Synthesis, characterization, and demulsification of water in crude oil emulsion via a corn oil-based demulsifier

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ABSTRACT

Natural product-based materials have gained significant interest in replacing the petroleum-based oil chemicals with environmentally friendly materials. A corn oil-based demulsifier has been successfully synthesized by the condensation reaction of corn oil with diethanolamine in the presence of a catalyst applied during separation via a water-in-oil (W/O) emulsion. The demulsifier was characterized by FTIR, GC-MS, and LC-QTOF-MS analyses. The surfactant's separation efficacy was studied using the Sany-glass test. The results showed that this new product efficiently demulsified the W/O emulsion with 98% separation achieved. The influence of settling time, demulsifier dosage, and temperature on the demulsification efficiency were investigated. The separation efficiency increased with increasing settling time, demulsifier dose and the temperature conditions accelerate the demulsification process. As well, the interfacial tension decreases with increases of the demulsifier dose.

1. Introduction

Water often accompanies crude oil production—, particularly in offshore oil fields. In general, crude oil consisted of 30–90% of oil, 30–70 percent of water and 2–15 percent of solids by mass and was identified as a complex emulsion [1]. In most cases, a constant water in oil emulsion (W/O) is generated via active interfacial materials (such as asphalt, resins and fine solid particles) and shear stress in pipes and valves while transporting oil [2]. The emulsion produced is often more complex than crude oil. This can reduce the use of pipelines and increase energy consumption and the degradation of pipes [3]. Also, the W/O emulsions are very viscous, creating difficulties in the transport of oil and catalyst contamination in downstream refinery processes [4].

Crude oil waste is produced from crude oil transport, storage, and refinery processes. Such waste cannot be used directly because of the high water content or released into the atmosphere because of their environmental/health threat [5]. Therefore, demulsification is essential to remove water from crude oil before shipping and refining [6]. Demulsification is a favorable approach to break emulsions, increase oil recovery, and enhance water purity. Demulsification techniques include the introduction of chemical and biological demulgators, membrane treatment, electrical demulsification, and demulsification by microwave irradiation [7–9]. Of these, the most widely used approach is the introduction of chemical demulsifiers. However, the demulsifier molecules themselves dissolve as additional contaminants in water after demulsification; therefore, it is difficult to follow more stringent discharge standards [10].

Surfactants are chemicals for use in crude oil, detergents, cosmetics and textile industries [11,12]. Surfactants minimize the interfacial tension to an ultra-low value between the water and residual oil trapped in the reservoir [13]. Demulsification requires a number of parameters, which can either decrease or improve emulsion stability like settling time, water volume, demulsifier concentration, and temperature [14–16]. Crude oil demulsification is a costly problem in the refinery and production sector, paving the need for demulsification of crude oil by using cheaper and active means [17–19]. Efforts have been made to develop low-cost, natural-based chemicals for further use in oil-related activities [20]. For example, the synthesis of fatty acid esters from plant oils through bio-enzyme-catalyzed esterification processes has been encouraged [21]. Babu reported the use of ricinoleic acid methyl ester of castor oil as an active renewable raw material for

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sodium methyl ester sulfonate (SMES) production to improve oil recovery [22]. In another work, Saxena used a *trans*-esterification method to make a surfactant from palm oil called alpha sulfonated ethyl ester (α-SEE). The surfactant was intended for use in processes for chemically enhanced oil recovery (EOR) [23]. The effectiveness and yield of surfactants depend on the synthesis process and the raw materials. Here, we selected corn oil as raw material for surfactant synthesis as a demulsifier for crude oil emulsion. Corn oil is a promising raw material among vegetable oils due to its cheap price, nontoxic nature, and renewable availability. The aim of this research was to synthesize a new demulsifier that is environmentally friendly and economical for use in the separation of w/o emulsions. The surfactant was characterized by FTIR, GC-MS, and LC-QTOF-MS. The suitability of the demulsifier was examined via the Sany-glass test.

2. Materials and experimental methods

2.1. Materials

Commercial corn oil was from a local supermarket (Daisy). Diethanolamine (liquid), reagent grade > 98.0% purity, and p-toluene sulfonic acid (solid), reagent Plus® ≥98%, was purchased from Sigma-Aldrich/USA. Petroleum ether (40–60) b.p, was collected from Fisher Chemical/UK for analysis. The sour crude oil sample was obtained from Petronas Refinery Melaka, Malaysia and its properties are shown in Table 1.

2.2. Synthesis of demulsifier

The demulsifier was synthesized by reacting corn oil (300 mL) with diethanolamine (100 mL) in the presence of a base catalyst. The corn oil and catalyst p-toluene sulfonic acid (2.5 g) was charged in laboratory reaction flask (1000 mL volume) equipped with a reflux condenser, magnetic stirrer, and thermometer. The sample was heated gently at a moderate level until of 140 °C with stirring until the catalyst was dissolved. The diethanolamine was then slowly added, and the temperature was increased gradually until it reached 180 °C; the reaction increased for another two hours with continuous stirring to obtain the expected amount of water. The product was obtained after collecting 12 mL of water. The sample was then detached from the heating mantle and cooled. The final product was purified and washed with petroleum ether and evaporated in a vacuum evaporator [24].

2.3. Emulsion preparation

The water-in-oil (W/O) emulsions were prepared at volumes of (30/70) vol.%. This work then used a homogenizer (IKA, Ultra Turax T25 Basic) at a mixing rate of 2000 rpm for 15 min at room temperature. Domestic tap water was used as the dispersed phase, and crude oil served as the continuous phase. The agent was followed in the oil process, i.e., the emulsifying agent was dissolved in the continuous step (oil). Water was slowly added to the mixture (oil + emulsifier). The UMP surfactant (NS-16-1) product used as emulsifier produced a stable emulsion.

