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Research Article

Ultrasound-assisted demulsification of heavy fuel oil using lemon peel powder: A sustainable natural approach

Hind A. Sami [*,a], Raheek I. Ibrahim [b], Manal K. Odah [c]

Electromechanical Engineering Department University of Technology-Iraq, Baghdad, Iraq

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Abstract

Heavy fuel oil (HFO) commonly forms highly stable water-in-oil (W/O) emulsions due to the presence of natural surfactants such as asphaltenes and resins, creating difficulties in transportation and refining. In this study, a green demulsification approach was developed by integrating ultrasonic treatment (28 kHz) with lemon peel powder, a low-cost and renewable natural additive. Experiments were performed at 85°C with ultrasonic powers ranging from 100 to 800 W for 2–10 minutes, while lemon peel concentrations varied between 3000 and 15000 ppm. The optimum condition of 5000 ppm at 800 W for 10 minutes achieved a maximum demulsification efficiency of 80%, surpassing the commercial demulsifier RQ35, which achieved 65% under similar conditions. The improvement in phase separation is attributed to the synergistic effect of acoustic cavitation and the active components of lemon peel, including pectin and limonene, which enhance droplet coalescence and reduce interfacial stability. This study introduces a novel and environmentally sustainable demulsification strategy that reduces reliance on synthetic chemicals and demonstrates strong potential for practical implementation in industrial heavy oil treatment.

1. Introduction

Water-in-oil (W/O) emulsions in heavy fuel oil (HFO) remain a major operational challenge due to their high stability [1], mainly caused by asphaltenes and natural surfactants that strengthen the interfacial films [2,3]. These emulsions increase viscosity, hinder pumping and transportation, and accelerate corrosion, making efficient demulsification essential [4]. Although several physical and chemical techniques exist, many are costly, require high energy input, or rely on synthetic demulsifiers that introduce environmental and disposal concerns [5].

Recent trends toward sustainable demulsification have explored natural materials and ultrasound-assisted separation. Ultrasound is effective because acoustic cavitation disrupts interfacial films and enhances coalescence; however, ultrasound alone often cannot sufficiently destabilize highly stable HFO emulsions [6]. Similarly, most bio-based demulsifiers reported in literature act through surface-active components, but their performance remains limited without an aiding physical mechanism [7]. Thus, the research gap lies in the lack of integrated approaches that combine a natural, renewable demulsifier with a physical enhancement technique capable of overcoming the strong interfacial strength in heavy emulsions [8].

In this context, combining lemon-peel powder with ultrasonic irradiation presents an innovative synergy:

*Corresponding author: adelhend548@gmail.com
[a]orcid.org/0009-0003-8109-6453; [b]orcid.org/0000-0002-7158-3376; [c]orcid.org/0000-0002-3406-709X
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- Ultrasound generates micro-jets and shear forces through cavitation, weakening the interfacial film.
- Lemon peel chemistry (pectin, limonene, polyphenols) reduces interfacial tension, adsorbs stabilizing agents, and promotes droplet coalescence.

The interplay between mechanical cavitation and natural surface-active compounds offers a dual-action, greener pathway for destabilizing stubborn W/O emulsions [9]. Ultrasonic emulsification techniques utilize the dynamics of acoustic cavitation. Acoustic cavitation denotes the process involving the development, expansion, and implosive collapse of minute bubbles in a liquid medium exposed to high-intensity ultrasonic waves. The Ultrasonic wave propagation also causes the medium to alternately compress and expand as the collapse of these bubbles produces significant local pressure and temperature variations, resulting in high-shear forces, shock waves, and micro-jets capable of disaggregating big particles and agglomerates into smaller fragments. The motion of the ultrasonic-induced media particle, despite the modest displacement and velocity, exhibits significant acceleration proportional to the square of the ultrasonic vibration frequency, occasionally surpassing tens of thousands of times the acceleration due to gravity; this substantial acceleration is sufficient to generate a pronounced mechanical effect in the medium as shown in Figure 1 [10].

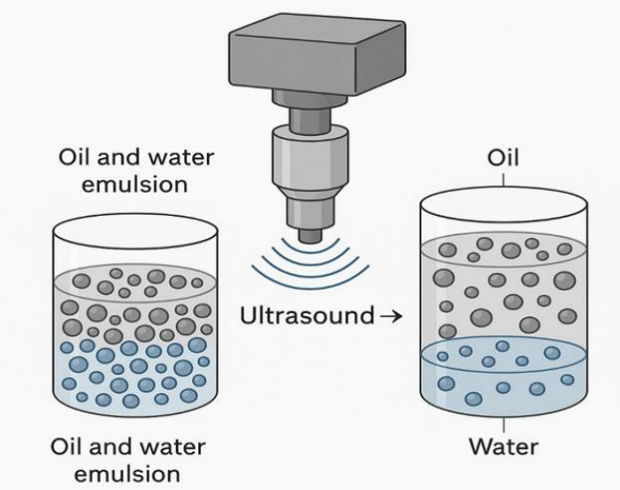


Fig. 1. Mechanism of ultrasonic activity in emulsion separation [11]

Ultrasonic treatment, now the focus of extensive research, can mitigate the drawbacks associated with classic extraction processes such as solvent extraction, distillation, and pressing [12]. The principle of ultrasonic demulsification is as follows: enhanced droplet oscillation speeds up droplet collisions, promoting their coalescence [13], and heat transfer from partial acoustic energy decreases emulsion viscosity and interfacial film strength [14]. Furthermore, droplets can increase the effectiveness of droplet coalescence by forming droplet bandings in ultrasonic standing waves (USWs) and directionally aggregating to pressure nodes or anti-nodes [12].

The environment and human health are still at risk from oil pollution, particularly when it comes to oil/water emulsions. This is explained by the fact that collecting such tiny oil droplets is more challenging [13]. Therefore, it is crucial to keep researching new approaches and techniques, effective oil capture systems, and cutting-edge wastewater treatment technologies, mainly for the separation of water and oil emulsions. Ultrasonic treatment is therefore believed to be a successful method of converting leftover oil and enabling subsequent processing in oil refineries. Moreover, it uses less energy while improving the results of physicochemical processing [14]. Ultrasonic treatment is essential for upgrading heavy molecules because it causes the bonds in heavy oil to thermally scission, producing hydrogen atoms. It is vital to continue investigating more effective solutions, possibly by combining different wettability types with the appropriate porous substrate, because the most popular methods, such as electro flotation and electrocoagulation [15], have disadvantages like high material requirements, expensive equipment, and high energy

consumption [6]. The demulsification of water-in-oil (W/O) emulsions has been widely investigated through three major categories of techniques.

