirms that the chemical demulsifier are made up of compounds such as carboxylic acids, phenols, terpenoid, flavonoid found in chemical demulsifiers.

The FT-IR spectrum (Figure 1b-e) of the calabash seed oil and the prepared demulsifiers, revealed similar characteristic vibrational banks observed in the chemical demulsifier O-H vibration around (3300-3600 cm^{-1}), C=O around 1700-1800cm^{-1}, C=C around 1450-1640 cm^{-1} and C-O around 1000-1150 cm^{-1}. But they differ in the intensity of the different vibrational peaks which is as a result of differences in the number of the compounds or functional groups absorbing the energies. The similarity shows that the oil contains the functional groups needed to formulate the demulsifier for emulsion separation. However, it was evident that the O-H vibrational peak of the ethanol and Nano-based demulsifiers are stronger in intensity when compared to those of the chemical demulsifier and the extracted seed oil. The reason may be attributed to the presence of ethanol is the solvent based for the preparation of the demulsifiers. Moreover, the FT-IR spectrum (Figure 1e) of the Nano-based demulsifier reveal the absence of the C-O functional group which demonstrates the absence or very little presence of the characteristic functional groups in sample. This may be attributed to the presence of the metallic sliver (nanoparticle). Studies have shown that FT-IR spectra of silver nanoparticles exhibited distinctive peaks at 1600-1630 cm-1, and absence of the C-O bond which is attributed to surface bound metallic silver [25]. This functional presence plays a vital role in emulsion separation.

3.4 Results of GC-MS Analysis

GC-MS is a vital technique employed for qualitative and quantitative identification of compounds present in an analyte. GC-MS analysis was conducted to obtain detailed information about the chemical constituents of the biodemulsifier formulations, complementing the characterization through FTIR analysis. The combined use of FTIR analysis and GCMS provides valuable insights into the biodemulsifiers molecular structure, functional groups, and potential interactions, enabling a comprehensive understanding of their composition. These findings not only contribute to further optimization and evaluation of the biodemulsifiers efficacy in emulsion management but also offer insights into their potential applications in various industries. Previous studies have shown that soaps, fatty acids, fatty alcohols, amines, resins obtained from plant materials can be used in the production of demulsifiers [17]. Bio-based materials have been utilized for the formulation of biodemulsifier because of their hydrophilic-lipophilic characteristics which enable them to form interactions such as hydrogen bond formation with water thus forcing a separation from water-in-oil emulsion [26;27].

The results Figures 2 and Table 2 represent the spectra and biodata of the chemical demulsifier used as a reference in this study. The chemical constituent obtained from the GC-MS analysis of the demulsifiers prepared in this study shows that they all contains the hydrophilic-lipophilic character as reported in literature. The commercial chemical demulsifier contain a total of nineteen compounds (Table 2) with two major constituents (and their relative peak) of acetic acid (27.28%) and 1-hydroxy-2-propanone (16.40) and minor components like acetic acid methyl ester (3.65%), 2,3-dihydro-benzofuran (3.65%) and phenol (3.05%). The presence of C=O, O-H and C-O functional groups that produces the hydrophilic and lipophilic characteristics in demulsifiers found confirms that the sample is a demulsifier.

