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Professor Dr. Rosli Md Illias

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Dear Professor Dr. Rosli Md Illias,

Ms. "EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY"

We are submitting an article entitled EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY for possible publication in Jurnal Teknologi.

The submission requirements are listed in the table below:

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4	Keywords	emulsion liquid membrane; heavy metals; removal; emulsion breaking; demulsification
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Please kindly acknowledge me for the receipt of the manuscript. If you have any inquiries, please do not hesitate to contact me through my email at adhi_kusumastuti@mail.unnes.ac.id. Your cooperation regarding this matter is very much appreciated.

Thank you once again and with regards.

Sincerely yours

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EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY

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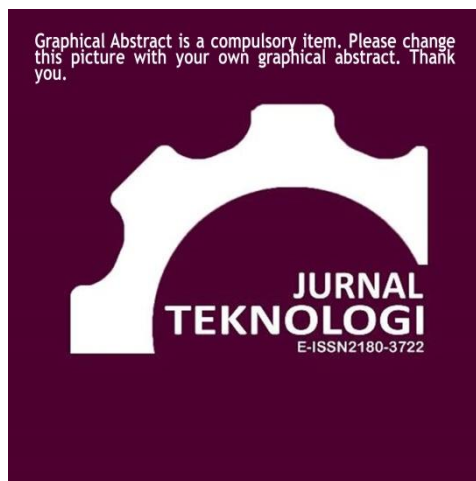
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Graphical abstract



Abstract

Emulsion liquid membrane (ELM) method has been widely applied in the separation process as the alternative of liquid/liquid extraction. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification. The results showed that the use of microwave to break the used emulsion provided demulsification efficiency of 98.10%, while application of ultrasonic probe was able to break emulsion at efficiency of 98.45%. In the meantime, demulsification efficiency of almost 97% was achieved when employing centrifuge at centrifugation speed of 3000 rpm. Considering the energy consumption, it is recommended to apply microwave irradiation for emulsion breaking. It could save energy up to 97% and 99% compared to that of ultrasonic probe and centrifuge, respectively.

Keywords: Emulsion liquid membrane, heavy metals, removal, emulsion breaking, efficiency

Abstrak

Kaedah membran cecair emulsi (ELM) telah digunakan secara meluas dalam proses pemisahan sebagai alternatif pengekstrakan cecair / cecair. Kajian ini membandingkan penggunaan gelombang haba, kuar ultrabunyi dan emparan dalam memecahkan emulsi yang digunakan. Kecekapan pengemulsian telah dikaji dari segi kandungan air dalam larutan fasa membran sebelum dan selepas proses penyahemulsi. Keputusan kajian menunjukkan bahawa penggunaan gelombang haba untuk memecahkan emulsi yang digunakan memberikan kecekapan demulsifikasi sebanyak 98.10%, manakala penggunaan kuar ultrabunyi mampu memecahkan emulsi pada kecekapan 98.45%. Sementara itu, kecekapan penyahemulsi hampir 97% dicapai apabila menggunakan emparan pada kelajuan 3000 rpm. Adalah disyorkan untuk menggunakan kaedah gelombang mikro bagi pemecahan emulsi berdasarkan penggunaan tenaganya. Kaedah ini boleh menjimatkan tenaga sehingga 97% daripada kuar ultrabunyi dan 99% daripada kuar emparan.

Kata kunci: Membran cecair emulsi, logam berat, penyingkiran, pecah emulsi, kecekapan

1.0 INTRODUCTION

Emulsion liquid membrane (ELM) is an established technology as a modification of liquid/liquid extraction. In ELM method, extraction and stripping processes occur in a single step thus make the method economically feasible. ELM involves the mixing of double emulsions, either water in oil in water or oil in water in oil. External phase contains impurities to be extracted. Membrane phase composed of organic solution act as a barrier of external and internal phases. The solute is transferred through the membrane phase towards internal phase [1, 2].

