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Effects of Vegetable Seed Oils Concentration in Bio-Demulsifiers on Demulsification of Nigerian Crude Oil

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Abstract: In search of environmentally friendly petroleum processing, three bio-demulsifiers were synthesized from Nigerian vegetable seed oils. The synthesized vegetable seed oils were Mahogany, Neem, and Calabash. Their oils were mechanically extracted and mixed with liquid detergent, camphor, starch, and paraffin wax to form bio-demulsifiers. The green demulsifiers produced were mixed with synthetic crude oil in the ratios of 0.5:50, 1:50, 1.5:50, 2:50, and 2.5:50 volume/volume in mL. Studies on the effects of their concentration in the demulsification of water-in-oil emulsion were conducted. Mahogany demulsifier of formulation M8 1.5:50 and M8 2:50 (volume of demulsifier to the volume of synthetic crude) had 78% performance. This was followed by N8 1.5:50 which had 77% performance. The highest 70% water removal performance by calabash demulsifiers was recorded by C1 0.5:50, C1 2:50, and C1 2.5:50. The lowest performance was recorded by N1 1:50 and N1 1.5:50 which had a performance of 35% water removal. With these results, Mahogany seed oil can be conveniently used to prepare bio-demulsifiers to save our environment and production cost.

Keywords: Bio-demulsifiers, concentration, crude oil, demulsification, effects, Vegetable Seed Oils

Introduction

Efficient, environmentally, and cost-effective separation of water in oil emulsion is key. Bio-demulsifiers are environmentally friendly and cost-effective as they are degradable and are produced locally from renewable and sustainable sources such as vegetable seed oils (Dhandhi et al., 2022). Before the downstream processing of crude oil, the emulsified water in the water/oil emulsion is first removed using a demulsifier for the safety of the processing materials (Ye et al., 2022). Normally, water is found in the form of droplets dispersed in the oil and gas exploration called water-in-oil emulsion (Arifin et al. 2016). Crude oil emulsion can occur naturally in the oil well, during drilling and processing, and transportation from the oil reservoirs to the processing stations (Yonguep et al., 2022: Arifin et al. 2016). The emulsion of water in oil or oil in water is usually aided by some natural emulsifiers such as asphaltenes, resins, naphthenic acids, and waxes (Ye et al., 2022). Some other notable emulsifiers are lectin, proteins, gums, and fatty acid esters (Flores-Andrade et al., 2021). These emulsifiers attract water at one end (hydrophilic end) and at the other end attract oil (lipophilic end) (Clark, 2013). Therefore, a typical emulsifier has an ionic end which is hydrophilic, and an organic end hydrophobic to stabilize water/oil emulsion (Han et al., 2022). Huang et al. (2020) and Severino et al. (2011) claimed that the emulsion form type depends on the emulsifier's hydrophilic-lipophilic balance.

Besides being formed in the wellbore due to turbulence agitation of the crude oil during production, an emulsion is also formed in the desalting unit of crude oil processing (Yonguep et al., 2022). The crude oil is usually washed to remove metals that may cause wearing and corrosion to the processing machines (Rajeev et al., 2012). The crude oil is also emulsified to enhance oil recovery (Rostami et al., 2019) and to reduce the viscosity of the crude oil as it is transported from the field of production to the refining station (Souas, et al., 2021). In the preparation of the emulsification of water in oil, highly amphiphilic compounds are used to form a stable emulsion (Umar et al., 2018). The demulsification of water-in-oil or oil-in-water emulsion is the breaking down of the emulsion of the two immiscible liquids (water and oil) by attacking the interface (Umar et al., 2018). The demulsification also mitigation catalysts' poison and hence, maximizes production capacity (Saad et al. 2019). Water/oil emulsion demulsification is achieved by any of the following applications; the addition of a demulsifier, mechanical agitation, heating, or electrostatic field (Sousa et al., 2022). The thermal method is the introduction of hot water or steam into the reservoir oil to raise the temperature thereby reducing the viscosity of the heavy or viscous oil (Bera and Babadagli, 2017). The chemical method of demulsification is the use of chemicals such as polymers, surfactants, or alkalis to break the interfacial tension of water and oil (Yonguep et al., 2017). In some cases, immiscible gas injection of light gases such as CO_2, N_2, CH_4, C_3H_8, and C_4H_{10} is used to facilitate the production of crude from the reservoir (Zheng et al. 2017).