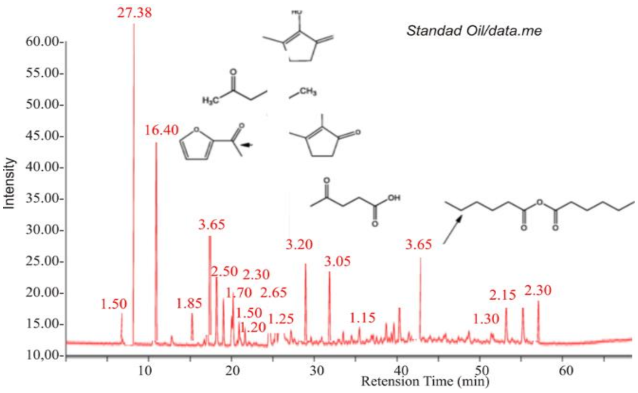

Figure 2: GC-MS spectrum of chemical demulsifier

Table 2: Biodata analysis of chemical demulsifier

S/N	RT(mins)	Compound Name	Area %
1	8.20	2-amino 1,3-propanediol	1.50
2	9.40	Acetic acid	27.38
3	10.95	1-hydroxyl 2-propanone	16.40
4	15.60	1-hydroxyl 2-butanone	1.85
5	15.85	Acetic acid-methylester	3.65
6	18.05	Butanedial	2.55
7	18.80	2-cyclopentane-1-one	1.70
8	18.60	Furfural	2.30
9	20.85	2,2,4-trimethyl 1,3dioxolane	1.50
10	21.65	1,2propanone	2.65
11	22.05	2-butanone	1.20
12	26.95	2,3-dimethyl-cyclopentane	1.25
13	27.80	2-furanone	1.15
14	29.70	3methyl 1,2cyclopentanedione	3.20
15	31.50	Phenol	3.05
16	35.70	4-methyl-phenol	1.30
17	39.70	4-ethyl-phenol	2.15
18	43.62	2,3-dihydro-benzofura	3.65
19	59.95	Glucosandi-one	2.30

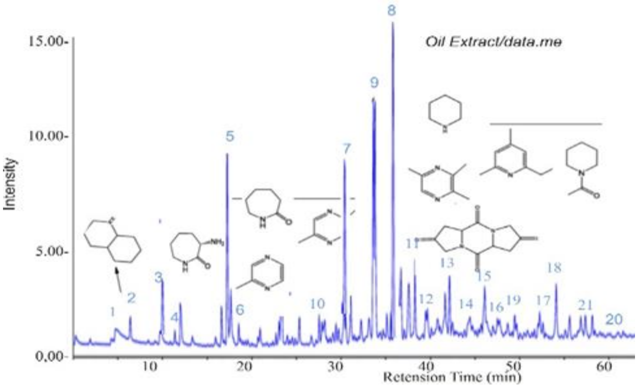

Figure 3: GC-MS spectrum of calabash seed oil

Table 3: Biodata analysis of the calabash oil

S/N	RT(mins)	Compound Name	Area%
1	5.60	Octane	1.20
2	7.70	Decanoic scid	1.60
3	12.35	1-undecene	3.60
4	13.20	1-dodecene	1.65
5	18.40	Dodecene	8.60
6	19.82	1, 12-tridecadiene	1.20
7	23.70	3-tetradecene	1.50
8	30.60	Tridecane	8.30
9	34.82	3-tetradecene	10.20
10	29.42	3-tetradecene	2.65
11	37.65	4-methyl phenol	19.20
12	40.20	Cyclohexane, 1,5-diiso propyl-2,3-dimethyl	1.22
13	42.60	1-hexadecene	3.60
14	45.40	Methyl-hexadecadienoate	1.10

15	45.90	Isopropylmyristate	3.65
16	46.40	3-octadecanone	0.70
17	53.50	1-octadecanethiol	1.15
18	55.22	Methyllinolelaidate	4.60
19	65.35	Methylelaidate	1.30
20	62.22	Methyl-octadecenoate	0.07
21	57.20	1-docosene	1.12

The result obtained for the extracted oil have a chemical constituent (Tables 3 and Figures 3) of twenty-one (21) compounds. The constituents with highest percentage composition are; 4-methyl phenol (19.20%), 3-Tetradecane (10.20%), Tridecane (8.30%) and dodecene (8.60%). The three major constituents identified belongs to the ten (10) carbon atom hydrocarbon with more lipophilic characteristics. The major hydrophilic constituents identified is 4-methyl phenol while others of low amount are Decanoic acid (1.60%), methyl, hexadecadienoate (1.10%). The GC-MS result obtained for the oil-based demulsifier appeared to have almost the same chemical constituents (Table 4) with that of the extracted oil with a total of twenty-one (21) compounds though the major constituent differs. The constituents with highest percentage composition are; Tridecane (16.30%), 3-Tetradecane (10.20%), 3-Tetradecene (8.50%), dodecene (8.60%) and hexadecane (5.20%). The constituents identified all belongs to the ten (10) carbon atom hydrocarbon thus making them to be more lipophilic in nature. The similarities in most of the constituent found in the oil based demulsifier arises to the fact that the extracted oil is the base of the prepared demulsifiers.