- Chemical demulsification, which relies on surfactant-based additives, remains the most common industrial practice due to its ability to weaken interfacial films. Studies such as Mi et al. and Okereke et al. reported high separation efficiencies using ionic liquids and chemically modified biomass, though concerns persist regarding cost, toxicity, and environmental accumulation [9,12].
- Mechanical and physical demulsification, including thermal, electrostatic, and particularly ultrasonic methods, offers alternatives that avoid chemical residues. Ultrasonic cavitation has been shown to accelerate droplet coalescence through microstreaming and localized turbulence, as demonstrated by Sadatshojaie et al. and Chen et al. However, ultrasound alone often requires high energy input or extended treatment times [13,14].
- Bio-based demulsifiers, derived from agricultural waste or natural fibers, have recently gained attention as sustainable alternatives. Natural materials such as coconut extracts, lotus leaf powder, and cellulose-based agents have achieved promising efficiencies due to their surface-active functional groups. Yet, most studies rely solely on passive chemical action without enhancing physical disruption.

According to Hassan et al. [15] conducted a technical and economic assessment of employing silica nanoparticles to improve the demulsification process in crude oil. A software model was created in MS Excel for the Central Processing Facility (CPF) that processes heavy crude oil from Fula in Balila, Sudan. A sensitivity analysis of the primary factors associated with production cost and net present value (NPV) for various flow schedule selection alternatives was conducted. Evaluating flow tables according to equivalent plant capacity yields a 19% decrease in production costs, but assessment based on consistent yearly crude oil processing leads to an only 3.7% reduction in production costs. Pal et al. [16] focused on breaking the emulsion to improve water separation using derived demulsifier (DEMLOCS) is formulated with extract of Cocos nucifera coconut that does not harm the environment. According to the results obtained, it was concluded that the prepared demulsifier works best at 2000 ppm. It efficiently separates oil and water within 24 hours and extracts a maximum amount of water of 88%. The emulsion is treated with DEMLOCS and the maximum water volume is separated at 45°C. There is abundant promising result for the use of bio-demulsifier in heavy crude oil and water emulsion. Ye et al. [17] employed naturally occurring lotus leaves, modified using a straightforward hydrothermal technique, to eliminate emulsions from crude oil mixtures.

The efficacy of HLLF powder in rapidly destabilizing W/O emulsions is demonstrated by its unique wettability and surface architecture. DE may reach 88.17% when the HLLF dose was 1000 mg/L and the settling period was 90 minutes at 70 °C. HLLF exhibited comparable demulsification efficacy to many widely used commercial demulsifiers. Furthermore, it could efficiently demulsify two varieties of crude oil emulsions from distinct oilfields. Parvasi et al. [18] demonstrated the impact of low-frequency ultrasonography on the demulsification of a crude oil wastewater unit with a low concentration of crude oil (500 mg/L). Subsequently, research has been conducted without chemical demulsifiers with a laboratory ultrasonic bath at frequencies of 25 kHz and 45 kHz. Perform studies to assess the impact of wastewater temperature, ultrasonic power, frequency, and irradiation time on separation efficiency. The findings indicated that, under ideal conditions, the efficiency of crude oil emulsion separation improved by 72%. Romanova et al. [19] demonstrated the feasibility of destabilizing stable water-in-oil (W/O) emulsions with an average diameter of 30 to 45 μm, including those containing "gel," by the combination of ultrasonic treatment and a nanosized additive. The impact of sonication parameters, such as power and exposure duration, on the separation efficiency of emulsions in batch mode has been examined. The study focused on submerged and reactor-type ultrasonic devices. Ultrasonic treatment at 1.0 kW, along with the incorporation of nanopowder AlN suspension in acetone, effectively eliminates over 99% of the emulsions examined. The additive concentration ranged from 4–8% vol, while the exposure duration varied from 0.5 to 3 minutes, contingent upon the emulsion's composition and properties. The oil phase, with a maximum water content of 0.5 weight percent, and the aqueous

phase, with a maximum oil content of 46 mg L−1, may be achieved by the developed demulsification method.

Nadirov et al. [20] examined the demulsifying efficacy of original and fresh ground quartz (FMQ) particles extracted from river sand, contrasting it with the absence of an emulsifier. Alongside conventional solid-liquid characterization methods, employ rheological assessments, surface tension evaluations, and demulsification experiments to examine the impact of 75-micron mesh-sized quartz on emulsion stability. Following 100 minutes of deposition, a demulsification efficiency of 97% was achieved with the incorporation of 3 weight percent FMQ, in contrast to 140 minutes for unmodified quartz. The objective of grinding quartz is to enhance water permeability, hence elevating the local pH level, which results in decreased emulsion stability and eventual dissolution. Abdullah [21] focused on using oleic acid (OA), a naturally occurring substance that is widely accessible, to create two novel ionic liquids (ILs) and utilizing them to break up water-in-oil (W/O) emulsions. Both Epoxidized Oleic Acid + Pentaethylenhexamine - Ionic Liquid (EAPA-IL) and Epoxidized Oleic Acid + Tetraethylenepentamine - Ionic Liquid (EATA-IL) demonstrated effective performance, attaining 100% at various concentrations of demulsifier. The statistics demonstrated that as their concentration grew over time, so did their performance. Moreover, pure water was segregated by EAPA-IL and EATA-IL. Notwithstanding the considerable advancements in oil-water separation research, several limits have been identified in the associated studies. Numerous studies have extensively examined chemical demulsifiers, which, while useful, frequently provoke environmental concerns due to their possible toxicity and non-biodegradable characteristics. The aim of the present work is to prepare and formulate a cheap and environmentally safe demulsifier farm locally sourced raw material (Lemon peels) and experimentally tested to separate W/O emulsion assisted with ultrasonic waves applications.

2. Experimental Methods

2.1 Heavy Ful oil (HFO)

Heavy fuel oil is a kind of fuel oils characterized by a viscosity similar to that of tar. HFO consists of the residuals from petroleum sources following the extraction of higher-quality hydrocarbons using methods such as thermal and catalytic cracking [11]. HFO is distinguished by its physical, processing, and end-use qualities due to its wide variety of composition. HFO, the final byproduct of the cracking process, also comprises mixtures of these compounds to variable degrees: "paraffins, cycloparaffins, aromatics, olefins, and asphaltenes as well as molecules containing sulfur, oxygen, nitrogen, and/or organometals" [22]. The Daura refinery in Baghdad, Iraq, which produced water-in-oil emulsions, provided the heavy fuel oil emulsion equipment used in this study. The physical properties of this oil are shown in Table 1.

Table 1. Physical properties of the Basra Heavy oil [Al-Doura refinery]

Heavy fuel oil properties	
Specific gravity at 15.6ºC	0.8724
API at 15.6ºC	15.8
Density at 15 ºC (g/Cm^3)	0.9657
Kinematc Viscosity at 50ºC cst (mm^2/s).	183
Pour point ºC	+3
Carbon residue %w/w	8.1
Sulfur content %w/w	4.5
Water & sediment %v/v	<0.025
Asphaltenes content (wt %)	3.09%
Calorific Value (gross) KJ/kg	10441

2.2 Salt Water

In this study utilized natural water (tap water). A precise quantity of sodium chloride solution (5500 ppm) was combined with several prepared samples in 100 ml beakers containing 40% water. Table (2) presents the water specifications.

