Jurnal Teknologi

Full Paper

FORMULATING AND CHARACTERIZING AN OIL-IN-WATER PALM OIL FREE FATTY ACID-BASED NANOEMULSIONS FOR CRUDE OIL EXTRACTION PERFORMANCE

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Article history
Received
14 August 2023
Received in revised form
5 October 2023
Accepted
5 October 2023
Published Online
20 April 2024

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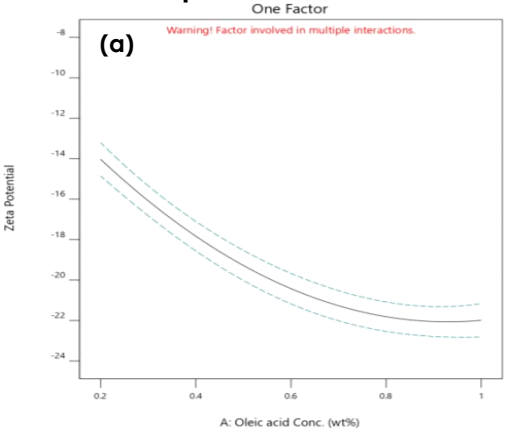
Graphical abstract



Abstract

Nanoemulsion is a promising medium for chemically enhanced oil recovery (cEOR) due to its ability to reduce interfacial tension and modify the wettability of reservoir rocks. This work focuses on formulating stable oil-in-water (O/W) nanoemulsions through high-energy ultrasonication method, with oleic acid as the primary component and is stabilized with a non-ionic Tween 40 surfactant in distilled water. Systematic experimental designs, employing response surface methodology (RSM), were implemented to develop polynomial models for various responses related to the dynamic and stability properties, and crude oil extraction performance. The p-value indicator (p-value < 0.05) is utilized to assess the significance of the models and independent variables. Overall, the formulation for achieving the lowest surface tension involves 0.41 wt.% oleic acid mixed with 0.81 wt.% Tween 40 at 60 °C. Meanwhile, the highest viscosity attained with 1.0 wt.% oleic acid mixed with 1.0 wt.% Tween 40 at 30 °C. For stable nanoemulsion, the best conditions are 1.69 wt.% oleic acid, sonicated for 15 minutes at 25 °C. Additionally, an optimal condition for effective crude oil extraction is at nanoemulsion preparation with sonication time of 15 minutes and contact time of 12 hours in the immersion experiment. To this end, this work contributes valuable insights into the formulation and characterization of stable oleic acid O/W nanoemulsions for potential EOR applications. The findings enhance understanding of nanoemulsion properties and their potential as effective agents in crude oil recovery.

Keywords: Colloid, enhanced oil recovery, nanoemulsion, response surface methodology, ultrasonication

Abstrak

Nanoemulsi adalah medium yang berpotensi untuk pemulihan minyak tertingkat kimia (cEOR) kerana keupayaannya untuk mengurangkan ketegangan antara dua permukaan dan mengubah kebolehbasahan batu. Kajian ini berfokus terhadap penghasilan nanoemulsi jenis minyak-dalam-air (O/W) melalui kaedah ultrasonikasi, menggunakan asid oleik sebagai bahan utama yang distabilkan oleh surfaktan jenis bukan-ion Tween 40 di dalam air suling. Reka bentuk eksperimen sistematik menggunakan metodologi permukaan tindak balas (RSM), telah dilaksanakan untuk membangun model

polinomial bagi pelbagai uji kaji yang berkaitan dengan sifat dinamik dan kestabilan, dan juga prestasi pengekstrakan minyak mentah. Penunjuk nilai-p (nilai-p < 0.05) digunakan untuk menilai kesignifikan model dan pembolehubah tak bersandar. Secara keseluruhan, formulasi untuk mencapai tegangan permukaan yang paling rendah melibatkan 0.41 wt.% asid oleik yang dicampur dengan 0.81 wt.% Tween 40 pada 60 °C. Sementara itu, kelikatan tertinggi dapat dicapai dengan 1.0 wt.% asid oleik dicampur dengan 1.0 wt.% Tween 40 pada 30 °C. Untuk menghasilkan nanoemulsi yang stabil, keadaan terbaik adalah 1.69 wt.% asid oleik, disonikasi selama 15 minit pada suhu 25 °C. Tambahan pula, keadaan optimum yang berkesan untuk pengekstrakan minyak mentah adalah pada penyediaan nanoemulsi dengan masa sonikasi selama 15 minit dan masa sentuhan selama 12 jam dalam eksperimen rendaman. Akhir kata, kerja ini memberi petunjuk penting terhadap perumusan dan pencirian nanoemulsi O/W daripada asid oleik yang stabil sebagai potensi untuk aplikasi EOR. Penemuan ini meningkatkan pemahaman tentang sifat nanoemulsi dan potensinya sebagai bahan yang berkesan dalam pemulihan minyak mentah.

Kata kunci: Koloid, pemulihan minyak tertingkat, nanoemulsi, metodologi permukaan tindak balas, ultrasonikasi

1.0 INTRODUCTION

Oil and gas are the main contributors to the world's energy resources. Despite the availability of other major non-renewable energy sources such as nuclear, coal, and uranium, the persistent high demand for the oil and gas remains relevant to meet basic needs. With the ever increasing of global population, maximizing oil and gas recovery has become imperative to satisfy this escalating demand [1]. However, as continuous production leads many existing oil fiels to maturity, the adoption of tertiary oil recovery techniques, known as enhanced oil recovery (EOR) has gained significance in extracting the residual oil from small pore spaces within the reservoir rocks.

EOR methods helps to discover more oil beneath the surface. Once the primary and secondary recoveries end due to reduced pressure, they cease at a particular stage, which causes a pertubation in the recovery process despite a significant amount of oil remains trapped in the reservoir rocks. At this instant, EOR methods are implemented to fulfill the economic aspects of exploration. Various EOR methods have been employed over the years, depending on reservoir conditions and the fluid and rock characteristics. One such method is nanoemulsion flooding, a chemically enhanced oil recovery (cEOR) technique by providing mechanisms such as interfacial tension (IFT) reduction and wettability alteration (WA) [2,3].

Nanoemulsion refers to collodial disperision system formed by two immiscible liquids with particle sizes in the nano-scale range, typically ranging from 50 to 500 nanometers, usually stabilized by surfactant [4]. It can be synthesized using low- and high-energy methods. However, the most widely applied methods for creating stable nanoemulsions for extended periods is high-energy ultrasonication, making it favourable for EOR applications [5]. Nanoemulsion flooding EOR utilizes three fundamental principles: interfacial tension reduction, wettability modification, and emulsification [6]. Notably, nanoemulsions significantly increase oil recovery efficiency by reducing the interfacial tension between oil and water in the reservoir to ultra-low levels [7]. Moreover, the small size of nanoemulsion particles allows for enhanced effectivity and penetration into reservoir rocks without filtration [4].