ELM system involves three main processes, i.e. emulsification, extraction, and demulsification. Emulsion could be produced using blender [3, 4], homogenizer [5, 6], ultrasonic probe [7, 8], and stirrer [9]. Those researches characterised the produced emulsion in term of emulsion diameter, membrane breakage, and emulsion swelling. The emulsion performance was also tested in the extractions of various impurities.

The ELM method has been widely applied in the separation process. Heavy metal removals using ELM have been intensively studied by many researchers. Cadmium recoveries under ELM system have been investigated by Ahmad, et.al. [10, 11], Kumbasar [12, 13], and Mortaheb, et.al. [14]. Other researchers conducted experiments on copper removal by ELM [8, 15, 16]. Chromium extractions have been studied by some other researchers [17-19].

The last process in ELM system is demulsification. The used emulsion must be broken that the entrapped solutes could be recovered for further necessities. The liquid membrane and internal phase solution could be reused in the following emulsification process. Emulsion breaking occurs through three steps, i.e. flocculation, coagulation and coalescence. In the first step, flocculation of the dispersed droplets of internal phase occurs, forming some larger groups. Furthermore, the drops in groups coalesce into a large group, leads to the decrease of drops numbers. Finally, due to gravity effect, the large internal drops sink in the interface of membrane and internal phase, coagulate with the water phase, and generate the emulsion breaking [20].

There are several methods of demulsification [21], i.e. chemical demulsification [22, 23], gravity or centrifugal settling [24], pH adjustment, filtration, heating treatment, electrostatic demulsification [25, 26], and membrane technique [27]. Demulsification process based on the gravity effect occurs in a centrifuge. Centrifugation accelerates sedimentation of an immiscible mixture. Moreover, in the mixtures of solutions in similar densities, gravity separations might take hours. The use of centrifuge could minimise the

separation time to be few minutes. Centripetal force could separate greater and lesser density solutions leading to emulsion breaking [24].

Heating has also been used in demulsification, but it is energy-intensive. Emulsion breaking is achieved by applying heat. It has been known that surfactant induces the formation of micelle by interactions of polar hydrophilic head and non-polar hydrophobic tail groups in the mixture. The applied heat interrupts the micelle interactions leading to micelles breakdown and liquids separation. Euston, et.al [28] investigated destabilization of oil in water emulsion by heat induction. They found that large increase of emulsion breakdown occurred at degree of hydrolysis > 27%. Electric field methods have been used to demulsify water-in-oil emulsions [20]. It promotes an irreversible rupturing of the stabilizing emulsions and the droplets coalesce if the external field exceeds a certain critical value. However, it is ineffective for the water-in-oil emulsion having high water content or a swelling. It can produce a "sponge" phase which contains abundant internal aqueous phase in the interface of oil and aqueous phase, so that demulsification efficiency is seriously affected. Another demulsification method is microwave irradiation. This process has similar mechanism with that of dielectric heating. Internal heating occurs when emulsion exposed to electromagnetic field of microwave resulting in molecular rotation and ionic conduction. It is therefore accelerated the emulsion separation process. Chan and Chen [29] investigated the performance of microwave in breaking water in oil emulsion by microwave irradiation by testing the effects of emulsion conditions and microwave operating conditions on the demulsification rate and the separation efficiency of W/O emulsion. Some studies about application of sonicator in breaking the emulsion have been reported. Issaka [30] studied the use of chemically assisted ultrasonic demulsification method in separating water from crude petroleum oil. Pure crude petroleum oil was used and 20 KHz ultrasonic bath was employed in the experiment. Addition of silicon origin chemical demulsifier could significantly reduce emulsion viscosity. In turn, it destabilised the emulsion by interrupting the emulsifiers. Emulsion destabilisation led to the aggregation of water droplets to form bigger emulsion. Application of ultrasonic took a role in uniformly dispersed the chemicals and created air bubbles in the emulsion. At low power level ultrasonic application, these air bubbles in the emulsion were disrupted and finally evaporate. Another study on ultrasonic demulsification was carried out by Yang et al. [31]. The study investigated separation of crude-oil emulsions by combining demulsifier and ultrasonic irradiation. Effects of ultrasonic output power,