Table 2. Physical properties of the water

Water properties	
Physiologic (pH)	9.8
Electrical conductivity (EC)	3460 µs/cm
Temperature ºC	Between 20 and 25°C
Viscosity at 25°C	1 mPa/s

2.3 Natural Demulsifier

The natural material utilized in the separation process is lemon peels with a particle size of less than (100 microns). The lemon peels were removed, cleansed, desiccated, and sun-dried for a week. The specimens were subsequently subjected to an electric oven at 80°C and pulverized using a 1000-watt grinder.

2.4 Experimental Apparatus

The Lab Scale Ultrasonic Probe Sonicator (HC-SG-28800). The main components of the ultrasonic vibrating rod are the ultrasonic transducer, ultrasonic horn, and ultrasonic generator. The features of the ultrasonic apparatus used in the experiment are listed in Table 3.

Table 3. Specifications of the ultrasonic machine

Specifications	Value
Type	HC-SG-28800
Input voltage	220V 50-60 Hz
Frequency	28 kHz
Rated power	100-400-600-800 W
Power adjustment	50-100% gear adjustable
Working ambient temperature	+5 to +50℃
Tool head material	Titanium alloy
Length of the tool head	182 mm
Maximum operating temperature	150 degrees
Weight	16 kg
Power supply size	380×285×135 mm
Real-time display	Resonance, current
Cooling device	Transducer fan cooling
Connecting length	5 m
Reference processing capacity	1000

2.5 Emulsion Preparation

Samples were prepared following a stringent methodology to guarantee experimental consistency and reliability of results. Experimental reactors comprised clean 100-ml glass beakers. A mixture of 40% brine and 60% oil by volume created a two-phase system that simulates real separation conditions. Where 20 experiments were conducted. The components were meticulously combined using a magnetic stirrer to guarantee uniform distribution prior to ultrasonication. All preparations were conducted under regulated conditions to guarantee reproducibility and analytical precision. The procedure for applying ultrasonic waves to petroleum emulsions in a 300 ml beaker is depicted in Figure 2. After separation, the water content is drained into a 500 ml conical flask using a regulated tap at the bottom of a borosilicate glass 500 ml conical separatory funnel.

In experiments, lemon peel particles at varying concentrations (3,000, 5,000, 10,000, 15,000, and 20,000) ppm were included into the emulsion at 85°C with an operational frequency of 28 kHz. The results illustrate the impact of these concentrations on demulsification efficiency when ultrasound was utilized within conical glass reactors. Separation efficiency increased with higher lemon peel content, achieving an 80% water removal rate from the emulsion at 5,000 ppm, particularly when the combination underwent ultrasonic treatment. Separation efficiency fluctuated at different concentrations, suggesting an interplay between the applied energy level and the quantity of

additive. Moreover, it was noted that ultrasound-induced friction elevated the emulsion temperature as processing duration rose, hence enhancing the separation process. Experiments indicate that at elevated energy levels, the separation process accelerates; nevertheless, further investigation is necessary to comprehend the influence of varying concentrations on characteristics such as viscosity and color.

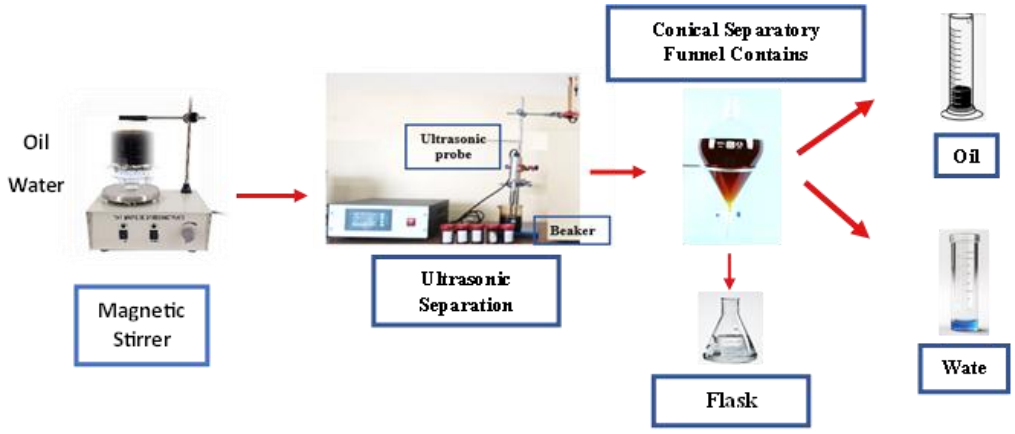


Fig. 2 Diagram of emulsion separation process

To guarantee the stability of the emulsion, the containers containing the oil/water emulsion were allowed to rest for a complete day prior to being segregated for each experiment. A reading is obtained after the materials are exposed to ultrasonography and allowed to sit for five minutes. The initial water content in the emulsion prior to ultrasound (IWC) and the final water content obtained after ultrasonic exposure (FWC) were taken into consideration when calculating the demulsification efficiency (ED) for each experiment in which the water-emulsion separation was achieved. The following equation was used to do this [25]:

$$ED\% = \frac{I_{WC} - F_{WC}}{I_{WC}} \times 100 \quad (1)$$

Where; I_{WC}: The emulsion's initial water content prior to ultrasonography, F_{WC}: The ultimate water content measured during ultrasonic exposure.

Cannon-Fenske-Routine Viscometer was used to determine the kinematic viscosity of heavy oil. The relationship applied to calculate the kinematic viscosity is [26]:

$$v = K \times t \quad (2)$$

The instrument constant k refers to the timing marks during the visual survey of the meniscus passage. It comes to: k=0.02688 mm^2/S^2.

3. Results and Discussion

3.1 Effects of Adding A 3000 ppm Concentration of Lemon Peels Molecules

Figure 3 illustrates the incorporation of lemon peel particles, a natural material, into the water/heavy oil combination, followed by the application of ultrasonic waves to the sample. The duration of ultrasound waves administered over 10 minutes at several energy (100 W, 400 W, 600 W, 800 W) influenced the concentration of the mixture. The concentration of the isolated water augmented over time, signifying that the separation process progressively enhances. At a low power of 400 W, the concentration of the separated water is inferior to that at higher energies of 600 W and 800 W. At 600 W and 800 W, the separation efficiency is enhanced; nevertheless, the disparity between these power levels is minimal, suggesting that elevating the power beyond 600 W may not yield substantial advancements in separation efficacy. The pulverized lemon peel particles assist in separation by disrupting the emulsion, absorbing water, or owing to their inherent physical and chemical characteristics. It comprises organic chemicals, including limonene,

a hydrophobic substance that can dissolve some hydrocarbon constituents. It also has other components like pectin and polyphenols, which may alter the surface tension between water and oil, so aiding in the separation of the two phases.