Table 1
Characteristics of the crude oil.

Density	0.8628 (g/cm^3)
Viscosity	35 (N/m^2)
API Gravity	26
Surface Tension	24.678 (mN/m)
Interfacial Tension	14.731 (mN/m)

3. Sample characterization

3.1. Fourier transform infrared spectroscopy (FTIR)

A Nicolet iS5 FTIR spectrophotometer (Thermo Science, Germany) coupled with OMNIC software was used to perform the FTIR analysis. IR spectra were measured within 4000–400 cm^{-1}. The KBr approach was used to evaluate the functional groups in the demulsifier. Nearly one drop of the sample was reported on the diamond crystal surface for infrared spectrometry analysis and immediate reading.

3.2. Gas chromatography-mass spectrometry analysis (GC-MS)

GC-MS demulsifier analysis was performed with an Agilent GC-MS 7890A-model specification equipment and injector 7683B USA equipment. A C-18 column with a 30-mm diameter, 0.25-mm internal diameter, and 0.25-μm film thickness was used. Temperatures for the injector and detector were 230 °C and 250 °C, respectively. The opening oven temperature was held for five minutes at 50 °C and then allowed to increase to 230 °C at a rate of 5 °C/min. The flow rate for the helium gas was fixed at 1 mL/min. Prior to injection, the sample was diluted at a ratio of 1:10 in petroleum ether and purified using a 0.2 μm filter with syringe attachment. The collected components were matched with NIST05.LIB database equipped with GC-MS method to classify the sample's chemical compounds.

3.3. Compound analysis via liquid chromatography-quadrupole-time-of-flight mass spectrometry (LC-QTOF-MS)

LC-QTOF-MS used a mass spectrometer (IMS QTOF Vion; Waters, USA). The mobile phase was prepared via water and acetonitrile composition at different concentrations and worked with 20 mL injection volume and 0.5 mL/min flow rate. Mass spectrometry (MS) had a start time: 0.00 min, end time: 13.00 min, low mass: 50 m/z, high mass: 1000 m/z, low collision energy: 4.00 ev, high collision energy ramp start: 10.00 ev and high collision energy ramp end: 40.00 eV. The sample, column, and desolvation temperatures were set to 15, 40 and 550 °C, respectively. The capillary voltage was around 2 kV. Surfactant identifications were unequal in positive and negative ion modes.

4. Results and discussion

4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the functional groups on the surfactant Fig. 1. The broad peak at 3363 cm^{-1} is assigned to secondary aliphatic alcohols indicating O–H stretching. The sharp absorption peaks at 3007.19–2852.08 cm^{-1} are given to both symmetrical and asymmetrical alkane stretching (–CH$_3$) and alkenes (=CH$_2$) within the aliphatic hydrocarbon groups. The peaks at 1737 and 1165 cm^{-1} refer to the presence of fatty acids (C=O) stretching of esters; [15]. The band at 1049 cm^{-1} is the primary aliphatic alcoholic (C–OH) group. Finally, the peak at 568.5 cm^{-1} is a chlorinated linear alkane. Specific functional groups were identified in surfactants such as carboxyl, hydroxyl, fats, alkanes, and aliphatic alcoholic compounds based on the FTIR spectral result obtained.

4.2. GC-MS analysis

The surfactant was characterized with GC-MS. There were 35 composites with 100% compositions. Table 2 displays the detected constituents together with their retention time (RT), composition rate, and molecular formula obtained from PubChem. Fig. 2 shows
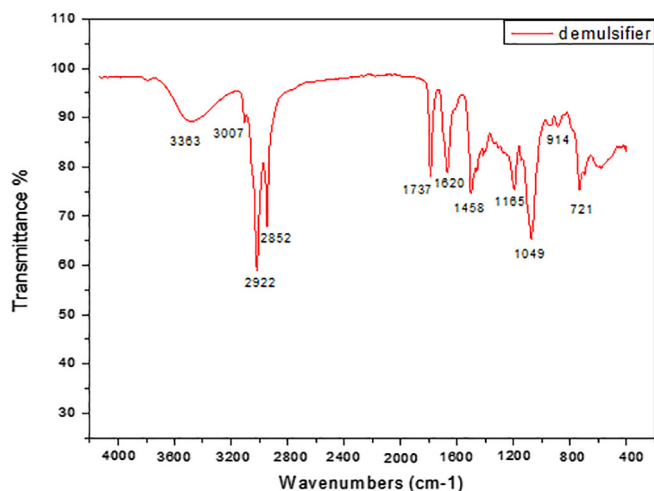
Fig. 1. FTIR analysis of demulsifier.

the GC-MS characterization of the surfactant in terms of retention time (min) and compound abundance. The compounds found included esters, amines, hydrocarbons, carboxyles, amides, and fatty acids.

4.3. LC-QTOF-MS analysis of surfactant

The identification of surfactant was performed using LC-QTOF-MS analysis. Table 3 shows 14 compounds containing pirimeta-

phos, α-aminobutyric acid, spinetoram minor component, dufulin, fosmethilan, quwenzhi, oxamate, fucaomi, dodicin, fluazuron, halosulfuron, chlorimuron, pyriprole, and sulcofuron. These chemically active substances are important for many naturally occurring and agricultural activities such as pesticide for inducing plant disease resistance and veterinary use. The α-aminobutyric acid is one of the three isomers of aminobutyric acid and is known for inducing plant disease resistance. Dufulin is a modern highly efficient antiviral agent against farm pathogens and works in plants by inducing systemically acquired resistance (SAR). It is commonly used in recent years in China for tobacco and rice viral diseases [25].