irradiating time, demulsifier dosage, and water content to dehydration ratio were examined. The best condition was obtained by applying ultrasonic output power of 100 W, irradiating time of 10 min, demulsifier concentration of 50 mg/L and water bath at 75°C. It was found that crude-oil emulsion provided higher demulsification velocity as well as final dehydrating ratio than that of lower water content emulsion. Chemical ultrasonic demulsification was able to separate most of water from emulsion, however, it triggered the emulsification of the residual water droplets.

In spite of the available reports of emulsion breaking processes through many methods, there is limited articles reveals the comprehensive studies of demulsification in ELM system. Whereas ELM performance also determined by successful demulsification process. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification.

2.0 METHODOLOGY

2.1 Material and Reagent

The aqueous copper solutions were prepared by dissolving copper nitrate (Merck) in deionised water. HCl (Merck) was added to the feed solution to adjust the pH. Trioctylamine (Merck) and Span 80 (Merck) were used as extractant and surfactant, respectively. Low odour kerosene purchased from Sigma Aldrich was used as diluent. Ammonia (Merck) was used as internal phase solution.

2.2 Experimental Procedures

After the extraction process, the organic membrane phase was recovered for its diluents. The demulsification processes using physical treatment process were applied. The water content in the emulsion before demulsification and in the membrane phase after demulsification was measured. The demulsification efficiency (Br) was calculated as:

$$Br = \frac{\theta_0 - \theta_1}{\theta_0 \times (1 - \theta_1)} \times 100\% \quad (1)$$

Br refers to demulsification efficiency, θ_0 is the fraction of water content in the emulsion before demulsification, and θ_1 is the fraction of water content in the membrane phase after demulsification. Energy consumption (Ec) for emulsion breaking was determined as:

$$Ec = P_{in} \times t \quad (2)$$

where P_{in} is the power consumed (J/s) and t is the demulsification time (s).

2.2.1 Microwave demulsification

A beaker glass was used to collect used emulsion. It was then placed in defined position in the microwave (domestic microwave oven, Panasonic, NN-SM330 M) thus every experiment got the same heating irradiation. Experiments were done at irradiation power of 50 W, 380 W, 540 W, and 700 W for 8 s, 10 s, 12 s, and 15 s irradiation time. The irradiated sample was settled down until 15 minutes and then collected for water content analysis.

2.2.2 Ultrasound demulsification

Used emulsion was placed in a beaker glass. The 22.5 kHz ultrasonic irradiation (ultrasonic USG-150) equipped with a titanium horn (3 mm diameter) was mounted at the top of the cylindrical glass cell. The emulsion was treated for 2, 4, 8, and 10 minutes at frequency of 20 kHz in different intensities of about 20%, 60%, and 80%. Water content analysis was also done to the demulsified samples.

2.2.3 Centrifuge Demulsification

Certain volume of the used emulsion was put in the centrifuge bottle. The demulsifying method was conducted in a centrifuge (Kubota 5220) that accelerates the sedimentation at 2500-3500 rpm. The centrifugation time was varied from 5 to 15 minutes with interval of 5 minutes. After centrifugation process, the organic sample on the top layer of the solution is collected for water content analysis.

GC-MS analysis by using a Perkin Elmer GC Clarus 680 MS Clarus SQ 8T was also applied to quantify the organic membrane phase after demulsification. The length of column is 30 m with 250 μ m of diameter. Maximum temperature of oven was set at about 300°C. Helium was used as carrier gas with 0.8 ml/min of flow rate. The sample was filtered by using a filter paper before injected into the GC at one μ l.