Evaluating nanoemulsion characteristics is essential to determine its suitability for cEOR. Characteristics such as surface tension [8–11], rheology [8,12–14], turbidity [12], and thermal stability are among the widely employed properties measured for nanoemulsion characterization. Another important aspect is the stability of nanoemulsions, which plays a crucial role in maximizing its functionality. Typically, nanoemulsion stability is gauged by by its zeta potential and droplet size, as evident from extensive research [8–14]. It is established that nanoemulsions with a zeta potential falling within the range of > 30 or <-30 mV are labeled as stable. This increase in the absolute zeta potential value is attributed to the enhanced adsorption of surfactant molecules at the droplet interface, resulting in a smaller droplet size and consequently reinforcing nanoemulsion stability [8,15,16]. Thus, evaluating both the physical chracteristics and stability of nanoemulsions is essential for their successful application in EOR.

In fact, in formulating nanoemulsions, various factors could affect the final characteristics of a prepared nanoemulsion. Most researchers in the field have investigated the effect of the nanoemulsions

preparation conditions towards the characteristics and stability of the nanoemulsions. The preparation conditions includes oil phase concentration [17,18], surfactant concentration [13,17,18], ultrasonication time and power [16,19–21], co-addition of different surfactant [16,18,19], incorporation of nanoparticles [14,17], etc. Meanwhile, surfactant concentration significantly affects the stability of the emulsion, as surfactants reduce the interfacial tension between the immiscible liquids, inhibiting droplet coalescence. Sonication time also directly impacts nanoemulsion stability, as longer sonication times result in smaller droplet sizes, which are crucial for stability [22]. The choice of surfactant also influences the nanoemulsion stability, whereby the surfactant's hydrophilic-lipophilic balance (HLB) value could influence nanoemulsion stability [4].

Recently, the use of low-cost or waster materials for dispersed medium has attracted researchers in formulating their nanoemulsions, particularly due to economic concerns, and some towards the environment as well. The use of expensive dispersed mediums render them less favourable from economic and environmental perspectives. Therefore, replacing these expensive dispersed mediums with waste materials will reduce the environmental and cost penalty of the associated with nanoemulsion applications. As part of this innovative approach, oleic acid was specifically chosen in this study to formulate and characterize cost-effective nanoemulsions. This decision was motivated by the fact that oleic acid, a key component of palm oil, at which can also be abundantly found in the palm oil mill effluent, can be obtained at a low or even no cost.

To this end, in this study, a new formulation based on oleic acid, non-ionic Tween 40 surfactant, and distilled water was proposed to study the EOR of nanoemulsion through response surface methodology. Various nanoemulsion preparation parameters were systematically investigated on the produced nanoemulsions characteristics involving both the dynamic and stability properties. Then, an immersion test is conducted to assess the crude oil extraction performance by nanoemulsion on a core rock sample saturated with crude oil at varying conditions. The results will establish a foundation for further studies on nanoemulsion systems.

2.0 METHODOLOGY

2.1 Materials

Oleic acid ($C_{18}H_{34}O_2$), a palm oil free fatty acid was chosen as the dispersed phase. It was obtained in an analytical grade from Nacalai Tesque Inc. Polyoxyethylene sorbitan monopalmitate ($C_{62}H_{122}O_{26}$), also known as Tween 40 with a HLB value of 15.6 was selected as a surfactant or emulsifier. Tween 40 was procured from Sigma-Aldrich (St. Louis, U.S.A.). Distilled water was used as the continuous phase for the nanoemulsion formulation. The properties of the core rock sample were sandstone type with 136.7 g weight and 13.49 % porosity. The properties of crude oil were 0.86 g/ml density with viscosity of 5.11 cP.

2.2 Nanoemulsion Preparation and Characterization

2.2.1 Nanoemulsion Preparation

The nanoemulsion preparation method was adapted from the work of Kumar & Mandal [10]. The nanoemulsion prepared is composed of oleic acid, Tween 40, and distilled water. The quantities of these components and the time taken for sonication were determined from the experimental design as described in the next Section 2.4. Ultrasonication process was used for the preparation of nanoemulsion. Firstly, a coarse emulsion was prepared by stirring a mixture containing oleic acid, Tween 40, and distilled water at 800 rpm for 5 minutes with the help of a magnetic stirrer. Then, the formed coarse emulsions were sonicated with a handheld ultrasonicator, supplying a power of 375 W to the emulsion at a certain sonication time (discussed in later section). The ultrasonication process ensures the formation of O/W nanoemulsion [10]. To verify the successful preparation of the nanoemulsions, conductivity measurements were conducted for all samples before proceeding with the nanoemulsion characterization analysis.

2.2.2 Nanoemulsion Characterization and Measurement

The prepared nanoemulsions were subjected to dynamic properties and stability properties characterization, including surface tension (liquid-gas), viscosity, droplet size, and zeta potential.

The surface tension (liquid-gas) of nanoemulsion samples was measured using the drop shape analysis technique performed by the DSA 25 drop shape analyzer. Many researchers commonly used this technique to measure surface tension. For example, Kumar & Mandal [5] employed this method to assess the IFT of a nanoemulsion, evaluating its efficacy in reducing IFT to an ultra-low level under diverse temperature conditions.

The viscosity of nanoemulsions was measured with the help of a Brookfield viscometer. Viscosity is used to approximate the type of nanoemulsion system, whether it is an O/W or W/O emulsion [23].

The average nanoemulsion droplet size was analyzed using dynamic light scattering technology with the help of Zetasizer Nano S90 (Malvern Instruments Ltd., U.K.) instrument. The instrument used a scattering angle of 90°. Formulations are dispersed in double-distilled water for immediate analysis [23]. The emulsions were diluted in the ratio of 1:100 with distilled water to ensure Brownian motion identification of the droplets.

Another important nanoemulsion characteristic is the charge density at the surface of the emulsion droplets, which can be inferred from zeta potential measurements. Thus, the zeta potential values of all the O/W emulsions formulated in this work were determine using Zetasizer Nano S90 (Malvern Instruments Ltd., U.K.) immediately after nanoemulsion preparation. Emulsions were diluted using the continuous phase (distilled water) before subjecting them to the zeta potential measurement in order to avoid multiple scattering effect commonly encountered with concentration emulsions. Zeta potential of ±30 mV is believed to be sufficient for ensuring the physical stability of nanoemulsion [23].