Quwenzhi is the hexyl ester of (5-aminolevulinic acid) with photodynamic properties and drug product. It is commonly used in the treatment of non-muscle intrusive bladder papillary cancer with cystoscopy. Oxamate is an inhibitor of lactate dehydrogenase LDH and is an effective drug against cancer [26]. Pyriprole is a phenylpyrazole derivative similar to fipronil for veterinary use on dogs against external parasites such as fleas and ticks. Figs. 3 and 4 display demulsifier compounds detected by LC-QTOF-MS analysis based on retention time and negative and positive ion modes strength observed, respectively.

5. Effecting parameters on the demulsification efficiency

To better understand the demulsification efficiency of the most stable emulsions (W/O emulsions), the influence of the settling time, demulsifier dosage, and temperature on demulsification efficiency was evaluated as follows:

Table 2
GC-MS chemical composition of surfactant.

| RT (min)	Area%	Compound name	Molecular formula
4.237	9.22	1,4-Bis(2-hydroxyethyl) piperazine	$C_8H_{18}N_2O_2$
6.426	0.42	Triethanolamine	$C_6H_{15}NO_3$
6.555	1.14	Triethanolamine	$C_6H_{15}NO_3$
10.614	2.12	Zuclopenthixol	$C_{22}H_{25}ClN_2OS$
11.030	0.14	9-Eicosyne	$C_{20}H_{38}$
11.297	0.24	9,17-Octadecadienal, (Z)-	$C_{18}H_{32}O$
11.906	0.51	E-12-Tetradecenal	$C_{14}H_{26}O$
11.970	0.25	9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$
12.686	0.37	9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$
12.739	0.30	9,17-Octadecadienal, (Z)-	$C_{18}H_{32}O$
12.932	0.32	1,3,4-Thiadiazol-2-amine,5-(4 flluorophenoxymethyl)-	$C_9H_8FN_3OS$
13.498	13.70	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	$C_{19}H_{38}O_4$
13.765	3.09	4-Chlorophenyl methyl carbinol	C_8H_9ClO
14.181	0.90	Butanoic acid, 2-methyl-	$C_5H_{10}O_2$
14.246	0.61	1-Propanamine, N,N-dipropyl-	$C_9H_{21}N$
14.299	0.61	1H-Azepin-1-amine, hexahydro-	$C_6H_{14}N_2$
14.352	1.31	[1,3,5]triazine-2,4-diamine	$C_3H_5N_5$
14.630	2.48	Butanamide,N,N-dihexyl-	$C_{16}H_{33}NO$
14.908	18.81	(R)-(-)-14-Methyl-8-hexadecyn-1-ol	$C_{17}H_{32}O$
14.940	6.16	2-hydroxy-1-(hydroxymethyl)ethyl ester	$C_{23}H_{46}O_4$
15.057	3.41	1,5-diazocine-2,6(1H,3H)-dione	$C_6H_{10}N_2O_2$
15.474	2.26	Octadecanoic acid, 9,10-dichloro-,methyl ester	$C_{19}H_{36}Cl_2O_2$
15.506	2.41	Butanoic acid, 2-methyl-	$C_5H_{10}O_2$
15.613	1.75	3-Acetamido-3-methylheptane	$C_8H_{19}N$
15.656	3.95	4-Morpholinepropanamine	$C_7H_{16}N_2O$
15.944	4.47	2-Amino-4-methyl-4-pentenoic acid	$C_6H_{11}NO_2$
16.286	1.39	Pyrimidine, 2-chloro-	$C_4H_3ClN_2$
16.329	0.65	1,5-Diazocane-2,6-dione	$C_6H_{10}N_2O_2$
16.489	1.46	1,5-diazocine-2,6(1H,3H)-dione	$C_6H_{10}N_2O_2$
16.660	0.66	Benzene,1,2 difluoro-	$C_6H_4F_2$
16.884	1.99	Octanoic acid, 2-amino-,trimethylsilyl ester	$C_{12}H_{25}NO_3Si$
17.204	8.46	Heptanoic acid, methyl ester	$C_8H_{16}O_2$
17.493	2.59	Isoquinoline, 1-methyl-	$C_{10}H_9N$
17.685	0.68	[1,3,4]Thiadiazol-2-ylamine,5-(4-chlorophenoxymethyl)-	$C_9H_8ClN_3S$
17.835	1.19	Benzenepropanamine,	$C_9H_{13}N$
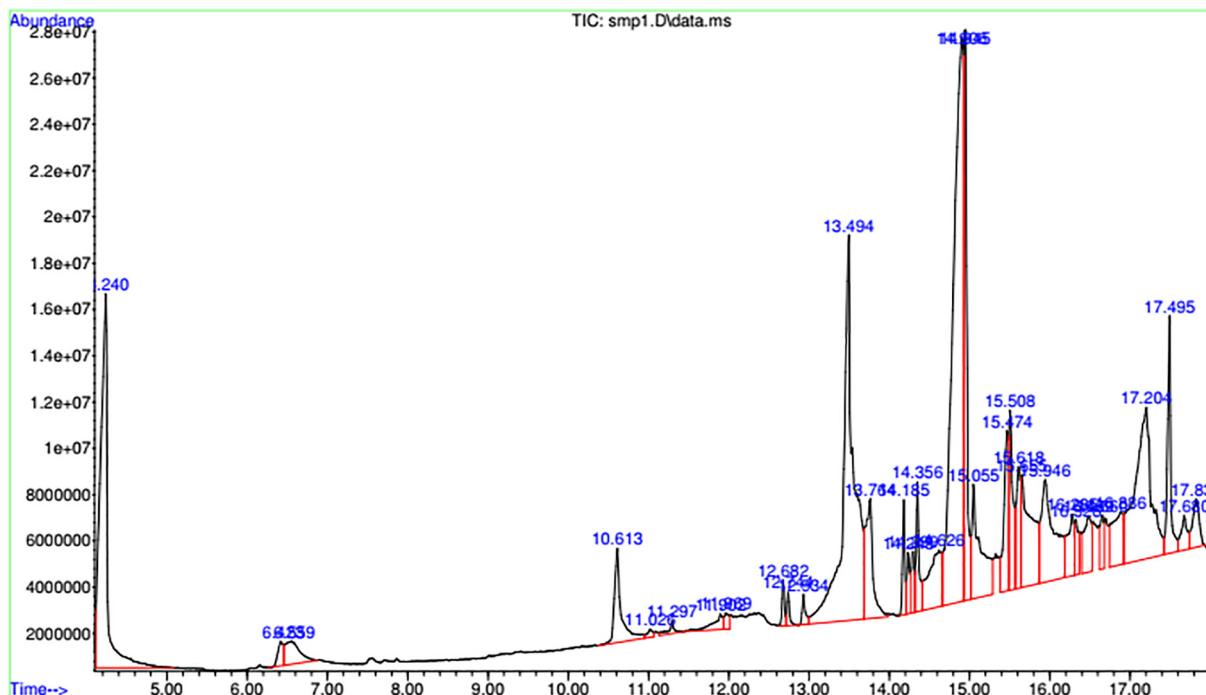
Fig. 2. GC-MS characterization of the surfactant in terms of retention time (min) and product abundance.