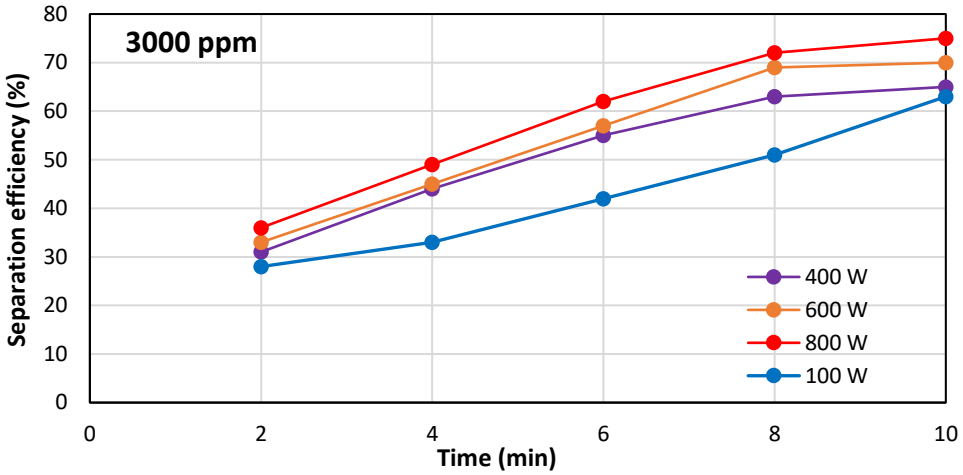


Fig. 3. Effect of adding 3000 ppm concentration of lemon peel particles

3.2 Effects of Adding a 5000 ppm Concentration of Lemon Peel Molecules

Upon increasing the concentration of lemon peel particles to 5000 ppm, as seen in Figure 4, a significant improvement in separation efficiency was observed relative to the 3000-ppm concentration. At all power levels, the percentage of separated water increases compared to the prior Figure 3, attaining 80% at a power of 800 W after 10 minutes. The distinction between 600 W and 800 W in the latter minutes is less perceptible, suggesting that the separation efficiency attains a saturation point around 5000 ppm, beyond which augmenting the power has no impact after a certain threshold. Lemon peel particles have been demonstrated to function as adsorbents, absorbing water or impurities that stabilize the emulsion. Moreover, they encompass acidic and alkaline substances that alter these emulsions and diminish their stability, hence facilitating coalescence and the separation of water and oil. The ultrasonic waves augmented the interaction by facilitating the cavitation effect, therefore accelerating the disintegration of emulsified water droplets and enhancing the reduction of surface tension, which results in the water being less adherent to the heavy oil.

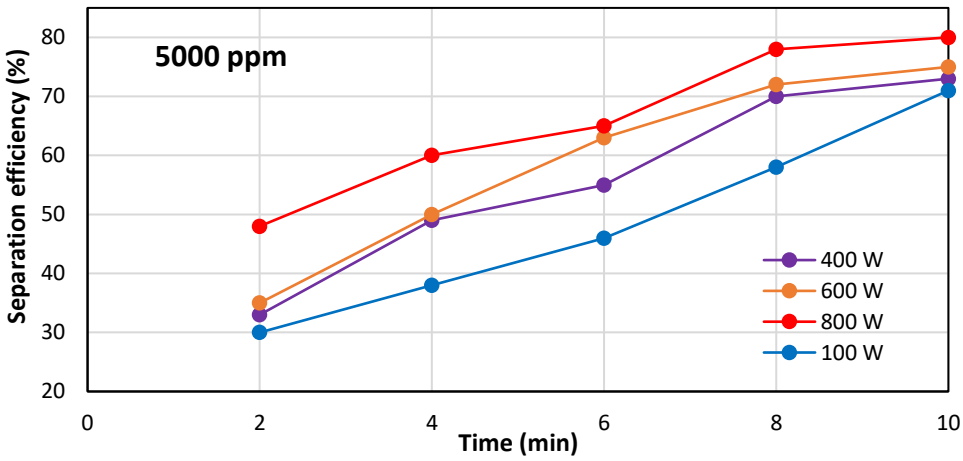


Fig. 4: Effect of adding 5000 ppm concentration of lemon peel particles

The demulsification efficiency showed a strong dependence on both ultrasound power and demulsifier concentration. Increasing ultrasound power enhanced acoustic cavitation intensity, resulting in more effective disruption of the interfacial film and higher droplet coalescence rates.

Efficiency increased significantly up to 600 W and reached near saturation at 800 W. Similarly, increasing lemon peel concentration improved efficiency up to an optimal value of 5000 ppm due to the increased availability of active surface-modifying compounds. However, concentrations above 5000 ppm led to reduced efficiency because viscosity increased and particle crowding hindered droplet mobility and cavitation performance.

3.3 Effects of Adding a 10000 ppm Concentration of Lemon Peel Molecules

Figure 5 indicates that elevating the particle concentration to 10,000 ppm did not markedly enhance the separation relative to 5,000 ppm, suggesting that the system may have attained saturation. The disparity between 600 W and 800 W diminished, suggesting that elevated particle concentration mitigated the impact of high power. This may result from heightened viscosity or the restabilization of the emulsion owing to particle saturation, which restricts ultrasound's efficacy in enhancing separation. Furthermore, the substantial quantity of particles may result in the establishment of a physical particle network that retains a portion of water within the system rather than allowing its total release.

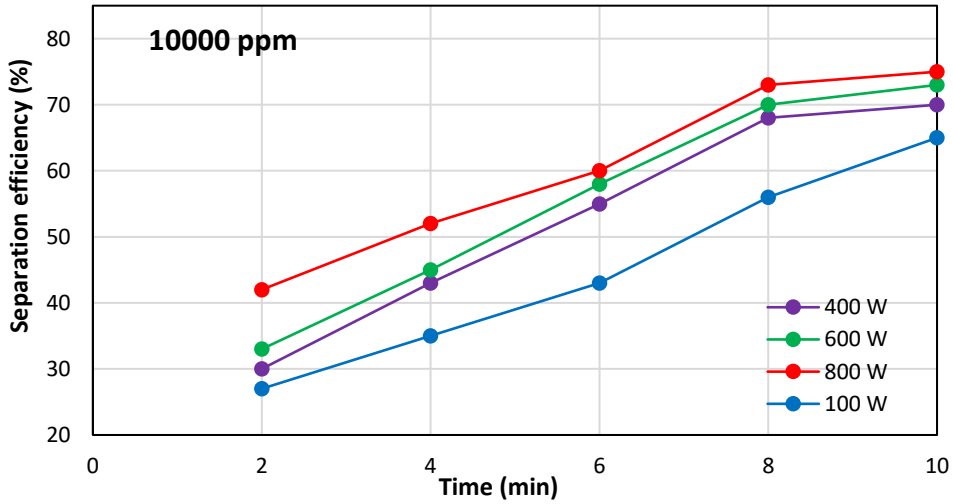


Fig. 5: Effect of adding 10000 ppm concentration of Lemon peel particles

3.4 Effects of Adding a 15000 ppm Concentration of Lemon Peel Molecules

In Figure 6, an increase in concentration to 15000 ppm in the water-oil combination resulted in a reversal of the separation process compared to 10000 ppm, suggesting that the lemon peel particles did not enhance the emulsion's effectiveness. The inefficiency arises from the heightened viscosity of the emulsion and the challenge of disrupting the links between the water and oil molecules. Conclude from the process of increasing concentrations that the best value at which we can get the highest efficiency is at a concentration of 5000 ppm at a power of 800 watts in ten minutes.