3.0 RESULTS AND DISCUSSION

3.1 Microwave Demulsification

The used emulsion needs to be broken so that membrane component can be reused for further emulsification process. After demulsification, the clear upper layer was sampled; pure kerosene indicated the success of demulsification process. The water content was then tested and the efficiency was calculated using Equation 1. Study of Henry [32] found that microwave irradiation was effective in reducing emulsion stability at relatively high water separation efficiency. It was also revealed that at equal irradiation exposure time and power, emulsion with higher water content achieved better demulsification efficiency. This is due to the nature

properties of water, in which energy absorption of water is higher than that of oil. Figure 1 shows the effects of both microwave irradiation and settling time on demulsification efficiency. It is seen that demulsification efficiency increase with the increase of irradiation and settling time. Right after separation at irradiation time of 8 s, almost no separation of water and oil phase occurred thus resulted in very low demulsification efficiency. Significant increase of demulsification efficiency was seen after prolonging settling times. Increment of demulsification rate by the increase of microwave irradiation time is affected by dielectric heating properties that able to separate water-in-oil emulsions. The highest demulsification efficiency of 82.45% was achieved by applying irradiation time of 15 s and settling time of 15 min.

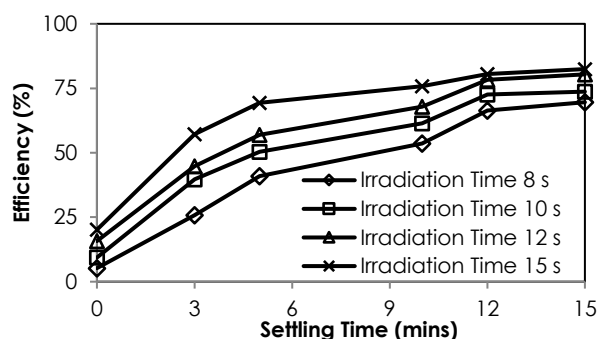


Figure 1 Demulsification efficiency (Microwave power 540 W; Irradiation time: 8, 10, 12, and 15 s; settling time: 0, 3, 5, 10, 12, 15 mins)

Figure 2 reveals that very small amount of aqueous phase can be separated with a 50 W power output. Even with power output above 380 W, a critical settling time greater than 5 min was necessary to give significant raise in demulsification rate. Along with settling time, demulsification rate increases with the increase of microwave power. The increase of microwave irradiation power resulted in higher separation efficiency as well as sample temperature. Improvement of microwave irradiation power from 50 W to 380 W gave insignificant effect of demulsification efficiency. Neither did further improvement to 540 W. Mohammed and Mohammed [33] found that this phenomenon was triggered by the increase of wavelength and penetration depth as the increase of microwave power.

3.2 Ultrasound demulsification

Among the important factors affecting emulsions breaking is sound intensity. In which, energy level is varied depend on the sound intensities given to emulsions. Dehydration process of emulsions is only determined by mechanical effects of ultrasound. It was revealed that the increment of sound intensity resulted in the lower emulsion water content [34].

They found that the lowest water content was achieved at sound intensity of 0.66 W/cm², further increase in sound intensity actually increased water content. This also applies in this study, where sound intensity of 60% resulted in the best demulsification efficiency, shown in Figure 3. This is due to higher sound intensity triggered the reduction of water-oil interface tension leading to emulsion breaking. However, further increment of sound intensity to be 80% leading to the decrease of demulsification efficiency. This is because excessive sound intensity caused re-emulsification phenomenon [34].

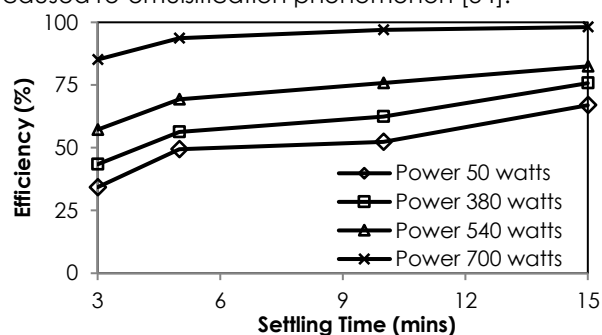


Figure 2 Demulsification efficiency (Irradiation time: 15 s; Microwave power 50, 380, 540, and 700 W)