Chemical demulsification is among the most widely used application in the demulsification of water and hydrophilic substances in water-in-oil emulsion (Gómez-Jaimes et al., 2020). In this method, chemicals with a strong affinity (i.e. highly hydrophilic) to water are used (Shehzad et al., 2018). The commercial demulsifiers currently in use in the refineries such as triblock EO-PO copolymer are nonbiodegradable and hence require to be replaced with sustainable and environmentally friendly ones (Husain et al., 2022). The imported chemical demulsifiers are not biodegradable. In this study, three bio-demulsifiers were produced from three Nigerian vegetable seed oils; namely; Mahogany, Neem, and Calabash.

Materials and Methods

Materials

Materials used in this study include; Mahogany seed oil, neem seed oil, calabash seed oil, camphor, paraffin oil, starch, liquid soap, and distilled water. The apparatus used includes; a density bottle, hot plate magnetic stirrer, weighing balance, beakers, syringe, graduated bottles, centrifuge machine, thermometer, plastic buckets, and water bath.

Experimental

Preparation of oil field brine

A synthetic oilfield brine was prepared by dissolving sodium chloride into crude oil (Dardor et al., 2019) collected from Kaduna Refinery and Petrochemical Company (KRPC). It was produced to a salinity similar to that of the crude used in KRPC which is about 2.4 % (Adebanjo and Aduroja, 2015) as presented in Equ. 1.

$$Y = 8.3566X - 0.3582 \quad (1)$$

Y = Salinity (%w/w); % in per thousand

X = NaCl concentration (g/100 ml)

Emulsion preparation

Water in oil emulsion was prepared by mixing 50 mL of distilled water with 50 mL of synthetic oilfield brine (1:1 v/v) (Adebanjo and Aduroja, 2015). The mixture was agitated with a mechanical stirrer at a speed of 1300rpm for 3 hours to get a stable emulsion (Raji, 2021).

Extraction of oils

The Mahogany and Neem seeds were collected within NARICT environs while the calabash seeds were collected around Katsina Axis. The seeds were dehulled and extracted through mechanical pressing (Koubaa et al., 2016) in the NARICT neem extraction laboratory.

Production of liquid soap from locally sourced materials

A mass of 125 g of Sodium hydroxide (NaOH) was soaked in 150 g of distilled water for 24 hours in a bowl. Meanwhile, a solution of 192 g of sodium lauryl sulphate (SLS), 270 g of Sodium trioxocarbonate (iv) (Na_2CO_3), and 520 g of sulphonic acid were prepared in another bowl. The sodium hydroxide and distilled water were then added to the solution of sodium lauryl sulphate, sodium trioxocarbonate (iv), and sulphonic acid. The mixture was gently stirred and more distilled water was added to produce a homogeneous mixture of 10 litres with a pH of 9.0.

Production of local starch from Cassava

Some quantity of dry cassava starch was purchased from a local market around Sabon Garin market in Zaria. A mass of 262 g of the dry cassava starch was dissolved in 261 g of cold distilled water to form a solution. Meanwhile, some quantity of distilled water was made to boil on a gas burner at 100 ^{0}C. A mass of 300.9 g of the boiled distilled water was then added to the starch solution and gently stirred to form a paste-like solution as reported by Francis et al, (2016).

Production of Local Demulsifiers

A 5 g mass of camphor powder was measured and poured into a 500 mL beaker containing 35 g of Mahogany oil, placed on a hot plate magnetic stirrer at a temperature of 40 ^{0}C, and gently stirred to dissolve the camphor. A mass of 25 g of paraffin oil was then added to the hot camphorated mahogany oil. Next, 30 g of prepared cassava starch was added to the mixture while stirring continued. Finally, 30 g of prepared liquid soap was added to the entire mixture and stirred gently for 60 minutes on the hot plate to obtain a homogenous blend of bio-demulsifiers as reported by Francis et al. (2016). In the second phase, the neem and calabash demulsifiers were prepared using the same procedure described for the mahogany demulsifier as presented in Tables 1, 2, and 3.