2.3 Core Rock Sample Immersion Experiment

The core rock sample immersion experiment method was described in our previous work [16], whereby the potential use of the prepared nanoemulsion for displacing oil in an enhanced oil recovery method is simulated by the extraction of oil from a core rock sample, previously saturated with crude oil immersed in the said nanoemulsion. The amount of crude oil extracted is presented in a percentage form as in Equation 1.

$$\text{Crude oil extracted}(\%) = \frac{b - c}{b - a} \times 100 \quad (1)$$

where a (g) is the weight of the core rock sample, b (g) is the weight of the core rock sample after being immersed in crude oil, and c (g) is the weight of the core rock sample after being immersed in nanoemulsion.

2.4 Experimental Design using Box-Behnken Design (BBD)

Three experimental designs, each for the characterization of nanoemulsion (dynamic properties and stability properties) and core rock sample immersion experiment were implemented using the BBD in the Design-Expert (V12, Stat-Ease, U.S.A.) statistical software. The experimental data were then statistically analyzed, and the significance difference was determined through analysis of variance (ANOVA) by the software.

The physical or dynamic characteristics of the nanoemulsion, focusing on surface tension and viscosity, were investigated through experimental design. This analysis entails varying oleic acid concentration, Tween 40 concentration, and temperature as the independent variables. Table 1 details the range of the independent variables and responses considered for dynamic characterization phase. A total of 20 experiments were run and the corresponding responses were recorded.

Table 1 Parameter ranges and corresponding responses for dynamic properties characterization

Independent variables	Real values of coded levels	
	-1	1
X_1: Oleic acid concentration (wt.%)	0.2	1.0
X_2: Tween 40 concentration (wt.%)	0.1	1.0
X_3: Temperature (°C)	25	70
Responses		
Y_1: Surface tension (mN/m)		
Y_2: Viscosity (cP)		

In characterizing stability properties, a systematic experimental design is employed at varying oleic acid concentration, sonication time, and temperature as independent variables towards the stability properties of droplet size and zeta potential as responses. The independent variables, along with their respective ranges, and the responses are detailed in Table 2. A total of 20 experiments were run and the corresponding responses were recorded.

Table 2 Parameter ranges and corresponding responses for stability properties characterization

Independent variables	Real values of coded levels	
	-1	1
X_1: Oleic acid concentration (wt.%)	0.2	1.0
X_2: Sonication time (min)	1	20
X_3: Temperature (°C)	25	70
Responses		
Y_1: Droplet size (nm)		
Y_2: Zeta potential (mV)		

In the immersion test phase, nanoemulsions were prepared using a fixed 0.7 wt.% oleic acid concentration, 0.8 wt.% Tween 40 concentration, and at room temperature, following the previously determined optimum formulation. The experimental design includes variations of the sonication time for the nanoemulsion preparation and contact time for the immersion test, as outlined in Table 3. A total of 13 experiments were run and the corresponding responses were recorded.

Table 3 Parameter ranges and corresponding responses for crude oil extraction performance

Independent variables	Real values of coded levels	
	-1	1
X_1: Sonication time (min)	1	20
X_2: Contact time (hrs)	3	12
Responses		
Y_1: Crude oil extracted (%)		

Response surface regression is used to analyze the experimental data, and the anticipated form of the response surface second-order polynomial model is developed as in Equation 2.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{j^2 i}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y = response, X = factor, ε = error, and β = coefficient. β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for the model's intercept, linear, quadratic, and interaction terms, respectively. While X_i and X_j are the independent variables.

Then, the developed models and independent variables were evaluated for their significance based on p-value, whereby p-value of less than 0.05 is considered significant.

3.0 RESULTS AND DISCUSSION

3.1 Nanoemulsion Dynamic Properties

The nanoemulsion dynamic properties considered are surface tension and viscosity, analyzed through the developed polynomial model from the response surface regression. The model equations are presented in terms of the actual factors.

3.1.1 Surface Tension of Nanoemulsion

By measuring the surface tension, it is possible to investigate the formation and properties of a nanoemulsion. The co-existence of surfactant phase or middle-phase nanoemulsions with equilibrium between the aqueous and oil phases is the primary factor in the phase behaviour of ultra-low interfacial tension [23]. The surface tension measurement can estimate a particular nanoemulsion's critical micelle concentration (CMC) at a given temperature for a given formulation and fluid type.

Equation 3 is the regressed polynomial equation relating the surface tension with the independent variables considered (oleic acid concentration, surfactant concentration, and temperature). In the model equation, the p-values for oleic acid concentration, surfactant concentration, and temperature are all less than 0.001 (p-value < 0.05), indicating a significant effect toward surface tension.

$$\begin{aligned}&\text{Surface tension (mN/m)}\\&= 64.92312 - 7.83251 * \text{Oleic acid conc}\\&-15.11901 * \text{Surfactant conc} - 1.13863 * \text{Temp}\\&+8.75284 * \text{Oleic acid conc}^2 + 11.82941 *\\&\text{Surfactant conc}^2 + 0.010339 * \text{Temp}^2\end{aligned} \quad (3)$$

From the Equation 3, it is possible to predict the surface tension for a particular combination of oleic acid concentration, Tween 40 concentration, and temperature in terms of the actual factors. The surface tension will either increase or decrease in accordance with the equation's positive and negative terms for the respective variables. Higher coefficient values substantially influence surface tension more than lower values and vice versa. Figure 1 presents the graphs for the surface tension response for each independent variable.