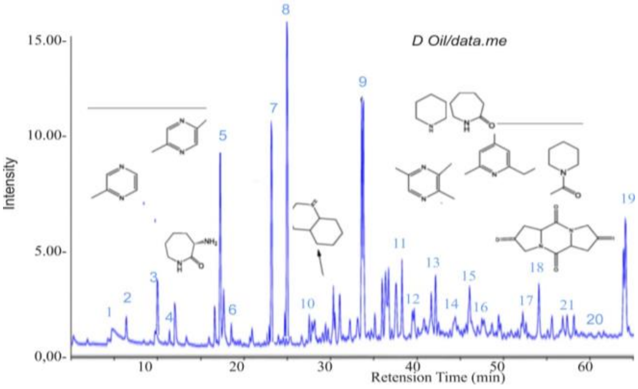

Figure 4: GC-MS spectrum of oil-based demulsifier

Table 4: Biodata analysis of the oil-based emulsifier

S/No.	RT (mins)	Compound Name	Area %
1.	5.60	Octane	1.20
2.	7.70	Decanoic acid	1.60
3.	12.35	1-undecene	3.60
4.	13.20	1-dodecene	1.65
5.	18.40	Dodecene	8.60
6.	19.82	1, 12-tridecadiene	1.20
7.	23.70	3-tetradecene	8.50
8.	25.60	Tridecane	16.30
9.	34.82	3-tetradecane	10.20
10.	29.42	3-tetradecene	2.65
11.	38.65	Hexadecane	5.20
12.	40.20	Cyclohexane, 1,5-diisopropyl-2,3-dimethyl	1.22
13.	42.60	1-hexadecene	3.60
14.	45.40	Methyl-hexadecadienoate	1.10
15.	45.90	Isopropylmyristate	3.65
16.	46.40	3-octadecanone	0.70
17.	53.50	1-octadecanethiol	1.15
18.	55.22	Methyllinolelaidate	4.60
19.	65.35	Methylelaidate	1.30
20.	62.22	Methyl-octadecenoate	0.07
21.	67.20	1-docosene	7.12

There were 22 composites in the GC-MS analysis of ethanol based demulsifier (Figure 5). Table 5 displays the detected constituents together with their retention time and percentage concentration. Among the 22 compounds, 1,2-dihydroxyl 2-proanone, 3-octadecanone and 9-octadecenoic acid with percentage abundance of 33.65%, 27.38% and 16.40 % respectively are the most occurring compounds. The result exhibits a hydrophilic character arising from the presence of the carboxylic groups, esters, phenolic group and a minor constituent elatol with percentage composition of 3.65 %. Elatol is a halogenated sesquiterpene in the chamiqrene natural product family. A two-ring cyclic unsaturated compound with O-H, Cl and Br attached at the 1,2 and 6 carbon atoms. It has been reported to play important roles in ecological interactions such as anti-herbivores activity and potential defense against infection by microorganisms [28]. Previous studies have reported that the development and effectiveness of cellulose-based materials as surfactant for emulsion separation [29;30].

The Nano-based demulsifier represents an innovative biodemulsifier formulation based on nanoparticles, specifically silver nanoparticles, known for their unique properties and versatile applications [31]. These nanoparticles serve as active agents in destabilizing and separating emulsions, contributing to the emulsion-breaking capabilities of demulsifiers.