Table 1: Formulation of Mahogany Seed Oil Demulsifier

Components	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Oil	35	15	34	20	33	20	32	10	31	0
Camphor	5	5	6	0	7	15	8	10	9	20
Starch	5	25	6	10	7	10	8	0	9	10
Paraffin oil	25	25	24	35	23	35	22	40	21	50
Soap(g)	30	30	30	35	30	20	30	40	30	20

Table 2: Formulation of Neem Seed Oil Demulsifier

Components	N 1	N 2	N 3	N 4	N 5	N 6	N 7	N 8	N 9	N 10
Oil (g)	35	15	34	20	33	20	32	10	31	0
Camphor(g)	5	5	6	0	7	15	8	10	9	20
Starch(g)	5	25	6	10	7	10	8	0	9	10
Paraffin oil(g)	25	25	24	35	23	35	22	40	21	50
Soap(g)	30	30	30	35	30	20	30	40	30	20

Table 3: Formulation of Calabash Seed Oil Demulsifier

Components	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Oil (g)	35	15	34	20	33	20	32	10	31	0
Camphor (g)	5	5	6	0	7	15	8	10	9	20
Starch (g)	5	25	6	10	7	10	8	0	9	10
Paraffin oil (g)	25	25	24	35	23	35	22	40	21	50
Soap (g)	30	30	30	35	30	20	30	40	30	20

Demulsification of the synthetic oilfield brine with synthesized demulsifier at room temperature

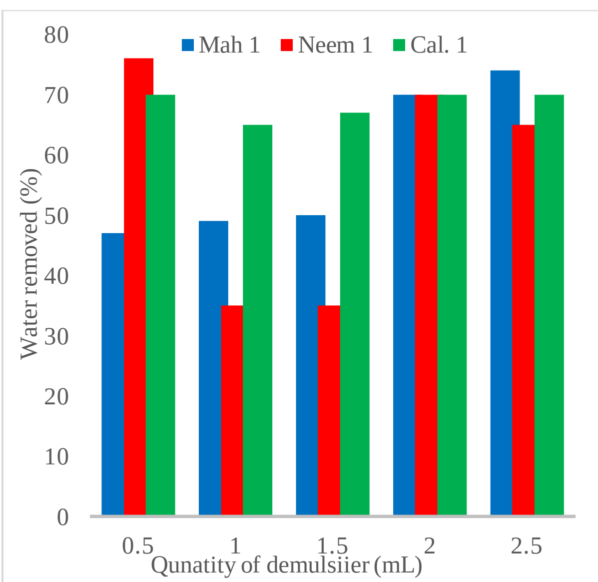
The synthesized demulsifiers produced were contacted with the crude oil samples in a ratio of 0.5:50 as reported by Sulaiman et al. (2015). A 50 ml of the crude oil emulsion sample was introduced into a bottle. Then, with the aid of a syringe, 0.5 ml of the mahogany synthesized demulsifier was added to the sample. The mixtures were vigorously mixed to homogenize and left to stand at room temperature. The process was monitored for four hundred and eighty (480) minutes, first at thirty 30-minute intervals followed by 60-minute intervals. This same process was repeated for neem oil and the calabash oil demulsifiers. The demulsifiers to synthetic oilfield ratios were increased to 1:50, 1.5:50, 2:50, and 2.5:50.

Results and Discussion

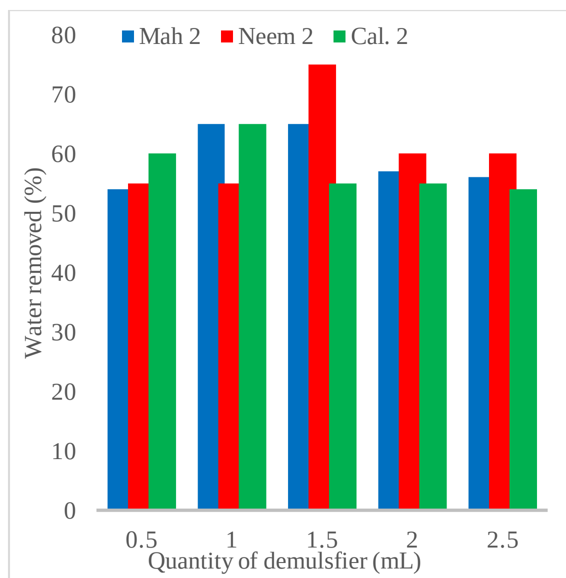
In the first formulation of M1, N1, and C1, which contained 35% vegetable oil in the demulsifiers, a 2.5:50 mahogany demulsifier separated 74 % water closely followed by a 2:50 ratio which separated 70