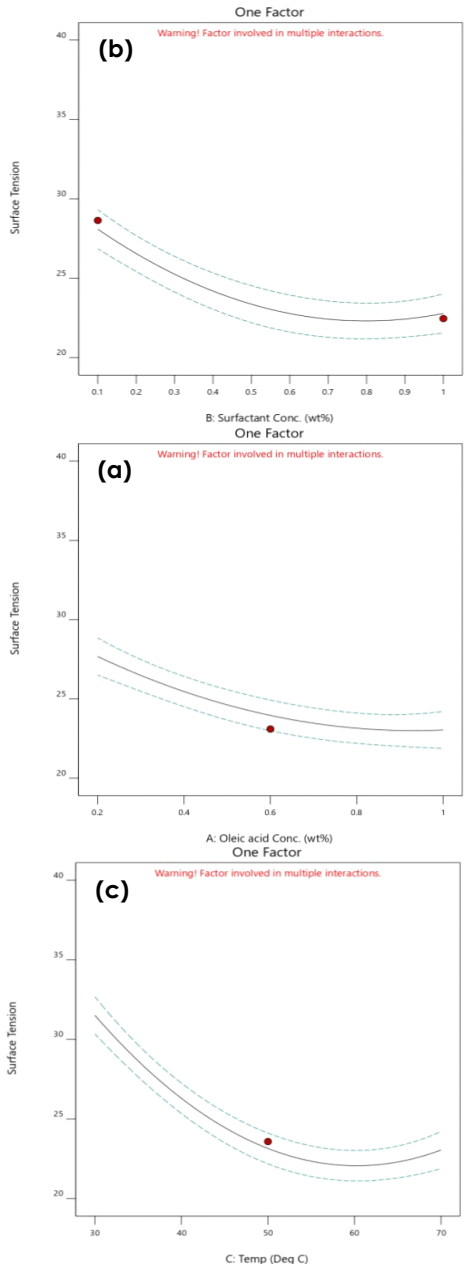


Figure 1 Single interaction graphs for surface tension of nanoemulsion against (a) oleic acid concentration, (b) surfactant concentration, and (c) temperature

According to Figure 1(a), the surface tension decreases from 27.76 to 24.56 mN/m as the oleic acid concentration is increased from 0.2 to 1.0 wt.%, and remained constant at around 0.41 wt.% surfactant. Surfactant concentration followed a similar decreasing trend, reaching a minimum of

23.35 mN/m at 0.81 wt.% surfactant and remaining near constant up to 1.0 wt.% surfactant. This phenomenon corresponds to the critical micelle concentration (CMC), a point where all surfactant molecules have adsorbed onto the surfaces of droplets, prompting the formation of micelles without further affecting the surface tension. Interestingly, when oleic acid is added, a slightly higher CMC is expected, indicating an increased requirement for surfactant in the presence of a dispersed phase component. This result in attributed to the nature of a surfactant, which readily adsorbed onto the surfaces of droplets of a dispersed phase. When there are fewer droplets, the surfactant aggregates more rapidly since less surface is available to be adsorbed onto. Thus, the CMC is increased with higher oleic acid concentration, requiring more surfactant as the dispersed phase is increased.

As for temperature, the surface tension of the nanoemulsion starts to decreases as the temperature increases from 30 to 60 °C and then increases beyond 60 °C. This suggests an optimum point of temperature at 60 °C, which results in the lowest surface tension. The observed decrease in surface tension with increasing temperature is attributed to molecules moving rapidly over fluid surfaces at higher temperature, which tends to counterbalance the stiff imbalance forces. This trend aligns with the findings of Dehaghani & Badizad [24], where the IFT of their nanoemulsion decreased with increasing temperature from 25 to 60 °C using CTAB as an emulsifier.

3.1.2 Viscosity of Nanoemulsion

It is imperative to examine the viscosity of nanoemulsions as it is one of the critical factors that could affect the areal and sweep efficiency of crude oil displacement. Nanoemulsion is less mobile than crude oil, with a mobility ratio of less than 1 (higher displacing fluid viscosity), resulting in improved displacement and recovery of oil. Therefore, the results of this section may provide insight into how temperature, surfactant concentration, and oleic concentration affect the viscosity of the nanoemulsion.

Equation 4 describes the relation of viscosity on the considered independent variables. All the three independent variables considered, which are oleic acid concentration, Tween 40 concentration, and temperature are significant in affecting the viscosity of nanoemulsions, each with a p-value of less than 0.001, 0.0028, and 0.0002, respectively.

$$\begin{aligned}\text{Viscosity (cP)} &= 3.50462 + 1.09170 * \text{Oleic acid conc} - 2.53148 * \text{Surfactant conc} - 0.004869 * \text{Temp} + 1.07955 * \text{Oleic acid conc}^2 + 1.3468 * \text{Surfactant conc}^2 \\ &\quad - 0.000068 * \text{Temp}^2\end{aligned} \tag{4}$$

The equation allows to determine an increase or decrease in viscosity based on the sign (positive or negative) of the variables, with the amplitude of the variation influenced by the magnitude of the variables' coefficients. Figure 2 displays the trends in viscosity response for each independent variable.

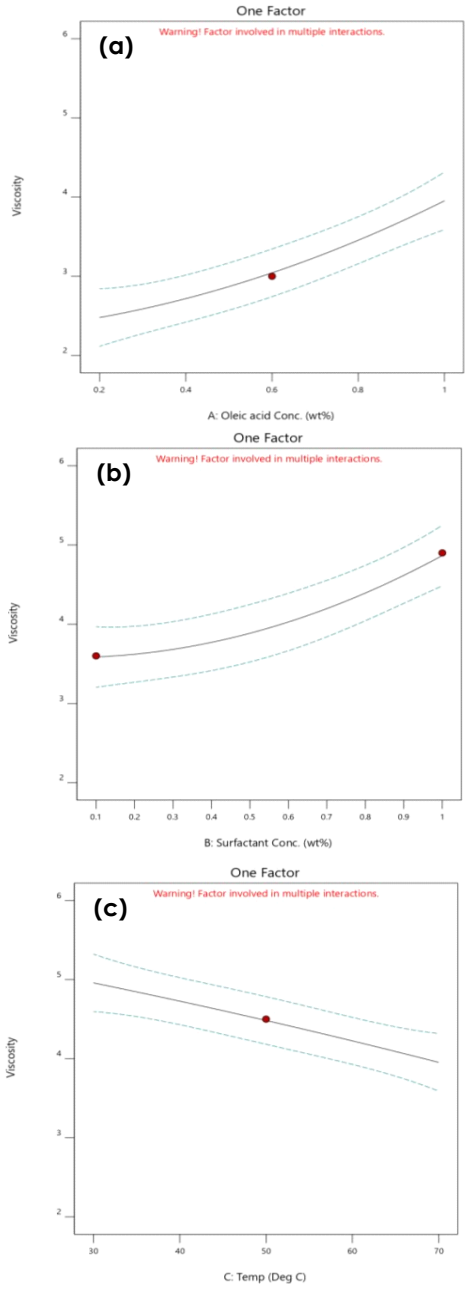


Figure 2 Single interaction graphs for the viscocity of nanoemulsion against (a) oleic acid concentration, (b) surfactant concentration, and (c) temperature

Increasing oleic acid concentration and surfactant concentration causes viscosity to rise slightly. However, temperature shows the opposite trend, in which viscosity decreases as temperature increases, indicating the more significant impact of oleic acid concentration on nanoemulsion viscosity at low

temperatures. The surfactant's Hydrophilic Lipophilic Balance (HLB) influences this phenomenon, with high HLB nonionic. Surfactants like Tween 40 have a lower impact due to their higher solubility in water. In contrast, oleic acid, being insoluble in water and forming droplets in the nanoemulsion, significantly affects viscosity. Once the critical micelle concentration (CMC) is reached at around 0.41 wt.% surfactant concentration, as previously mentioned, viscosity increases significantly due to micelle formation. This result is because, around this point, the CMC has been reached, and the micelles of surfactant molecules start to form, explaining the more significant increment in viscosity variations.