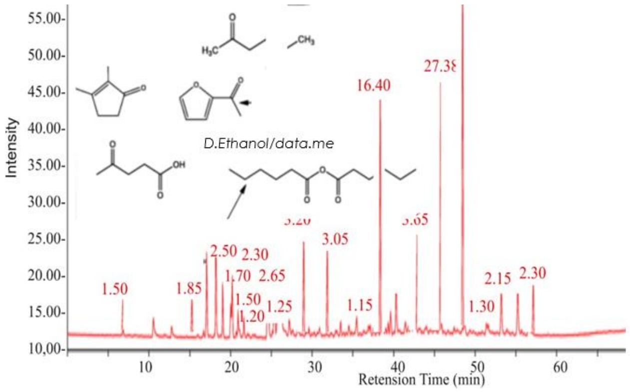

Figure 5: GC-MS spectrum of Ethanol based demulsifier

Table 5: Biodata analysis of ethanol based demulsifier

S/No.	RT (mins)	Compound Name	Area %
1.	7.50	Decanoic acid	1.20
2.	10.55	1-Hydroxyl-2-propanone	1.15
3.	15.60	1-Hydroxyl-2-butanone	1.85
4.	17.15	2-Butanol	2.50
5.	18.80	2-Cyclopentane-i-one	2.55
6.	19.30	2-Cyclopentane-1-one	1.70
7.	20.10	Pentanedecanoic acid 1,4-dimethyl ester	2.30
8.	20.85	2,2,4-Trimethyl-3-dioxalane	1.50
9.	21.65	1,2-Propanone	2.65
10.	22.05	2-Butanone	1.20
11.	26.95	2,3-Dimethyl-1-cyclopentanone	1.25
12.	29.70	3-Methyl-1,2-cyclopentanedione	3.20
13.	31.50	Phenol	3.05
14.	35.70	4-Methyphenol	1.30
15.	38.50	9-Octadecanoic acid	16.40
16.	40.10	4-Ethylphenol	2.15
17.	43.62	Elatol	3.65
18.	46.50	3-Octadecanone	27.38
19.	49.10	1,3-Dihydroxyl-2-propanone	33.65
20	53.70	1-Octadecanol	2.15
21.	55.20	9-Octadecanate	2.15
22.	57.95	1-Docoacene	2.30

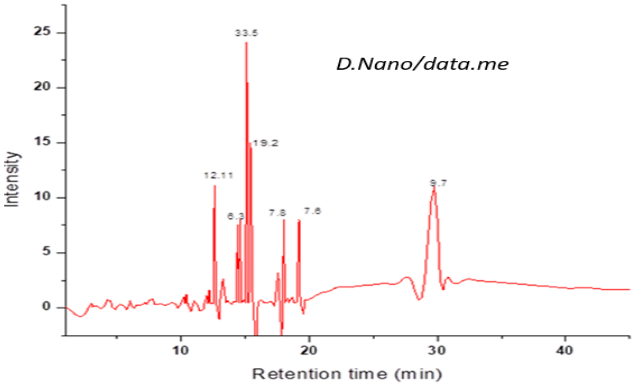

Figure 6: GC-MS spectrum of Nano-based demulsifier

Table 6: Biodata analysis of nano-based demulsifier

S/No	Retention Time	Compound Name	Area %
1.	10.2	Acetic acid methyl ester	0.6
2.	10.6	1-Hydroxyl-propanone	1.0
3.	12.5	Tetrachloropentane	12.11
4.	13.1	3-Chloro-2-nitrobenzyl Alcohol	1.3
5.	14.4	1-Oxaspiro-chlorophenyl	6.3
6.	15.11	1,3-Dihydroxyl-2-butanone	33.3
7.	15.53	Acetic acid-butyl ester	19.2
8.	21.60	1,4-Cyclohexadiene	7.8
9.	19.50	3-Cyclohexen-1-ol	7.6
10.	29.8	3-Methyl-5-nitro-1-2-cyclopentanedione	9.7

The GC-MS analysis of nano-based demulsifier (Figure 6) revealed that presence of ten compounds (Table 6). The major compound identified and their abundance are 1,3-dihydroxyl-2-butanone (33.5%), Acetic acid-butyl ester (19.2%) and Tetrachloropentane (12.11%). The presence of nitro (nitrogen containing) groups is evident that the agitation of the silver nitrate with the corncob could have led to a displacement reaction between the compounds and nitrates in silver nitrate. The presence of these compounds shows great presence of hydrophilic character. The efficiency of Nano-based particles to break emulsion was reported by [32] who utilized magnetic cellulose nanocrystal-supported silver nanoparticle to effectively break the oil-in-water emulsion. Hence, the results obtained from the formulated eco-friendly demulsifiers demonstrated that they contain the compounds with the ability to break a water-in-oil or oil-in-water emulsions. It also agrees with works in literature on the use of biomaterials for effective emulsion management.

3.5 Result for Bottle Test Analysis

The bottle test analysis was carried out with the three formulated eco-friendly demulsifiers: oil-based, ethanol-based and nano-based demulsifier in comparison with a commercial chemical demulsifier (Phase treat) to determine their capability to break the film during emulsion management. The bottle test was used to investigate the effectiveness of the formulated demulsifiers to break emulsions in comparison with a commercial chemical demulsifier at 70 °C. The emulsion breaking potential of any demulsifier depends majorly on the crude oil emulsion stability and the demulsifiers inherent properties.