Table 3
Compounds of surfactant identified by LC-QTOF-MS.

Component name	Formula	Observed neutral mass (Da)	Observed m/z	Mass error (mDa)	Mass error (ppm)	Observed RT (min)	Response	Adducts	Observed CCS (Å²)
pirimetaphos	C11H21N4O3P	288.1317	347.1455	−3.5	−10.0	0.57	110	+CH3COO	313.67
α-Aminobutyric acid	C4H9NO2	103.0643	162.0781	1.0	5.9	0.58	85	+CH3COO	192.24
Spinetoram minor component	C43H69NO10	759.4987	818.5125	6.5	7.9	0.58	132	+CH3COO	277.31
dufulin	C19H22FN2 O3PS	408.1053	407.0980	−2.0	−4.9	0.59	315	-H	181.80
fosmethilan	C13H19ClN O3PS2	367.0257	366.0184	2.4	6.7	0.62	209	-H	296.46
quwenzhi	C11H21NO3	215.1540	274.1678	1.8	6.7	6.01	283	+CH3COO	161.54
oxamate	C12H23NO3	229.1701	288.1840	2.4	8.2	7.82	115	+CH3COO	165.37
fucaomi	C19H16ClF3 N2O7	476.0641	475.0568	4.3	9.0	9.02	168	-H	181.55
dodicin	$C_{18}H_{39}N_3O_2$	329.3019	352.2911	−2.3	−6.6	2.73	2283	+Na	204.18
fluazuron	C20H10Cl2F 5N3O3	505.0063	543.9695	4.4	8.1	5.63	3468	+K	209.57
halosulfuron	C12H13ClN6 O7S	420.0215	438.0553	−4.0	−9.1	7.83	4016	+NH4	220.34
chlorimuron	C13H11ClN4 O6S	386.0049	404.0388	−3.8	−9.5	9.16	3323	+NH4	171.58
pyriprole	C18H10Cl2F5N5S	492.9933	531.95	65–2.1	−3.9	11.76	2414	+K	195.84
sulcofuron	C19H12Cl4N 2O5S	519.9272	537.96	11 5.1	9.5	12.04	2702	+NH4	196.18

5.1. Effect of settling time on the effectiveness of separation

A water-in-oil emulsion was prepared at a ratio of 30:70 (vol %) in a total volume sample of 250 mL. The microscopic emulsion images display the creation of uniform emulsion droplets with small sizes to support emulsion stability as shown in Fig. 5. Sany-glass test was used to determine the emulsion breaking efficiency of the demulsifier. Various demulsifier concentrations (1000–6000 ppm) were applied to every 50 mL of the emulsion. The percentage of water separation efficiency (SE %) was determined using Equation (1) from the observed volume of water in the graduated measuring container in mL. The separation of phases was reported as a function of time. The average separation

efficiency as a function of time obtained during four various concentrations (1000–6000 ppm) are shown in Fig. 6. The results indicated that the separation of water increased with increase in settling time; within 36 hr, the average separation efficiency approached 94.5%. In general, the graph indicates three rates of separation.