3.5 Effect of Concentrations of Lemon Peel Particles

Figure 7 indicates that augmenting the ultrasonic power from 100 W to 800 W enhanced the concentration of water-oil separation across all examined concentrations of lemon peel powder. The augmentation of power enhances the acoustic cavitation effect, facilitating the disruption of emulsions and promoting water-oil separation. The 3000-ppm concentration exhibited suboptimal performance, maybe attributable to an insufficient availability of active chemicals necessary for emulsion breakdown. The 5000-ppm concentration attained the greatest separation efficiency, exhibiting the highest water concentration across all power levels. At 10,000 ppm, a threshold was observed beyond which the separation efficiency began to decline at this concentration. At 15,000 ppm, the separation appears to be less efficient than anticipated, potentially due to the saturation effect; elevating the concentration to this level may augment the medium's viscosity, thereby diminishing the efficacy of acoustic cavitation and its impact on emulsification disruption. At low

energies, separation is constrained at all concentrations, highlighting the significance of ultrasonic power in improving the separation process for this material. The incorporation of lemon peel particles into a water-oil emulsion influences the separation process in many manners, contingent upon their chemical composition and surface characteristics. Besides the ultrasound's mechanism of disrupting emulsions by the mechanical fragmentation of emulsion particles, the findings on lemon peel particles indicate the following:

- Enhanced separation: Lemon peels contain essential oils and active chemicals like limonene, which exhibit hydrophobic qualities that may improve the surface tension between water and oil, hence aiding separation.
- Minimize emulsification: Lemon peel particles may function as a demulsifier due to their natural components, including pectin and flavonoids, which can influence emulsion stability, facilitating the separation of water from heavy oil.
- Enhanced environmental efficiency: Utilizing natural materials like lemon peels provide an eco-friendly alternative to synthetic chemicals, hence reducing the detrimental environmental effects of the separation process.
- Viscosity modification: Certain components in lemon peels may influence the viscosity of the oil, facilitating the separation of water and enhancing efficiency.

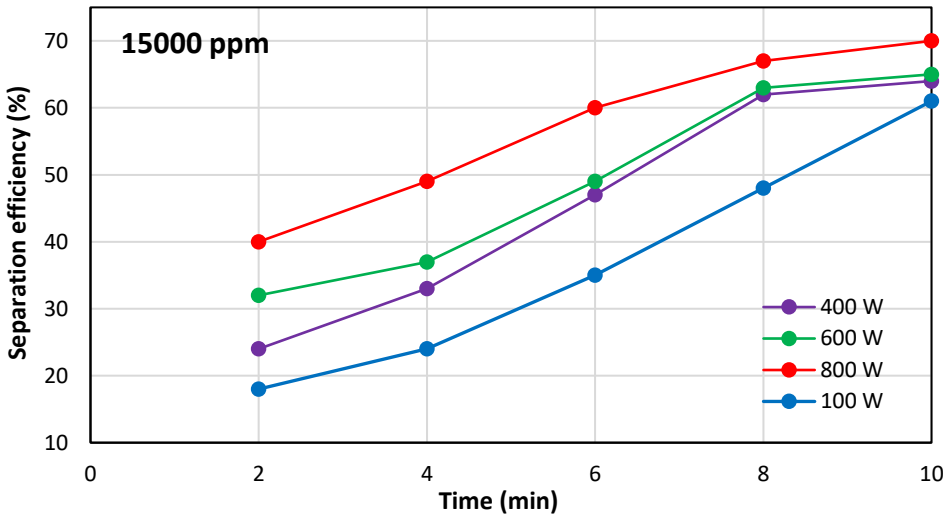


Fig. 6. Effect of adding 15000 ppm concentration of lemon peel particles

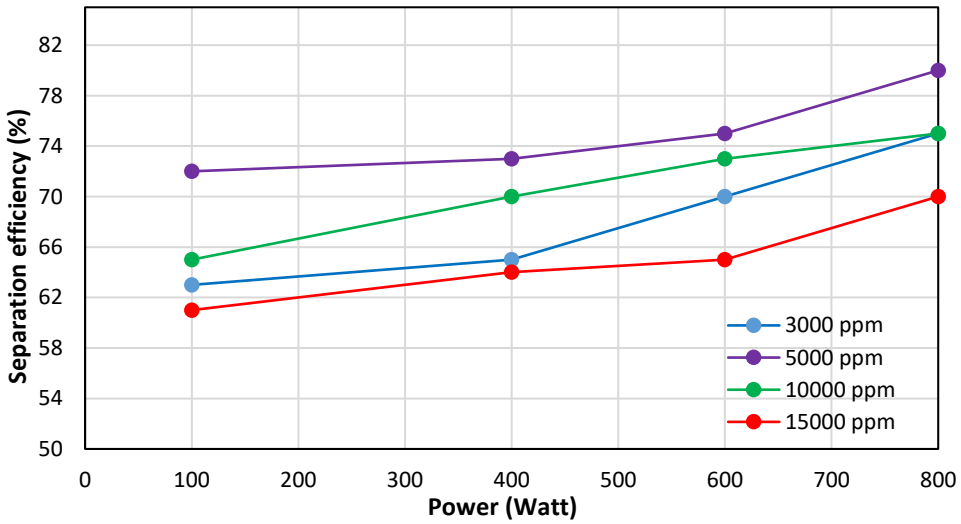
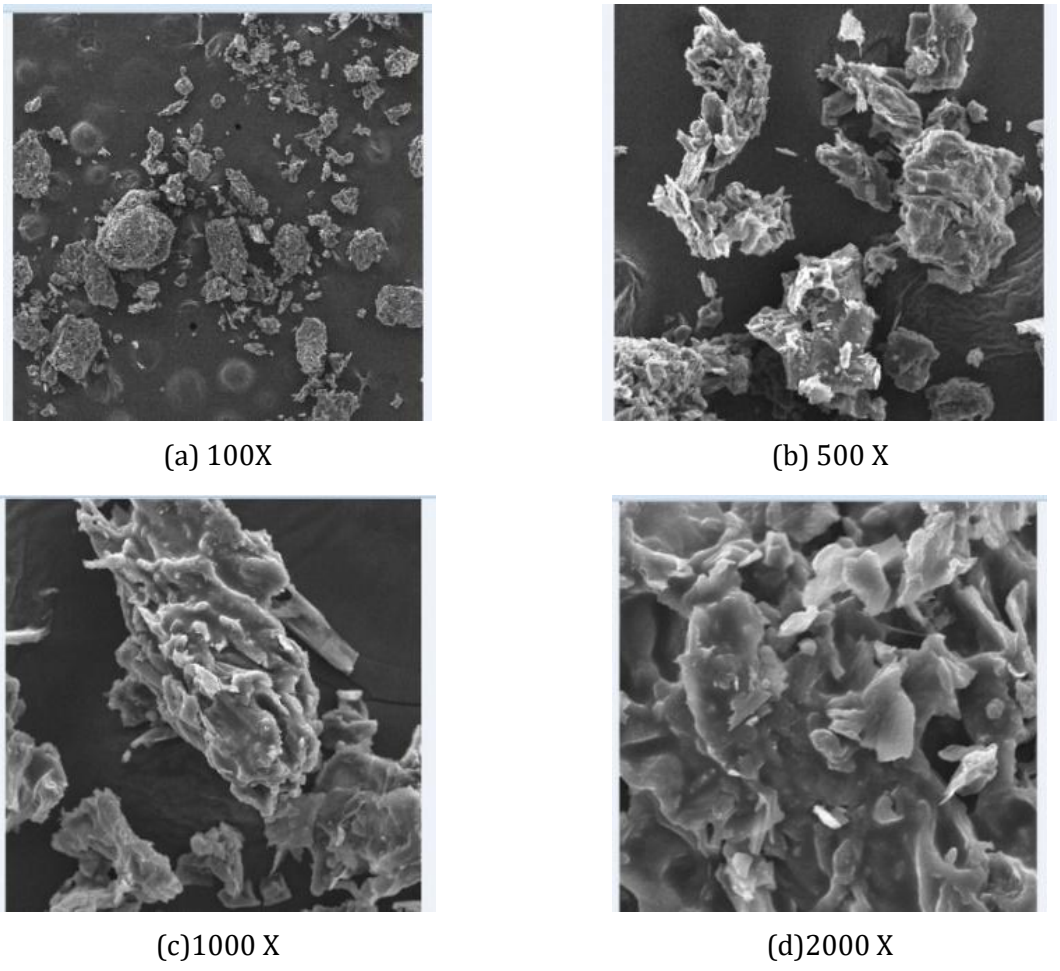