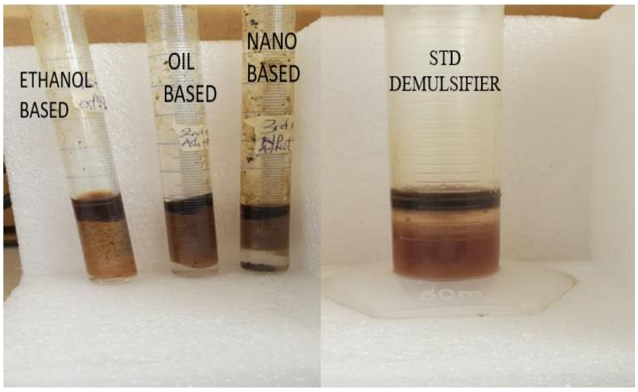

Figure 7: Bottle test analysis of the different eco-friendly demulsifiers

3.6 Efficiency of Separation

The efficiency of the separation was determined after 60 mins. According to the results (Figures 7 and 8), It showed that the eco-friendly formulated demulsifiers performed very favorably with the standard demulsifier (Phase treat). The Nano-based demulsifier produced the best separation with 25.8 % efficiency. This performance was followed by chemical demulsifier with 16.5% and ethanol based demulsifier with 11.4% whereas, the oil-based demulsifier produced the least with 3.9% separation.

The efficiency of separating emulsions basically rests on the particle size and hydrophilic substances on their surface, which is credited to the existence of the hydrophilic components of the bio-materials. Thus, the excellent demulsification performance (Figure 7) of the Nano-based demulsifier could be attributed to the small particle size of the synthesized silver Nano particle and the presence of hydrophilic groups such as the carboxylic acids. It is possible for nanoparticles to adhere to the emulsion interface and interfere with the stability of the emulsion droplets due to their special surface-active capabilities. According to [32] and [33], this behavior makes it easier for the oil and water phases to combine and then separate. This result is in line with the work of [34] who observed that the composition of carbon and silicon oxide could effectively improve the demulsification of W/O emulsions.

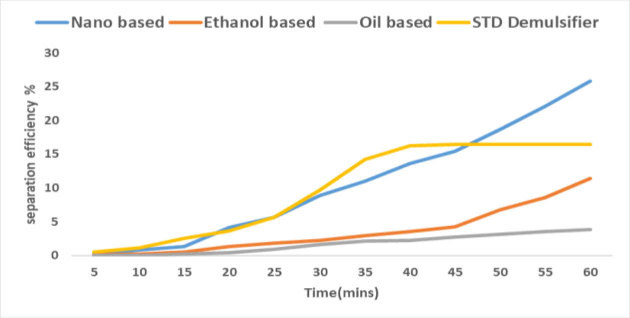

Figure 8: Separation Efficiency of the Eco-friendly Demulsifier

3.7 Effect of Separation Time on Emulsion Management

The effect of separation time on the demulsification process was carried out to determine the time each formulation will achieve maximum separation. It was observed (Figure 8) that the chemical demulsifier achieved its maximum separation at 40 mins after which it maintained a constant volume till the stipulated time of 60 mins. In contrast to the chemical demulsifier, the formulated eco-friendly demulsifiers demonstrated encouraging demulsification performance, but at a slightly slower rate and achieve their maximum separation time after 60 mins. Thus, the order of separation in respect to time is in the following trend: Chemical demulsifier > Nano-based > Ethanol-based > Oil-based.

4.0 CONCLUSION

The results obtained in this work demonstrated the effectiveness of bio-based and eco-friendly raw materials to break the interfacial attraction found in emulsions. The phytochemical analysis of Calabash seed oil extract exhibited the existence of both hydrophilic and hydrophobic substances which possesses the capacity and thus useful in the formulation of demulsifiers. The GC-MS and FTIR analysis conducted to determine the chemical constituents of the biodemulsifier formulated confirmed that most of the compounds present in the demulsifiers have the capacity of breaking the thin film created by the emulsion process. These findings not only contribute to further optimization and evaluation of the biodemulsifier' efficacy in emulsion management but also offer insights into their potential applications in various industries. The bottle tests showed that the Nano-based demulsifier formulated have excellent demulsification properties than the chemical demulsifier even though chemical demulsifier have faster settling time.

In conclusion, the various eco-friendly demulsifiers produced in this research demonstrated that they have the ability to break down the water-in-oil emulsion created during crude oil production. Moreover, the Nano-based demulsifier demonstrated high capability when compared with the commercial chemical demulsifier.

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