During the 24 hr period, the average demulsification recorded the highest separation at a rate of 3.3% per hour, which is equal to 79% of the separation emulsion. In the next 6 hr, the graph shows a decline in the separation rate of 10.5% over 30 hr; approximately 90% of the water has been separated from the emulsion. At this point, the presence of water droplets in the emulsion becomes minimal; hence, water molecules move apart and reduce the
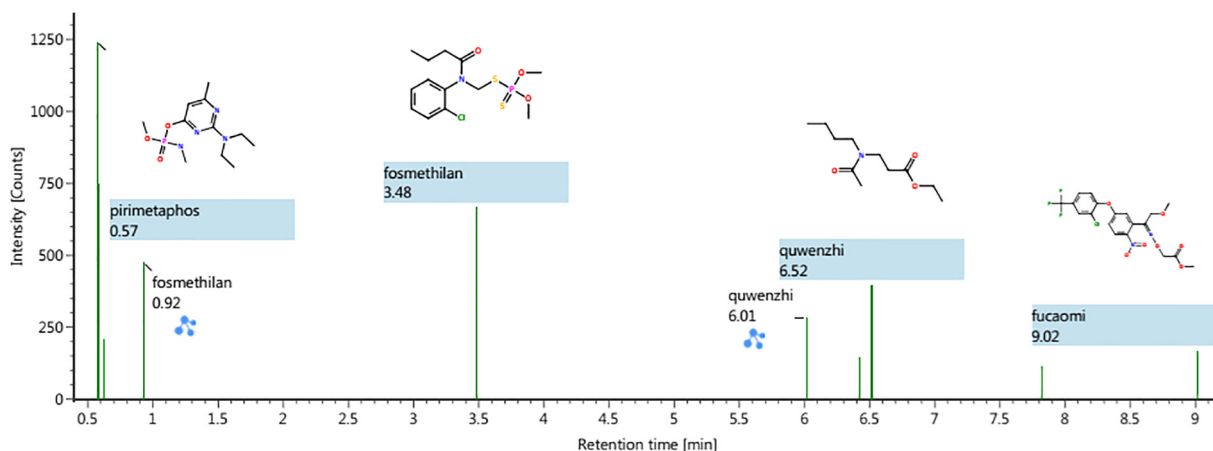
Fig. 3. LC-MS-QTOF chromatogram of the surfactant compounds temporarily allocated in negative ion form.
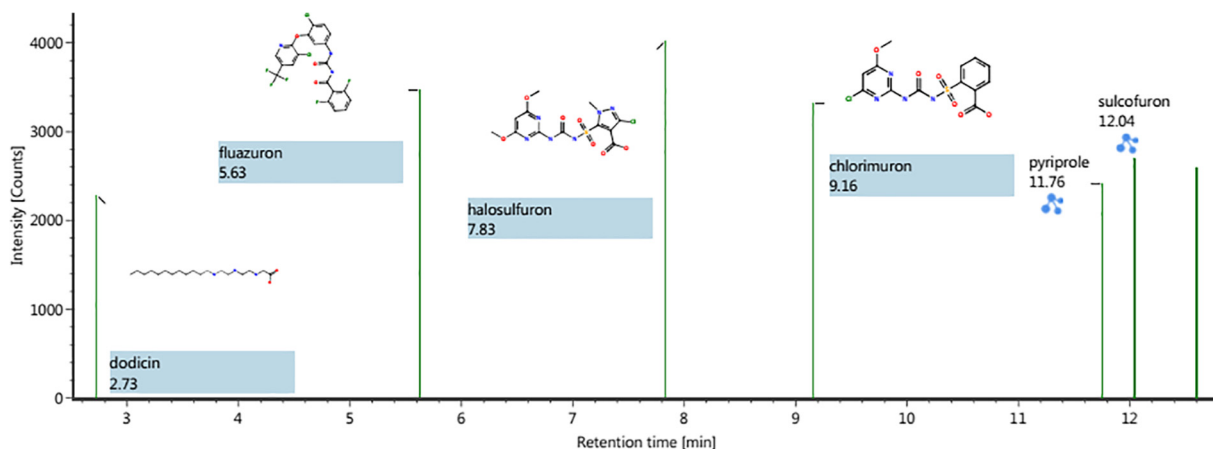

Fig. 4. LC-MS-QTOF chromatogram of the surfactant compounds temporarily allocated in positive ion form.
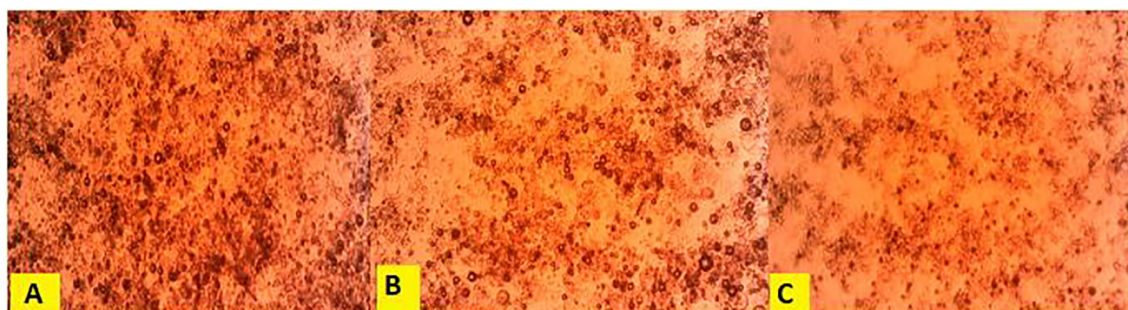

Fig. 5. Optical microscope photos of the emulsion at various times: a- (0 min), b- (15 min), and c- (30 min).

possibility of water droplets colliding and coalescing. As a result, a much slower separation rate was observed at hour 36 (5%). The average water removal was equal to 94.5% during 36 hr; no further separation was seen at longer settling times (up to 42 hr). The results indicated that settling time is a significant factor affecting demulsification efficiency. There was an exponential correlation with the separation efficiency [27]. Visual images of the separation performance are shown in Fig. 7.