Oleic acid concentration has a more pronounced effect on viscosity changes than surfactant concentration. This condition explains the viscosity reduction at high oleic acid concentration with increasing temperature. This phenomenon is simply due to the nature of a liquid's hydrodynamic characteristics. The more viscous a fluid is, the more sensitive it is to temperature changes. Because higher temperatures make both water and oil somewhat less viscous, the enhanced viscosity contrast improves oil flow considerably more than water flow. This heat input enables thermal recovery, mainly in heavy oil reservoirs.

3.2 Nanoemulsion Stability Properties

The nanoemulsion stability properties considered are droplet size and zeta potential, analyzed through the developed polynomial model from the response surface regression. The model equations are presented in terms of the actual factors.

3.2.1 Droplet Size of Nanoemulsion's Dispersed Phase

The investigation of droplet size of nanoemulsions is essential in determining the stability and interfacial behaviour, as droplet size and stability are affected by the type of surfactant used and its concentration [10]. Droplet size of the dispersed phase is a critical factor that affects the emulsion stability and rheology by reducing aggregation and decreasing susceptibility to Ostwald ripening [25]. The results of this investigation provide light on how differences in oleic acid content, sonication duration, and temperature affect droplet size.

The p-value analysis was conducted on the droplet size response of the nanoemulsion dispersed phase. In this regard, sonication time and temperature are significant for determining the nanoemulsion droplet size of the dispersed phase, with the p-value for each independent variable being less than 0.0001. At the same time, the oleic acid concentration is not significant, since its p-value is 0.405, greater that the 0.05 threshold. The insignificance of oleic acid concentration on the droplet size is graphically evidence from Figure 3, where within the range of oleic acid concentration studies, the droplet size variations appear constant. The Equation 5 below expresses the model equation of droplet size of nanoemulsion as a function of oleic acid concentration, sonication time, and temperature, in terms of the actual factor.

$$\begin{aligned}\text{Droplet size (nm)} &= 1221.86983 - 468.13098 * \text{Oleic acid conc} \\ &- 82.44068 * \text{Sonication time} - 17.56009 * \text{Temp} \\ &+ 445.45455 * \text{Oleic acid conc}^2 + 2.5238 * \\ &\text{Sonication time}^2 + 0.243502 * \text{Temp}^2\end{aligned} \quad (5)$$

Figure 3 shows the graphs for the droplet size of nanoemulsion against all investigated independent variables. According to Figure 3, the variations in the oleic acid concentration reveals a minimum point of droplet size at approximately 0.61 wt.% of oleic acid concentration, irrespective of sonication time and temperature. At a sonication time of 1 minute, the average droplet size measures around 866 nm.

The impact of the three independent variables (temperature, oleic acid concentration, and sonication time) on droplet size variations is evident. At a sonication time of 1 minute, the average droplet size was approximately 866 nm, attribute to insufficient energy for producing a stable nanoemulsion with reasonable droplet sizes.

Sonication time emerges as the most significant factor affecting droplet size, with the average size decreasing significantly as the sonication time is increased up to 15 minutes. A prolonged sonication leads to smaller droplet sizes, as it enhances surfactant adsorption, but excessive sonication becomes inefficient due to increased cavitation, turbulence, and shear force, causing more droplet breakup and smaller nanoemulsion droplet sizes. However, an excessive sonication time is avoidable since it increases the droplet size, as evidence from Figure 3(b), beyond 15 minutes of sonication time. Previous studies support the optimal sonication duration of approximately 15 minutes for achieving the smallest droplet size. Proper adjustment of the variables can result in stable nanoemulsions with smaller droplet sizes, improving overall quality and effectiveness [21,26–28].

With regard to temperature, the droplet size slightly decreased at low oleic acid concentration until reaching 35 °C, gradually increasing to around 400 nm at 70 °C. However, these larger droplet sizes are not considered nanoemulsions and are unstable due to the tendency for oleic acid droplets to aggregate.

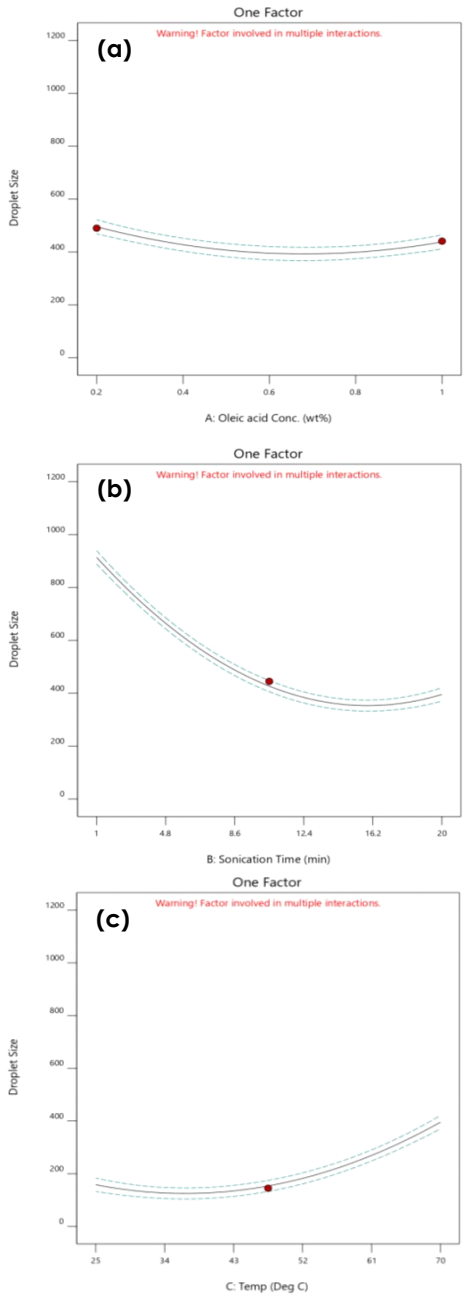


Figure 3 Single interaction graphs for droplet size of the nanoemulsion's dispersed phase against (a) oleic acid concentration, (b) sonication time, and (c) temperature

3.2.1 Zeta Potential of Nanoemulsion

An important technique for assessing colloidal dispersion is through zeta potential measurement, which determines the surface charge of particles when it is placed in liquid and helps understand the physic stability of nanoemulsions. Nanoemulsions with a large positive or negative zeta potential exhibit high physical stability due to high electrostatic interactions between individual particles.