% water. The lower ratios 1.5:50, 1:50, and 0.5:50 separated 50, 49, and 47 % water respectively. The trend is not the same as that of Neem oil formulations. In this case, 0.5:50 has the best performance of 76 % water separation followed by 2:50 which separated 70 % water, 2.5:50 separated 65 %, 1.5:50, and 1:50 separated 35 % water each. In the case of Calabash oil, 0.5:50, 2:50, and 2.5:50 separated 70 % water while 1.5: 50 and 1:50 separated 67 and 65 % respectively. In this group, the neem oil formulation of 0.5:50 had the best performance with 76 % water separation which can be compared to the application of TOCN-AMDC$_{12}$ and TOCN-AMDC$_{18}$ with 74% performance reported by Gómez-Jaimeset al, (2020). It was followed by Mahogany of formulations 2.5:50 which separated 74 % water as shown in Figure 1a and again can be compared with the performance obtained by Ejikeme et al., 2019 of 70% performance.

The second formulation of 15 % oil in the demulsifier content of M2, N2, and C2, neem N2 1.5:50 had the best performance of 75% which is still higher than TOCN-AMDC$_{12}$ and TOCN-AMDC$_{18}$ with 74% (Gómez-Jaimeset al., 2020). It was followed by mahogany at 1:50 and 1.5:50, and Calabash at 1:50 with a performance of 65 % each. This performance was followed by 60 % from N2 2:50, 2.5:50, and C2 0.5:50 as depicted in Figure 1b.



a) Formulation 1

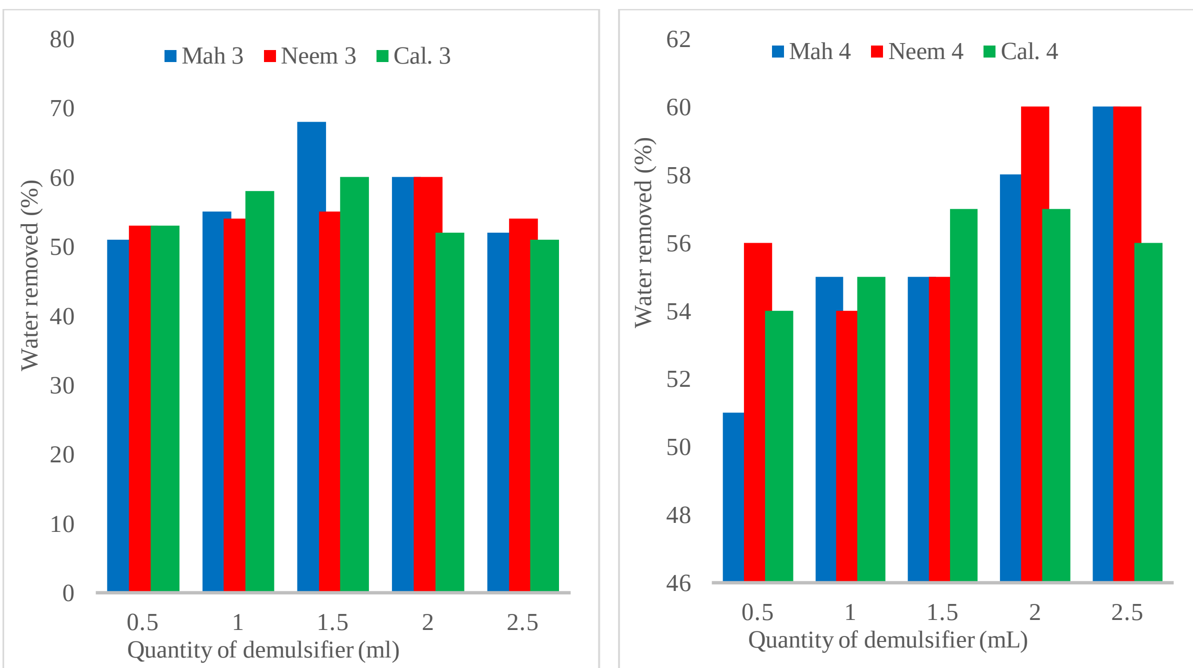


b) Formulation 2

Figure 1: Study of demulsification formulations 1 &2

The third formulation contained 34 % oil in the demulsifiers the M3, N3, and C3, M3 1.5:50 had the best performance with 68 % water separation. This was followed by M3 2:50, N3 2:50, and C3 1.5:50 each separating 60 % water as depicted in Figure 2a. The rest had below 60 % shown in Figure 2a.