$$separation\ efficiency(\%\ SE) = \frac{Volume\ of\ separated\ water\ in\ mL}{Original\ volume\ of\ water\ in\ the\ emulsion,\ mL} \times 100$$

(1)

5.2. Effect of demulsifier dosage on the separation performance

Higher chemical demulsifier concentrations are required for treatment of more stable emulsions. Some emulsions produced a method to recuperate tertiary oil during chemical enhanced oil recovery (EOR); these require a greater quantity of demulsifier than the main and secondary oil recoveries. In extreme circumstances, hundreds of ppm or more are required. Therefore, too little demulsifier could dissolve the emulsion formed from the chemical EOR whereas an overdose of demulsifier will stabilize the emulsion [28]. Alves et al. studied the influence of demulsifier concentration for water-in-oil emulsions including five types of chemical surfactants dependent on castor oil. The concentrations used for demul-
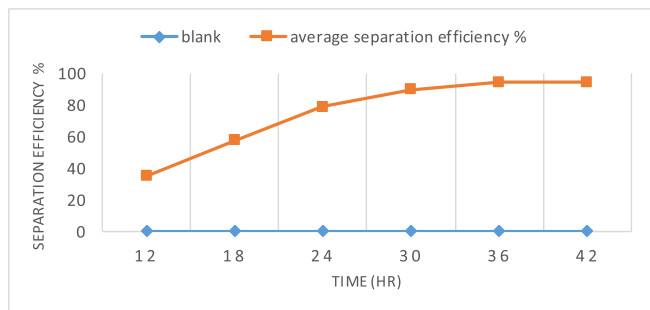
Fig. 6. The separation efficiency of the emulsion versus time.

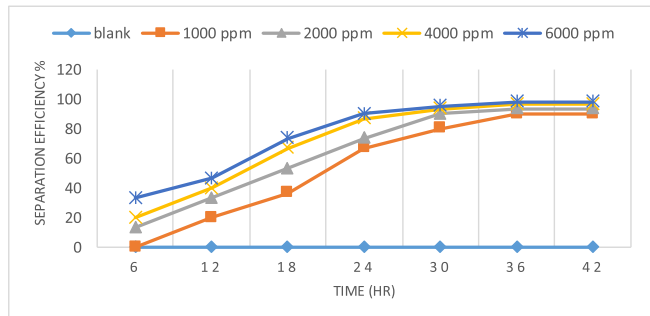**Fig. 7.** Demulsification photos for W/O emulsions.

Fig. 8. The separation efficiency of the emulsion versus demulsifier doses.

sifiers were 500, 1000, 2000, and 5000 ppm, respectively. The results showed an improvement in the separation water ratio with an increase in demulsifier concentration for different demulsifiers [29].

Our results show a similar trend. Fig. 8 presents the separation efficiency of the emulsion as a function of demulsifier concentration. All selected doses caused the water to separate from the emulsion with excellent efficiency: 98% water removal at 6000 ppm over 36 hr.

Of note, the water-in-oil emulsion may do not separate without using a demulsifier. The water-in-oil emulsions are breaking when the demulsifiers are added but are largely dependent on the concentration of the demulsifiers. In Fig. 8, the separation efficiency was observed to increase with an increasing amount of demulsifier. The separation efficiency of the emulsions is 20% and 46% at 1000 and 6000 ppm of demulsifier, respectively, over 12 hr of demulsification. The separation rate then continued to increase and reached 90% at 24 hr. At 6000 ppm, the highest separation rate reached 86.6%. The separation rate then began to decline due to the

lack of dispersed water droplets remaining in the emulsion. The highest separation rate was at 36 hr, which is 96 and 98% at concentrations of 4000 and 6000 ppm, respectively. The separation then continued significantly with a dose of 1000 and 2000 ppm to reach the highest separation efficiency of 90 and 93.3%, respectively. These data suggested that the rise in demulsifier concentration contributes to a rise in the demulsifier molecules being adsorbed on the W/O interface thus replacing the natural asphalt emulsifiers. This reduces the interfacial film's mechanical stability. This film's stability begins to decrease until it is weaker and then collapses entirely with more demulsifier agent adsorption on the interface [30]. In addition, the output improves even at the lowest concentration by increasing the settling time similar to Li et al. [31].

5.3. Influence of temperature

Heating can also be used to demulsify an emulsion. Temperature plays a significant role in various chemical activities including demulsification process. The stability of the emulsions can be decreased by factors that reduce the ability of crude oil to form the film. These films can then be reduced or their physical properties can be changed by a temperature increase through two routes [32]. The first is an improvement in the coalescence rate by providing sufficient energy to target two droplets that occur before coalescence. The second leads to a continuous reduction of the viscosity that facilitates the kinetic motion of the dispersed water droplets resulting in increased relaxation of the film, rupture of the film, and coalescence [33]. Fig. 9 shows the influence of heating on the demulsification process. The outcomes the separating of water from the emulsion gradually increased with change in temperature. There was a different proportion according to the demulsification. The process of separating the water from the emulsion was faster than the experiments conducted at room temperature. The separation rate reached 73% over 4 hr at 70 °C using a 3500 ppm dose of demulsifier.