Fig. 7. Effect of lemon peels particles

3.6 Morphological Analysis of Lemon Peels Particles Using Scanning Electron Microscopy (SEM)

Figure 8a is a SEM imaging at different magnifications illustrates lemon peel particles measuring between 50 and 150 μm, characterized by a porous and rough structure, potentially enhancing absorption or influencing emulsion stability. The surface has a rough and complex texture, reflecting the characteristics of plant fibers. There are evident agglomerates, perhaps due to dehydration or crushing during processing. The particles vary in size from microscopic fragments measuring 20-50 micrometers to bigger pieces measuring 100-300 micrometers, as seen in Figure (8b), showing a heterogeneous particle size distribution. Pores and interstitial spaces between the particles may influence their capacity to absorb and interact with liquids. Figure (8c) distinctly illustrates the fibrous layers, corroborating the notion that lemon peels have cellulose and hemicellulose, compounds that may influence the interaction with oil and water. Small particles and surface fibers range from 5 to 50 μm, whereas pores and microscopic holes may measure less than 5 μm.



(a) 100X (b) 500 X

(c)1000 X (d)2000 X

Fig. 8. SEM images of lemon peel particles at magnifications of (a) 100x, (b) 500x, (c) 1000x, and (d) 2000x

The surface is notably uneven, perhaps enhancing the physical and chemical interactions with the surrounding medium. Figure (8d) depicts irregularly shaped particles characterized by sharp edges, aggregated structures, and a rough surface exhibiting fractures and fragmented sections. A congregation of particles is observable, potentially revealing the characteristics of the material in its desiccated form, since the particles tend to stack upon one another. Some particles may range from 5 to 10 μm in size, whilst bigger particles may measure 20 to 30 μm or greater. The high porosity and fibrous composition—including cellulose and hemicellulose—facilitate adsorption of water droplets and interfacial interactions, which can limit water permeation through separation membranes. Additionally, the heterogeneous particle size distribution can form multi-layered

filtration paths, creating physical barriers that slow down water transport while allowing oil to pass more freely. Moreover, the rough texture and presence of micro- and nano-scale pores may contribute to modifying surface energy and interfacial tension, further stabilizing the separation process. The combination of sharp-edged particles, irregular geometry, and complex topography supports the idea that lemon peel powder could be an effective additive or functional material in oil–water separation membranes by enhancing both physical trapping and chemical affinity toward water. Table 4 shows how the surface structure contributes to the separation mechanism.

Table 4 .The surface structure contributes to the separation mechanism

Magnification	Key Observation	Contribution to Demulsification
100×	Rough, porous surface	Enhances water adsorption
500×	Irregular fibrous structure	Increases interfacial disruption
1000×	Visible micro-pores	Promotes droplet trapping
2000×	Sharp-edged fragments	Improves mechanical breakup of emulsion

3.7 X-ray Diffraction (XRD) Analysis to Determine the Crystal Structure of Lemon Peels Molecules

The results in Figure (9) show a broad peak at low angles (~20° - 30°) in crystalline systems, sharp peaks are due to the systematic reflection of X-rays from atomic planes, while the broad peak indicates the presence of amorphous or semi-crystalline materials. It also indicates that the sample contains materials with short-range atomic arrangement and not a regular crystalline structure. A gradual decrease in intensity at high angles (>30° Theta-2Theta) indicates the presence of non-crystalline materials such as organic materials or nanoparticles dispersed in the system. It could be due to oil residues, or products resulting from the decomposition of organic compounds present in lemon peels after exposure to ultrasound. the analysis of the raw signal (Profile) and the application of mathematical processing such as Smoothing Profile and Background Subtraction are shown, which helps in identifying the actual peaks and removing unwanted signals. The presence of a signal at low angles after background correction may indicate the remains of natural carbonaceous or silicate materials resulting from lemon peel particles.

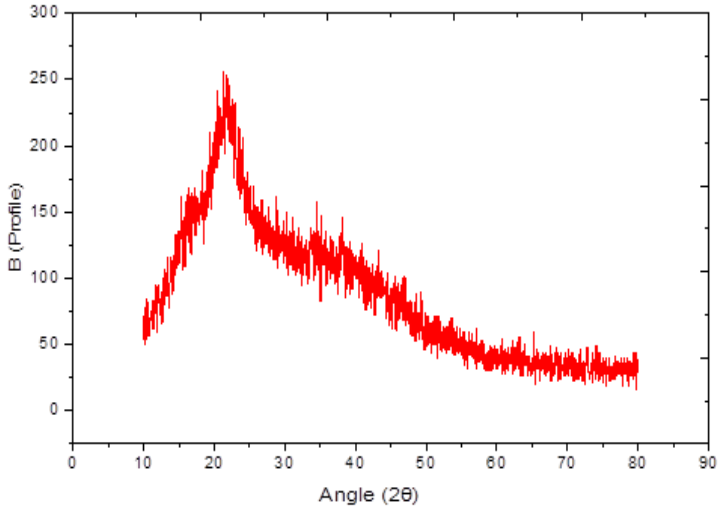


Fig. 9. X-ray diffraction (XRD) examination of an oil sample before exposure to ultrasound