The fourth formulation contained 20 % vegetable oils in the demulsifiers as presented in Figure 2b, the best performance was 66 % water separation obtained by N4 of 0.5:50 demulsifier to synthetic oilfield ratio. The performance was followed by M4 2.5:50, N4 2:50, and 2.5:50 which had 60 % each as depicted in Figure 2a. The highest performance obtained from C4 was 57 % from 1.5:50 and 2:50 ratio formulations.

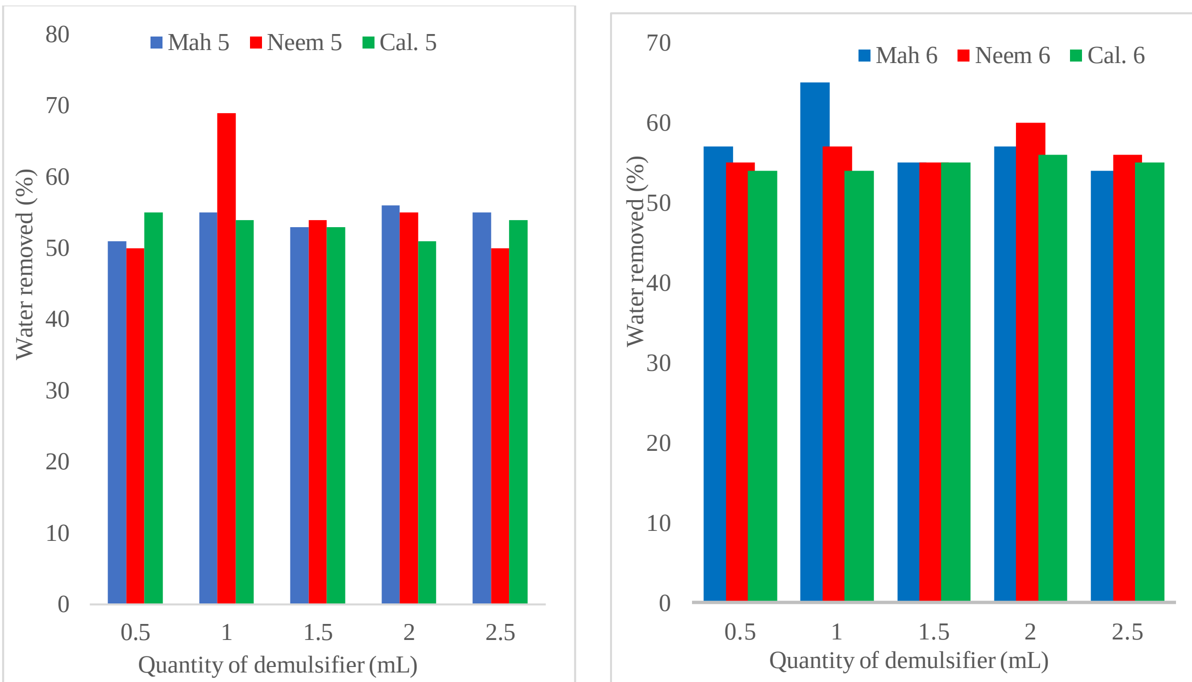


a) Formulation 3 b) Formulation 4

Figure 2: Study of demulsification formulation3 &4

In the fifth formulation which contained 33% vegetable oils in the demulsifiers, the highest performance of 69 % was obtained from the N5 1:50 ratio followed by 56 % from M5 2:50 and 55 %

M5 1:50, 2.5:50 and C5 0.5:50 ratios of demulsifier to synthetic oilfield as presented in Figure 3a. The sixth formulation contained 20 % vegetable oils in the demulsifiers and produced the highest performance of 65 % by M6 1:50. This was followed by N6 2:50 which had a 60 % performance as shown in Figure 3b.