As noted, when the temperature increased from 50 to 70 °C, the percentage of water removed increased dramatically at the first 4 h and then continued to steadily increase to the end of demulsification. The three samples recorded a separation rate of 53, 66.66, and 73.33% during 4 hr at a temperature of 50, 60 and 70 °C, respectively. The values then increased sharply to reach 80, 87, and 93% within 12 hr. Hence, the separation process continued moderately but with a lower separation rate versus the first hours of the experiment with a slight difference between the three temperatures. We recorded the highest values over 20 hr (97% at 70 °C). The values then reached 95 and 96% at temperatures of 50 and 60 °C. No further separation was seen during this period. Heating supports the demulsification of water in an oil emulsion. Introducing heating in the demulsification of emulsion helped reduce the settling time in
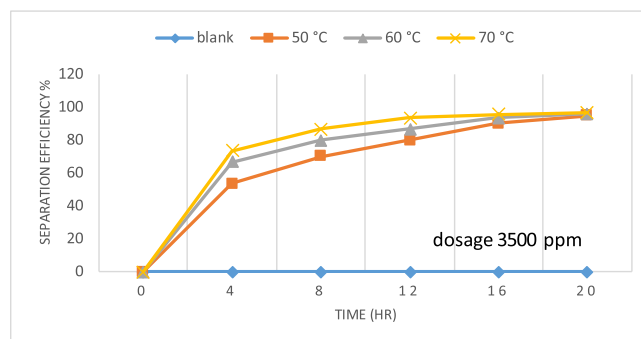

Fig. 9. The separation efficiency of the emulsion as a function of temperature.

Table 4
Results of IFT test at 25 °C.

Demulsifier	Dosage (ppm)	IFT (mN/m)
Blank	0	14.731
Demulsifier	1000	12
	2000	10
	4000	7
	6000	5

the process. Nevertheless, heat alone is insufficient to achieve a good separation of water from the emulsion.

5.4. Effect of demulsifier dosage on IFT

The interfacial tension of the oil–water interface at various dosed tested at 25 °C with pendant drop tension meter (KRUSS DSA 100). Surfactant solutions were used at different ratios, 1000 to 6000 ppm. The test consisted of calculating the IFT of a droplet of crude oil produced in a phase of water. IFT result have been calculated and recorded in Table 4. The crude oil/ water interfacial tension was 14.731 mN/m. With the addition of various demulsifier concentrations, interfacial tension decrease was obtained down to 5 mN/m at 6000 ppm of surfactant. The results revealed that the IFT reduced with increasing of demulsifier concentration and increasing the efficiency of separation is related to the reduction of demulsifier interfacial tension.

6. Conclusion

In this paper, a new demulsifier was synthesized based on corn oil as a raw material. The effect of settling time, demulsifier dosage, temperature, and pH on the demulsification of water-in-oil emulsions was investigated. The demulsifer was characterized by FTIR, GC-MS, and LC-QTOF-MS analyses. Demulsification experiments were conducted at 50–70 °C and 1000–6000 ppm of demulsifier. The demulsification experiments showed that the removal of water increases with increased setting time. The demulsification increases with increasing demulsifier dosage, and the maximum separation of water was 98% at 6000 ppm. The applied heating on emulsion improves the separation efficiency and accelerates the demulsification. The interfacial tension reduced with increase dosage of demulsifier to about 5 mN/m at 6000 ppm. The new demulsifier showed excellent performance and was promising for the W/O emulsion demulsification. Nonetheless, more research is needed for a deeper understanding of the mechanisms involved.

CRediT authorship contribution statement

M.A. Saad: Writing - original draft. **N.H. Abdurahman:** Conceptualization, Methodology, Writing - review & editing. **Rosli Mohd Yunus:** Supervision, Visualization, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] J. Zhang, J. Li, R.W. Thring, X. Hu, X. Song, Oil recovery from refinery oily sludge via ultrasound and freeze/thaw, J. Hazard. Mater. 203 (2012) 195–203.

[2] J. Peng, Q. Liu, Z. Xu, J. Masliyah, Novel magnetic demulsifier for water removal from diluted bitumen emulsion, Energy Fuels 26 (2012) 2705–2710.

[3] M.A. Saad, M. Kamil, N. Abdurahman, R.M. Yunus, O.I. Awad, An overview of recent advances in state-of-the-art techniques in the demulsification of crude oil emulsions, Processes 7 (2019) 470.

[4] W. Fang-Hui, Z. Hong, The application and research of dispersing in situ nano-SiO2 in polyether demulsifier TA1031, J. Dispersion Sci. Technol. 29 (2008) 1081–1084.

[5] A. Cambiella, E. Ortea, G. Rios, J.M. Benito, C. Pazos, J. Coca, Treatment of oil-in-water emulsions: performance of a sawdust bed filter, J. Hazard. Mater. 131 (2006) 195–199.

[6] L. Xia, K. Gong, S. Wang, J. Li, D. Yang, Microwave-assisted chemical demulsification of water-in-crude-oil emulsions, J. Dispersion Sci. Technol. 31 (2010) 1574–1578.

[7] R. Zolfaghari, A. Fakhru'l-Razi, L.C. Abdullah, S.S.E.H. Elnashaie, A. Pendashteh, Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry, Separation and Purification Technology, 170 (2016) 377-407.

[8] M. Chen, L. Zhu, Y. Dong, L. Li, J. Liu, Waste-to-resource strategy to fabricate highly porous whisker-structured mullite ceramic membrane for simulated oil-in-water emulsion wastewater treatment, ACS Sustain. Chem. Eng. 4 (2016) 2098–2106.

[9] K. Karakulski, A. Morawski, Recovery of process water from spent emulsions generated in copper cable factory, J. Hazard. Mater. 186 (2011) 1667–1671.

[10] A. Stocco, J. Crassous, A. Salonen, D. Langevin, Two-mode dynamics in dispersed systems: the case of particle-stabilized foams studied by diffusing wave spectroscopy, PCCP 13 (2011) 3064–3072.