Model equation terms are considered significant when the p-value is less than 0.05. In this scenario, oleic acid concentration and temperature are significant, with a value of less than 0.0001, while sonication time is insignificant, with a p-value of 0.2192. Equation 6 expressed the equation in terms of the actual factors of the nanoemulsion's zeta potential response.

$$\begin{aligned}\text{Zeta potential (mV)} &= -13.59848 - 30.46918 * \text{Oleic acid conc} \\ &- 0.350496 * \text{Sonication time} + 0.200808 * \text{Temp} \\ &+ 15.09659 * \text{Oleic acid conc}^2 + 0.017734 * \\ &\text{Sonication time}^2 - 0.001115 * \text{Temp}^2\end{aligned} \quad (6)$$

Predicting the response for specific values of each independent variable is possible with the aid of the equation stated in terms of the real components. The value of the zeta potential will increase or decrease depending on the positive and negative terms for the appropriate variables in the equation. Higher coefficient values affect zeta potential more than lower ones, and vice versa. Figure 4 demonstrates the zeta potential against a single interaction for the three manipulated variables.

Figure 4 illustrates that both oleic acid concentration and temperature exert a relatively more pronounced influence on the zeta potential of the nanoemulsion, whereas sonication time demonstrates minimal impact. The observed zeta potential in this study ranges from -23.56 to -14.11 mV. According to Figure 4(a), the negative magnitude of the zeta potential at higher oleic acid concentrations is more significant than at lower concentrations. This suggests that a high concentration of oleic acid enhances stability by promoting repulsion between droplets in the dispersed phase, thereby reducing flocculation and coalescence rates. Notably, beyond an oleic acid concentration of 0.8 wt.%, the zeta potential remains constant, most probably attributed to partially dissociated of negatively charged oleic acid molecules contributing to electrostatic repulsion. As more negatively charged oleic acid molecules are added, they saturate, further increasing the electrokinetic potential of the droplets.

For temperature aspect in Figure 4(c), a linear relationship between temperature and zeta potential is observed. The same trend for temperature effect was observed in the work by Mahrouqi *et al*. [29], where they examined natural carbonates under varying water salinity levels – both low and high. They observed that under both salinity conditions, the zeta potential exhibited a linear increase, providing an excellent fit to the temperature dependence of the zeta potential.

Overall, understanding the significant influence of temperature and oleic acid concentration on zeta potential adds to our knowledge of the factors involved in this study.

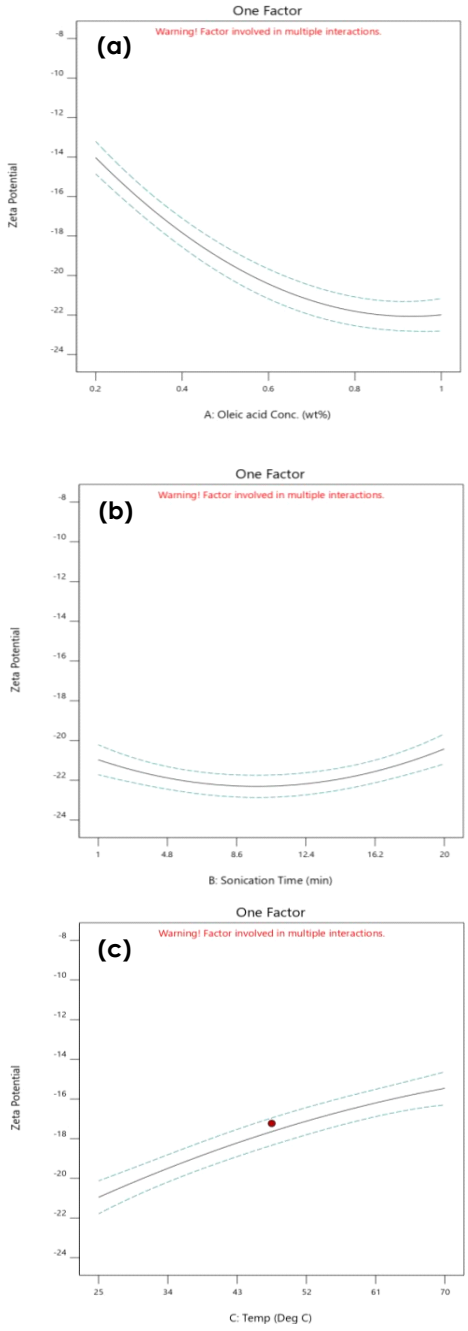


Figure 4 Single interaction graphs for zeta potential of nanoemulsion against (a) oleic acid concentration, (b) sonication time, and (c) temperature

3.2 Core Rock Sample Immersion Performance

Sonication time and nanoemulsion immersion duration in a core rock sample were used as independent variables to investigate the relationship between nanoemulsion formulation and crude oil extraction performance. This study was done to see the effect of the sonication process and to simulate the effectiveness of nanoemulsion in extracting the remaining crude oil in the reservoir, represented by a core rock sample. From the statistical analysis, the p-value for the independent variable of nanoemulsion crude oil extraction response was less than 0.0001 for both sonication and contact times, suggesting the sonication time and contact time substantially impact the effectiveness of oil extraction

In this case, the sonication time and contact time, are pertinent for further study. The length of the sonication process and the amount of time that the crude oil is in contact with the nanoemulsion determine the quantity of crude oil extraction. Equation 7 relates the crude oil extraction with the independent variables considered and Figure 5 shows the performance of crude oil extraction by nanoemulsion against the investigated independent variables (sonication time and contact time).

$$\text{Crude oil extracted (\%)} = 0.110222 + 0.222335 * \text{Sonication time} + 0.137044 * \text{Contact time} - 0.007049 * \text{Sonication time}^2 - 0.001294 * \text{Contact time}^2 \quad (7)$$