a) Formulation 5

b) Formulation 6

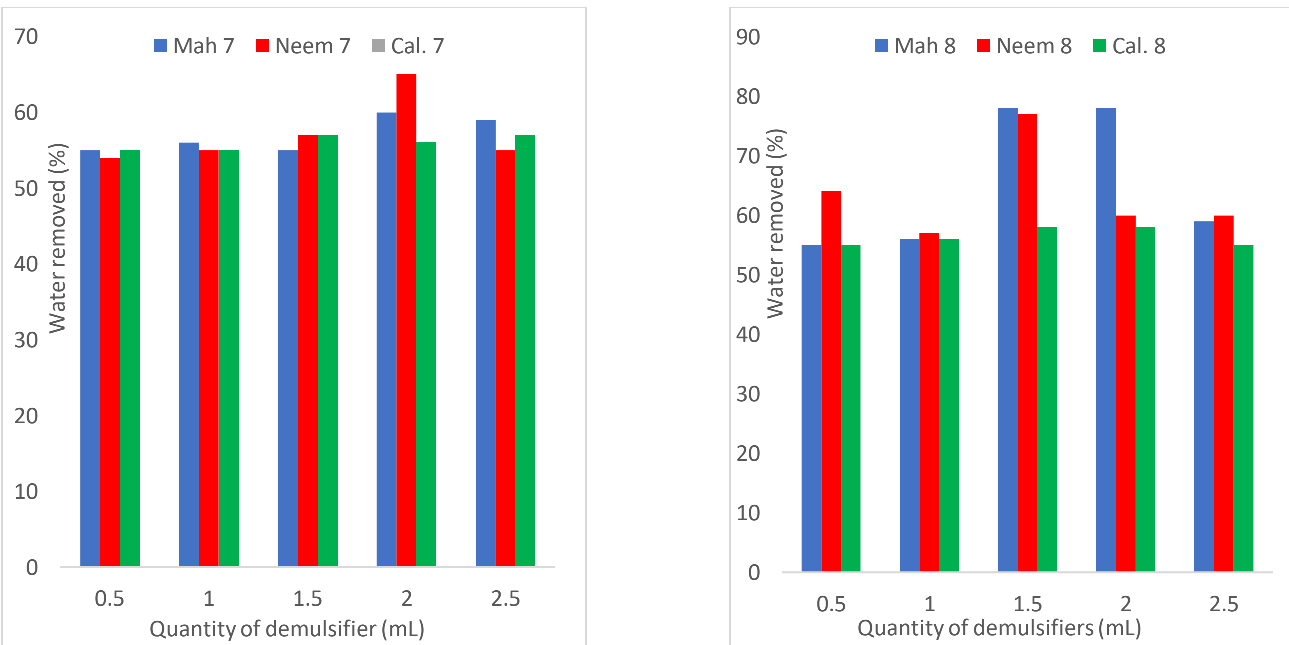
Figure 3: Study of demulsification of formulation 5 &6

The seventh formulation contained 32% vegetable oils in the demulsifiers, and the highest performance was 65 % obtained from N7 2:50. This was followed by 60 % and 59 % from M7 2:50 and M7 2.5:50 respectively. A 57 % performance was obtained from N7 1.5:50, C7 1.5:50, and C7 2.5:50. M7 1:50, C7 2.5:50 recorded 56 %, M7 0.5:50, M7 1.5:50, N7 1:50, 2.5:50, C7 0.5:50 and C7 1:50 recorded 55 %. The least was N7 0.5:50 which recorded 54 % performance as shown in Figure 4a.

Figure 4b depicts the performance of the 8th formulation which contained 10 % vegetable oils in the demulsifiers content. In this formulation, the best performance was 78 % obtained by M8 1.5:50 and

2:50, followed by 77 % from N8 1.5:50 which is higher than 75% obtained with TOCN-AMDC$_{12}$ and TOCN-AMDC$_{18}$ and 70% by Ejikeme et al, (2019). The next performances of 64 % and 60 % were obtained from N8 0.5:50, N8 2:50 and N8 2.5:50 shown in Figure 4b.