[11] N.A. Negm, A.S. El-Tabl, I.A. Aiad, K. Zakareya, A.H. Moustafa, Synthesis, characterization, biodegradation and evaluation of the surface active properties of nonionic surfactants derived from Jatropha oil, J. Surfactants Deterg. 16 (2013) 857–863.

[12] M. Saad, N. Abdurahman, R.M. Yunus, H. Ali, Surfactant for petroleum demulsification, structure, classification, and properties. A review, in IOP Conference Series: Materials Science and Engineering, 2020, vol. 991, no. 1, p. 012115: IOP Publishing.

[13] S. Abed, N. Abdurahman, R. Yunus, H. Abdulbari, S. Akbari, Oil emulsions and the different recent demulsification techniques in the petroleum industry-a review, in IOP Conference Series: Materials Science and Engineering, 2019, vol. 702, no. 1, p. 012060: IOP Publishing.

[14] M. Fortuny, C.B. Oliveira, R.L. Melo, M. Nele, R.C. Coutinho, A.F. Santos, Effect of salinity, temperature, water content, and pH on the microwave demulsification of crude oil emulsions, Energy Fuels 21 (2007) 1358–1364.

[15] P. Sar, Potential application of Micellar nanoreactor for electron transfer reactions mediated by a variety of oxidants: a review, Adv. Colloid Interface Sci. 284 (2020) 102241.

[16] M. Saad, N. Abdurahman, R.M. Yunus, H. Ali, An overview of recent technique and the affecting parameters in the demulsification of crude oil emulsions, in IOP Conference Series: Materials Science and Engineering, 2020, vol. 991, no. 1, p. 012105: IOP Publishing.

[17] D. Green, G.P. Willhite, Enhanced Oil Recovery, SPE textbook series, Society of Petroleum Engineers, Richardson, Texas, 1998.

[18] S. Majidaie, M. Muhammad, I.M. Tan, B. Demiral, Green surfactant for enhanced oil recovery, in 2011 National Postgraduate Conference, IEEE, 2011, pp. 1-5.

[19] P. Sar, A. Ghosh, A. Scarso, B. Saha, Surfactant for better tomorrow: applied aspect of surfactant aggregates from laboratory to industry, Res. Chem. Intermed. 45 (2019) 6021–6041.

[20] A. Flaaten, Q.P. Nguyen, G.A. Pope, J. Zhang, A systematic laboratory approach to low-cost, high-performance chemical flooding, in SPE Symposium on Improved Oil Recovery, 2008: Society of Petroleum Engineers.

[21] A.L. Matassoli, I.N. Corrêa, M.F. Portilho, C.O. Veloso, M.A. Langone, Enzymatic synthesis of biodiesel via alcoholysis of palm oil, Appl. Biochem. Biotechnol. 155 (2009) 44–52.

[22] K. Babu, N. Maurya, A. Mandal, V. Saxena, Synthesis and characterization of sodium methyl ester sulfonate for chemically-enhanced oil recovery, Braz. J. Chem. Eng. 32 (2015) 795–803.

[23] N. Saxena, N. Pal, S. Dey, A. Mandal, Characterizations of surfactant synthesized from palm oil and its application in enhanced oil recovery, J. Taiwan Inst. Chem. Eng. 81 (2017) 343–355.

[24] M. Saad, N. Abdurahman, R.M. Yunus, Eco-friendly surfactant to demulsification water in oil emulsion: synthesis, characterization and application, Chem. Data Collect. 13 (2020) 100582.

[25] Z. Chen et al., Dufulin activates HrBP1 to produce antiviral responses in tobacco, PLoS ONE 7 (2012).

[26] Z. Zhao, F. Han, S. Yang, J. Wu, W. Zhan, Oxamate-mediated inhibition of lactate dehydrogenase induces protective autophagy in gastric cancer cells: Involvement of the Akt–mTOR signaling pathway, Cancer Lett. 358 (2015) 17–26.

[27] L. Zhang, H. Ying, S. Yan, N. Zhan, Y. Guo, W. Fang, Hyperbranched poly(amido amine) as an effective demulsifier for oil-in-water emulsions of microdroplets, Fuel 211 (2018) 197–205.

[28] D. Nguyen, N. Sadeghi, C. Houston, Chemical interactions and demulsifier characteristics for enhanced oil recovery applications, Energy Fuels 26 (2012) 2742–2750.

[29] R.S. Alves, D.L. Maia, F.A. Fernandes, F.X. Feitosa, H.B. de Sant'Ana, Synthesis and application of castor oil maleate and castor oil maleate-styrene copolymers as demulsifier for water-in-oil emulsions, Fuel 269 (2020) 117429.

[30] A.M. Al-Sabagh, N.M. Nasser, E.A. Khamis, M. Abd-El-Raouf, Resolution of water in crude oil emulsion by some novel aromatic amine polyesters, Egypt. J. Pet. 24 (2015) 363–374.

[31] Z. Li, H. Geng, X. Wang, B. Jing, Y. Liu, Y. Tan, Noval tannic acid-based polyether as an effective demulsifier for water-in-aging crude oil emulsions, Chem. Eng. J. 354 (2018) 1110–1119.

[32] J.S. Eow, M. Ghadiri, Electrostatic enhancement of coalescence of water droplets in oil: a review of the technology, Chem. Eng. J. 85 (2002) 357–368.

[33] R.A. El-Ghazawy, A.M. Al-Sabagh, N.G. Kandile, M.R.N. El-Din, Synthesis and preliminary demulsification efficiency evaluation of new demulsifiers based on fatty oils, J. Dispersion Sci. Technol. 31 (2010) 1423–1431.