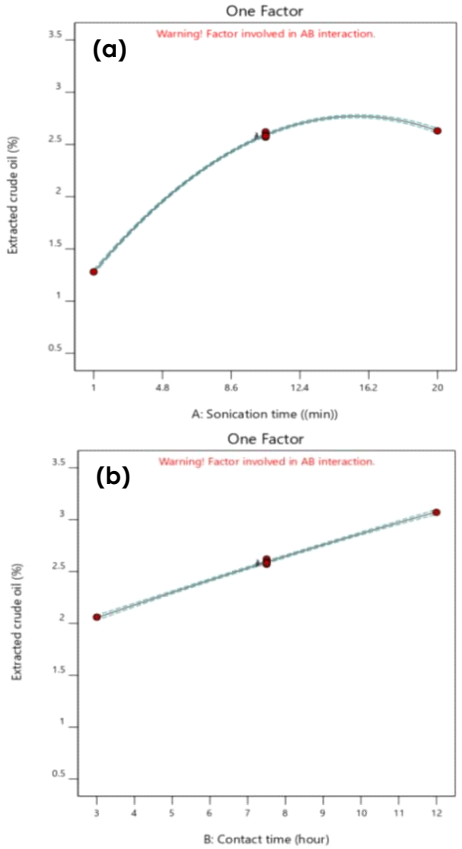


Figure 5 Single interaction graphs for the crude oil extraction performance against (a) sonication time and (b) contact time

From Figure 5, the recorded oil recovery in the range of 0.72 to 3.10% is notably low compared to real-life applications. This can be attributed to the fact that the maximum contact time during the immersion test was limited to 12 hours, whereas real reservoir during cEOR spans days, months or even years. The observed low crude oil recovery in this

study is a result of short contact and sonication times, with the lowest recovery associated with minimal contact and sonication durations, and the highest recovery achieved through prolonged contact and extended sonication.

Increasing immersion duration linearly improves oil recovery, as depicted in Figure 5(b). However, there is a point of diminishing returns, known as the residual oil concentration, where further increases in contact time does not significantly increase recovery. Beyond this point, the benefits of longer immersion contact duration start to diminish. Suitable chemical substances used in enhanced oil recovery can reduce this residual oil concentration, potentially allowing for increased recovery even beyond the point of diminishing returns.

Similarly, longer sonication time enhances oil recovery by reducing droplet size, promoting stability, and facilitating penetration into small pore spaces. To this end, understanding these interactions is crucial for optimizing crude oil extraction processes in realistic reservoir conditions.

4.0 CONCLUSION

This work formulates an O/W nanoemulsion derived from oleic acid as dispersed phase and stabilized by a non-ionic Tween 40 surfactant in a distilled water using ultrasonication for potential use in a chemical EOR flooding application. The nanoemulsion is prepared following the experimental designs using RSM at varying preparation parameters, including oleic acid concentration, surfactant concentration, sonication time, and temperature toward the characterization properties as responses, such as surface tension, viscosity, droplet size, and zeta potential. Then, an immersion test is conducted to determine the effectiveness of a stable nanoemulsion in extracting crude oil from a saturated core rock sample.

The best condition for obtaining the lowest surface tension is 0.41 wt.% of oleic acid and 0.81 wt.% of Tween 40 at 60 °C. Meanwhile, the ideal condition to obtain the highest viscosity is 1.0 wt.% of oleic acid, 1.0 wt.% of Tween 40 at 30 °C. In the aspect of stability, the optimum conditions for preparing a stable nanoemulsion are 0.69 wt.% of oleic acid and sonicated for 15 minutes at a temperature of 25 °C. For an effective crude oil extraction, it was obtained at a nanoemulsion preparation with 15 minutes of sonication time with an immersion duration of 12 hours.

However, at the current state of our findings, the zeta potential of the formulated nanoemulsions failed to obtain a stable range, which is within ±30 mV. Further research is therefore required to achieve the desired zeta potential values using different techniques or materials. It is also worth noting that the study did not explore the impact of surfactant types, even though the hydrophilic head charge of the surfactant can affect the nanoemulsion's zeta potential.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgement

This study is supported by the Ministry of Higher Education Malaysia under Fundamental Research Grant Scheme, FRGS/1/2019/TK05/UMS/03/1.

References

[1] S. Ahmed, K. A. Elraies. 2018. Microemulsion in Enhanced Oil Recovery, in: S. Karakuş (Ed.). Sci. Technol. Behind Nanoemulsions, 1st edition, IntechOpen. 145-165. https://doi.org/10.5772/intechopen.75778.

[2] O. Massarweh, A. S. Abushaikha. 2020. The Use of Surfactants in Enhanced Oil Recovery: A Review of Recent Advances. *Energy Reports*. 6: 3150-3178. https://doi.org/10.1016/j.egyr.2020.11.009.

[3] E. Jafarbeigi, Y. Ahmadi, M. Mansouri, S. Ayatollahi. 2022. Experimental Core Flooding Investigation of New ZnO-γAl2O3 Nanocomposites for Enhanced Oil Recovery in Carbonate Reservoirs. *ACS Omega*. 7: 39107-39121. https://doi.org/10.1021/acsomega.2c04868.

[4] I. Nor Bainun, N. H. Alias, S. S. A. Syed-Hassan. 2015. Nanoemulsion: Formation, Characterization, Properties and Applications - A Review. *Adv. Mater. Res.* 1113: 147-152. https://doi.org/10.4028/www.scientific.net/AMR.1113.147.

[5] N. Kumar, A. Mandal. 2018. Surfactant Stabilized Oil-in-Water Nanoemulsion: Stability, Interfacial Tension, and Rheology Study for Enhanced Oil Recovery Application. *Energy and Fuels*. 32: 6452-6466. https://doi.org/10.1021/acs.energyfuels.8b00043.

[6] N. Kumar, A. Mandal. 2018. Thermodynamic and Physicochemical Properties Evaluation for Formation and Characterization of Oil-in-water Nanoemulsion. *J. Mol. Liq.* 266: 147-159. https://doi.org/10.1016/j.molliq.2018.06.069.

[7] N. C. Dalibera, M. H. A. Zanin, K. L. Guimaraes, L. A. de Oliveira, A. M. de Oliveiraz. 2021. Optimized Formulation of Thermoresponsive Nanoemulsion-based Gel for Enhanced Oil Recovery (EOR) Application. *Appl. Petrochemical Res.* 11: 155-163. https://doi.org/10.1007/s13203-021-00269-9.

[8] M. K. Al-Sakkaf, S. A. Onaizi. 2023. Crude Oil/water Nanoemulsions Stabilized by Rhamnolipid Biosurfactant: Effects of Acidity/basicity and Salinity on Emulsion Characteristics, Stability, and Demulsification. *Fuel*. 344: 128052. https://doi.org/10.1016/j.fuel.2023.128052.

[9] R. K. Saw, D. Sinojiya, P. Pillai, S. Prakash, A. Mandal. 2023. Experimental Investigation of the Synergistic Effect of Two Nonionic Surfactants on Interfacial Properties and Their Application in Enhanced Oil Recovery. *ACS Omega*. 8: 12445-12455. https://doi.org/10.1021/acsomega.3c00401.