3.8 Effect of Ultrasound on Oil/Water Samples

The infrared spectra of the compounds prepared using the SHUMADZUFTIR-84005 were recorded as potassium bromide tablets in the region 400 - 4000 cm^2 at laboratory temperature. Where the device FTIR represents the effect of ultrasonic waves on the physical and chemical properties of oil samples. Figure 10 shows the peaks of the spectral waves, where the value of 3288 cm^{-1} indicates

the O-H bond (alcohols or water), i.e. this peak indicates the stretching vibration of the O-H bond, indicating the presence of water or alcohols in the sample. Since the sample contains water, it is likely that this absorption is due to the residual water after the ultrasound treatment. It is also shown that the peak is broad, i.e. there is water bound to hydrogen or alcohols such as phenols. The spectral wave peak of 2893 cm^{-1} indicates the C-H bonds in alkanes (saturated hydrocarbons). These peaks represent stretching vibrations of the C-H bond in the alkane's groups (-CH_3 and -CH_2), which are present in heavy oil. These peaks indicate saturated hydrocarbon compounds, which constitute a major part of oil. The rise of these peaks after ultrasound treatment indicates a change in the concentration of hydrocarbon compounds. Peak 2831 cm^{-1} This peak usually indicates the presence of alkynes (-C≡C-) or nitriles (-C≡N-). It due to the presence of alkynes or some nitrogen-containing compounds. Peak 1771 cm^{-1} indicates the presence of carbonyl bonds C=O, which are usually found in esters, carboxylic acids or ketones. That due to the decomposition of some organic compounds in the oil as a result of the ultrasonic waves, which leads to the formation of new oxygen compounds. Peak 1635 cm^{-1} This peak indicates the C=C bonds in alkenes, which means that the oil may contain unsaturated compounds. This peak may also be due to the vibrations of absorbed water (H-O-H bending mode), which may indicate the presence of residual water after separation. The peak at 426 cm^{-1} is very low in the spectrum, and often indicates the presence of silica (SiO_2) or metal oxides.

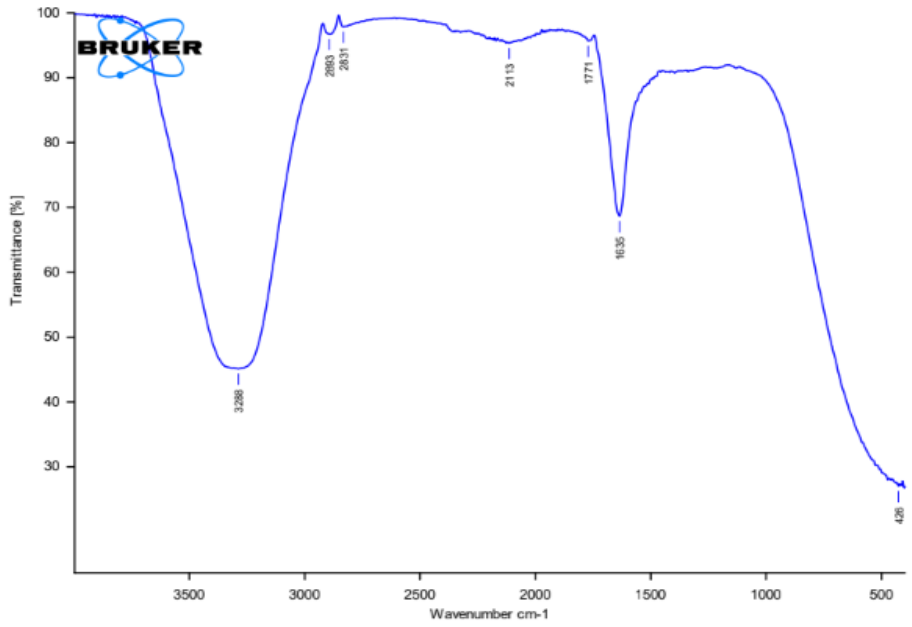


Fig.10 Effect of ultrasound on oil sample by FTIR device

While, Figure 11 represents the examination of oil samples before exposure to ultrasonic waves, the spectral wavelengths before ultrasound treatment, the broad peaks 3735 cm^{-1} and 3404 cm^{-1} indicate O-H vibrations associated with water or hydroxyl groups (alcohols or phenols). Peaks 2953, 2921 and 2852 cm^{-1} These short, narrow peaks represent the C-H stretching vibrations of methyl (-CH_3) and methylene (-CH_2-) typically found in hydrocarbons. Peak 1771 cm^{-1} A prominent peak represents the C=O vibration, indicating the presence of carbonyl groups, such as carboxylic acids, esters or ketones. Peak 1603 cm^{-1} These peaks can be associated with structural vibrations of aromatic rings or C=C bonds in organic compounds. The peaks of 1457 and 1376 cm^{-1} are usually associated with C-H bond bending vibrations in organic compounds, especially in alkanes, which indicate the C-H bending vibration in the -CH_2- and -CH_3 groups, and hydrocarbons, which often appear in oils and petroleum products, indicating the presence of long carbon chains. As this peak has changed (disappeared) after treatment, this is an indication of the cracking or rearrangement of hydrocarbons, which may affect the viscosity or chemical composition of the samples. The peak of 1032 cm^{-1} is usually associated with C-O vibrations, which can be found in alcohols, ethers. The peaks of 808 and 722 cm^{-1} can indicate out-of-plane C-H vibrations in aromatic or long-chain hydrocarbon compounds. It was also found that this peak decreased in

intensity after exposure to ultrasound due to the decomposition of some aromatic compounds as a result of the mechanical and chemical effects of ultrasound. Peak 501-432 cm^{-1} These peaks may be related to the structural vibrations of compounds other metal oxides. Table 5 shows the most important peaks and active variables associated with the deemulsification process.

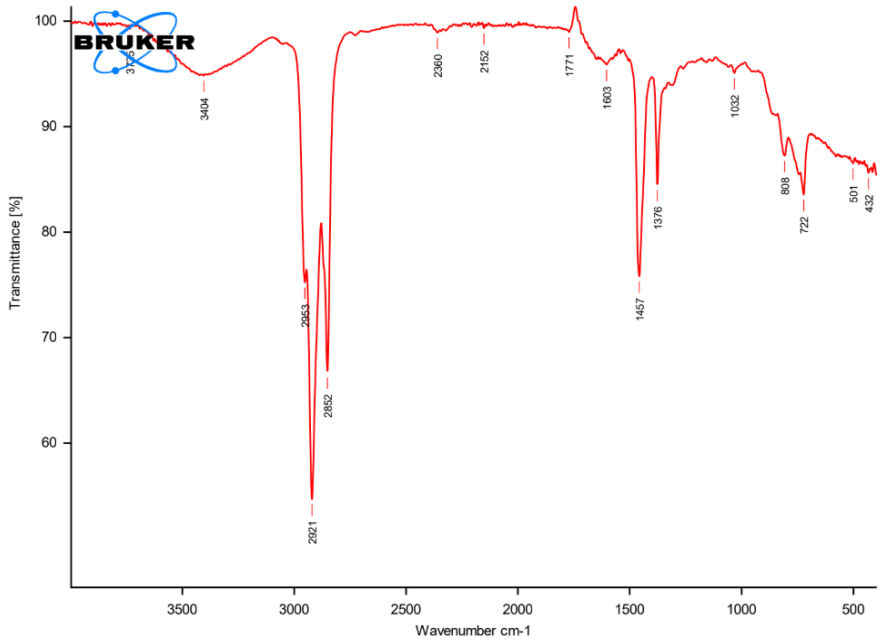


Fig. 11. FTIR examination of an oil sample before exposure to ultrasound

Table 5. The peaks and the active variables

Peak (cm^{-1})	Functional Group	Interpretation
3280	O–H	Moisture/pectin groups
2920, 2850	C–H (alkanes)	Hydrocarbon backbone
1730	C=O	Ester/carboxyl groups
1620	C=C	Unsaturated compounds
1030	C–O	Alcohol/ether groups