Figure 5 presents the performance of formulation 9 of the three bio-demulsifiers which contained 31% vegetable oils M9, N9, and C9. The highest performance was 64 % obtained from M9 2.5:50 followed by 59 % from N9 2:50 and N9 2.5:50 formulations. 57 % and 56 % were obtained from M9 1.5:50 and 2:50 respectively. A 55 % separation was obtained from M9 0.5:50, M9 1:50, N9 0.5:50, N9 1:50, C9 0.5:50, and C9 1.5:50 respectively. Others, C9 2.5:50, 2:50, and 1.5:50 recorded 54, 51, and 50 % respectively.



a) Formulation 7 b) Formulation 8

Figure 4: Studies of demulsification of formulation 7 & 8

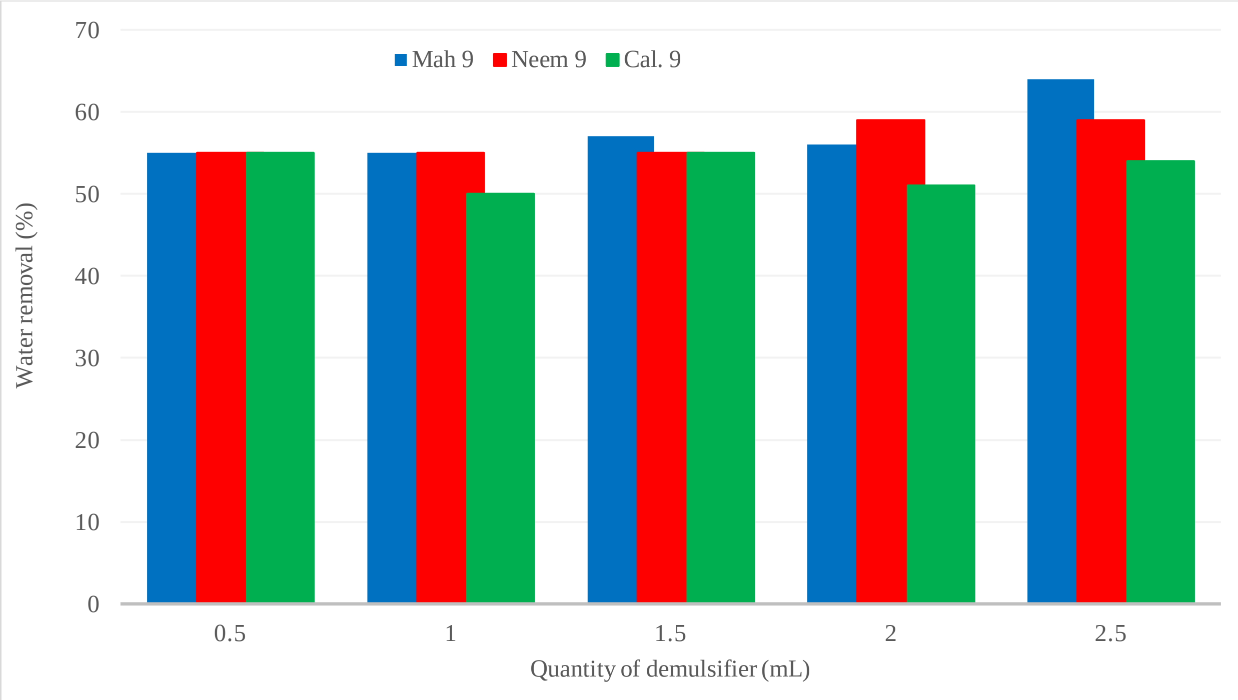


Figure 5: Studies of Formulation 9

Conclusions

Three bio-demulsifiers were synthesized from three Nigerian vegetable seed oils; Mahogany, Neem, and Calabash. The effects of their concentration on the demulsification of water-in-oil emulsion were conducted. Mahogany demulsifier of formulation M8 1.5:50 and 2:50 (volume of demulsifier to the volume of synthetic crude) had 78% performance. This was followed by N8 1.5:50 which had 77% performance. The lowest performance was exhibited by N1 1:50 and 1.5:50 which had the performance of 35% water removal. With these results, Mahogany seed oil can be conveniently used to prepare bio-demulsifiers to save our environment and production cost.

Recommendations

The demulsified samples should be tested to determine their extent of purification. Apply demulsifiers with the weight of vegetable oils less than 10 g to see if they can have a performance higher than 78% water removal. More local vegetable oils should be explored.

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