[10] N. Kumar, A. Mandal. 2020. Wettability Alteration of Sandstone Rock by Surfactant Stabilized Nanoemulsion for Enhanced Oil Recovery—A Mechanistic Study. *Colloids Surfaces A*. 601: 125043. https://doi.org/10.1016/j.colsurfa.2020.125043.

[11] Y. Zhao, F. Peng, Y. Ke. 2021. Design and Characterization of Oil-in-water Nanoemulsion for Enhanced Oil Recovery Stabilized by Amphiphilic Copolymer, Nonionic Surfactant, and LAPONITE RD. *RSC*. 11: 1952-1959.

https://doi.org/10.1039/d0ra06080a.
[12] G. W. Kim, S. Yun, J. Jang, J. B. Lee, S. Y. Kim. 2023. Enhanced Stability, Formulations, and Rheological Properties of Nanoemulsions Produced with Microfludization for Eco-friendly Process. *J. Colloid Interface Sci.* 646: 311-319. https://doi.org/10.1016/j.jcis.2023.05.005.
[13] M. Li, W. Kang, Z. Li, H. Yang, R. Jia, Y. He, X. Kang, Z. Zheng, Y. Wang, B. Sarsenbekuly, M. Gabdullin. 2021. Stability of Oil-in-water (O/W) Nanoemulsions and its Oil Washing Performance for Enhanced Oil Recovery. *Phys. Fluids*. 33: 072002. https://doi.org/10.1063/5.0058759.
[14] N. Kumar, A. Mandal. 2018. Oil-in-water Nanoemulsion Stabilized by Polymeric Surfactant : Characterization and Properties Evaluation for Enhanced Oil Recovery. *Eur. Polym. J.* 109: 265-276. https://doi.org/10.1016/j.eurpolymj.2018.09.058.
[15] S. Kumar, V. Mahto. 2017. Use of a Novel Surfactant to Prepare Oil-in-Water Emulsion of an Indian Heavy Crude Oil for Pipeline Transportation. *Energy and Fuels*. 31: 12010-12020. https://doi.org/10.1021/acs.energyfuels.7b02437.
[16] M. A. N. Aladin, M. H. W. Sani, M. H. V. Bahrun, Z. Kamin, A. Bono. 2022. Synthesis of Nanoemulsions from Palm Oil Stabilized by Sorbitan Monooleate and Polyoxyethylene Sorbitan Monopalmitate for Enhanced Oil Recovery Application. *AIP Conf. Proc.* 2610: 030005. https://doi.org/10.1063/5.0099660.
[17] M. Jalilian, A. Tabzar, V. Ghasemi, O. Mohammadzadeh. 2019. An Experimental Investigation of Nanoemulsion Enhanced Oil Recovery : Use of Unconsolidated Porous Systems. *Fuel*. 251: 754-762. https://doi.org/10.1016/j.fuel.2019.02.122.
[18] T. Mehmood, A. Ahmed, A. Ahmad, M. S. Ahmad, M. A. Sandhu. 2018. Optimization of Mixed Surfactants-based β-Carotene Nanoemulsions using Response Surface Methodology: An Ultrasonic Homogenization Approach, *Food Chem.* 253: 179-184. https://doi.org/10.1016/j.foodchem.2018.01.136.
[19] M. H. V. Bahrun, Z. Kamin, N. I. R. Idris, M. A. N. Aladin, A. Bono. 2022. Synthesis and Optimization of Surfactant-Stabilized Palm Oil-Based Nanoemulsion for Enhanced Oil Recovery. *AIP Conf. Proc.*
[20] T. Delmas, H. Piraux, A.-C. Couffin, I. Texier, F. Vinet, P. Poulin, M. E. Cates, J. Bibette. 2011. How to Prepare and Stabilize Very Small Nanoemulsions. *Langmuir.* 27: 1683-1692. https://doi.org/10.1021/la104221q.
[21] J. Carpenter, V. K. Saharan. 2017. Ultrasonic Assisted Formation and Stability of Mustard Oil in Water Nanoemulsion: Effect of Process Parameters and Their Optimization. *Ultrason. Sonochem.* 35: 422-430. https://doi.org/10.1016/j.ultsonch.2016.10.021.
[22] M. A. N. Aladin, M. H. V. Bahrun, Z. Kamin, Z. Zakaria, A. Bono. 2022. A Short Review on Application of Nanoemulsion for Enhanced Oil Recovery. *AIP Conf. Proc.* 2610: 050007. https://doi.org/10.1063/5.0099707.
[23] K. Gurpreet, S. K. Singh. 2018. Review of Nanoemulsion Formulation and Characterization Techniques. *Indian J. Pharm. Sci.* 80: 781-789.
[24] A. H. S. Dehaghani, M. H. Badizad. 2018. Effect of Magnetic Field Treatment on Interfacial Tension of CTAB Nano-emulsion: Developing a Novel Agent for Enhanced Oil Recovery. *J. Mol. Liq.* 261: 107-114. https://doi.org/10.1016/j.molliq.2018.03.111.
[25] M. K. Al-Sakkaf, S. A. Onaizi. 2022. Rheology, Characteristics, Stability, and pH-responsiveness of Biosurfactant-stabilized Crude Oil/water Nanoemulsions, *Fuel.* 307: 121845. https://doi.org/10.1016/j.fuel.2021.121845.
[26] P. Li, B. Chiang. 2012. Process Optimization and Stability of D-limonene-in-water Nanoemulsions Prepared by Ultrasonic Emulsification using Response Surface Methodology. *Ultrason. Sonochem*. 19: 192-197. https://doi.org/10.1016/j.ultsonch.2011.05.017.
[27] H. Rostami, A. Mehregan, G. Rajabzadeh, N. Niknia, S. Salehi. 2018. Development of Cumin Essential Oil Nanoemulsions and its Emulsion Filled Hydrogels. *Food Biosci.* 26: 126-132. https://doi.org/10.1016/j.fbio.2018.10.010.
[28] A. Gani, S. Benjakul. 2018. Impact of Virgin Coconut Oil Nanoemulsion on Properties of Croaker Surimi Gel. *Food Hydrocoll.* 82: 34-44. https://doi.org/10.1016/j.foodhyd.2018.03.037.
[29] D. Al Mahrouqi, J. Vinogradov, M. D. Jackson. 2016. Temperature Dependence of the Zeta Potential in Intact Natural Carbonates. *Geophys. Res. Lett*. 43: 11578-11587. https://doi.org/10.1002/2016GL071151.