Table 6. A comparison between the studies and the current study

Researchers	Material used	Results
This study (Lemon peel)	Natural (lemon peel powder)	the current study achieved 80% efficiency at 5000 ppm and 85°C employing lemon peel powder and ultrasound
Mi et al. [12]	Natural (CCDA ionic liquid)	documented a 99.78% oil removal efficacy utilizing CCDA at 20 ppm at 70°C
Sadatshojaie et al. [14]	0No demulsifier (ultrasound only)	the ultrasound-only technique employed attained an effectiveness of up to 88%
Okereke et al. [9]	Natural blend (local materials)	achieved over 90% separation efficiency under mild conditions

In comparison to analogous prior investigations, the lemon peel-derived demulsifier in this research attained competitive separation efficiency. For example, Mi et al. (2025) documented a 99.78% oil removal efficacy utilizing CCDA at 20 mg/L at 70°C [12], whereas the current study achieved 80% efficiency at 5000 ppm and 85°C employing lemon peel powder and ultrasound. Despite a little reduced removal rate, the cost-effectiveness and accessibility of lemon peels confer considerable sustainability advantages. Moreover, the ultrasound-only technique employed by Sadatshojaie et al. attained an effectiveness of up to 88% [14], which is comparable to our findings,

given that their methodology did not utilize any chemical demulsifier. This comparison highlights the efficacy and ecological suitability of natural demulsifiers, such as lemon peels, when combined with ultrasonic enhancement. Table 6 shows a comparison between the studies and the current study.

3.9 Commercial Breaker (RQ35) in Breaking Emulsification

Figure 12 shows the results of the commercial emulsification breaker (RQ35) where different concentrations were taken to break the emulsification and the results shown in Table 5 were obtained [23]. The commercial breaker gave a low separation rate compared to the prepared natural breaker, but when using a high temperature for the commercial breaker (RQ35), its efficiency increases, and this is what happens in most commercial breakers as they need a high temperature more than (70) m. Therefore, the effect of temperature on the commercial breaker and the prepared breakers was studied to increase the separation efficiency. The commercial emulsification breaker was added at concentrations of (500, 1000, 2000 and 3000) ppm and at different temperatures.

Table 7. Emulsification fraction by commercial breaker (35 RQ)

Amount of parasitic substance (ppm)	Amount of water separated (%) Separation time (minutes)					
	10	20	30	40	50	60
500	0	0	0	0	0	5
1000	0	0	0	0	5	10
2000	0	0	5	10	10	15
3000	0	5	10	10	15	20

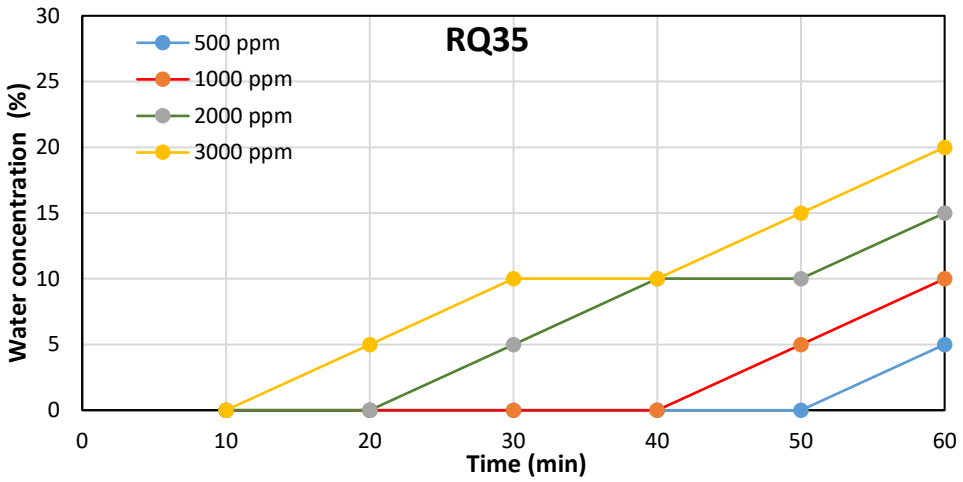


Fig. 12.Relationship between separation ratio and time with commercial emulsion breaker (RQ35)

4. Conclusion

This study provides clear evidence that integrating ultrasonic cavitation with lemon peel powder creates a synergistic demulsification mechanism capable of enhancing the separation of W/O emulsions in heavy fuel oil. Quantitative analysis of the experimental results revealed a strong dependency of demulsification efficiency on both ultrasound power and demulsifier concentration. The optimum operating conditions—5000 ppm lemon peel powder and 800 W ultrasonic power at 85 °C for 10 minutes—produced an efficiency of 80%. Compared with the commercial demulsifier RQ35 (65% under similar conditions), this demonstrates a measurable performance improvement of approximately 23%, supporting the viability of lemon peel as a competitive and sustainable alternative. The observed enhancement can be attributed to the combined physical and chemical actions of the system. Increasing ultrasonic power intensified acoustic cavitation, resulting in

violent microbubble collapse and high shear gradients that thinned and disrupted the interfacial films surrounding water droplets. Curve-fitting analysis showed that efficiency increased almost linearly with power up to 600 W before approaching a saturation trend at 800 W, indicating that the system reached the maximum effective cavitation threshold. Likewise, concentration-dependent behavior showed a logarithmic increase in efficiency up to 5000 ppm, followed by a decline at higher concentrations. This decrease corresponds with measured increases in viscosity at elevated particle loadings, which limited droplet mobility and partially suppressed cavitation effectiveness. The chemical contribution of lemon peel powder is linked to the functional groups present in pectin and limonene, as supported by FTIR analysis. Hydroxyl and carboxyl groups reduced interfacial tension and promoted droplet coalescence, while the hydrophobic nature of limonene modified surface energy at the oil–water interface. SEM observations further revealed a rough, porous morphology that enhanced adsorption and interfacial disruption, and XRD results confirmed the predominantly amorphous structure of the material, consistent with its high surface reactivity. Future efforts should therefore include pilot-scale continuous-flow testing, optimization of the particle size distribution to maximize active surface area, and comparative studies of other agro-waste–derived demulsifiers with similar biochemical functionality.

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