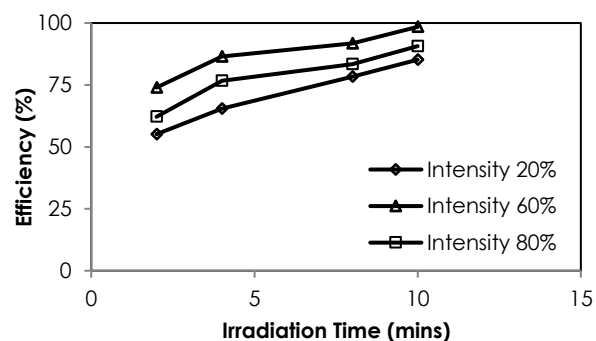


Figure 3 Demulsification efficiency (Intensity: 20%, 60%, and 80%; Irradiation time: 2, 4, 8, 10 min)

3.3 Centrifuge Demulsification

Demulsification under centrifuge force was investigated in terms of time and speed. To see the compounds, some of the samples were tested using GC-MS. The demulsification results are presented in Figure 4.

It is revealed in Figure 4 that due to the principles of gravity separation, increasing centrifugation speed could enhance demulsification efficiency. Each phase is separated due to the density difference between each phase. Higher centrifugation speed as well as longer centrifugation time is able to accelerate the separation process. The graph also shows that at centrifugation speed of 2000 rpm, efficiency was governed by time. At 5 min, efficiency was only about 86%, it gradually increased to be 90% at 10 min, and at the end of the process it succeeded to reach 92%. On the contrary, at high

centrifugation speed of 3500 rpm, there was no significant increase in efficiency with the time extension. At 5, 10, and 15 min of demulsification process, the efficiencies were about 96%. It is also seen that at 15 min, demulsification efficiency increased from 95% at 2000 rpm to be 97% at 3500 rpm.

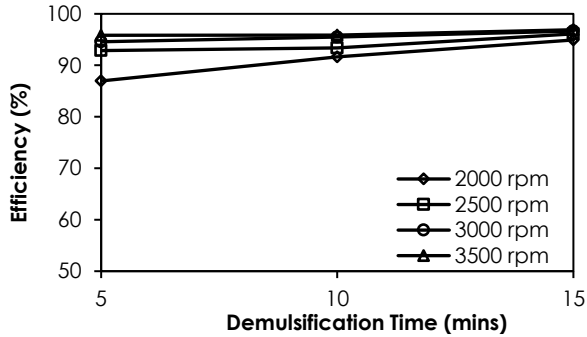


Figure 4 Demulsification efficiency (centrifugation speed: 2000, 2500, 3000, and 3500 rpm; centrifugation time: 5, 10, and 15 min)

GC-MS testing was done to qualitatively describe 20 major compounds of total ion chromatogram (TIC) detected from the organic membrane phase sample. GC-MS result for each centrifugation speed was revealed in Figures 5-8. The figures define that in retention time of 5-15 min, kerosene compounds were exclusively detected. TOA was detected at around 21 min and after 25 min of retention time for centrifugation speeds above and below 3000 rpm, respectively.

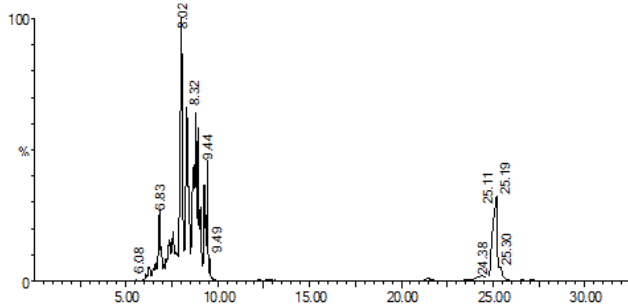


Figure 5 Demulsification efficiency (Total ion chromatogram of demulsification process at 2000 rpm)

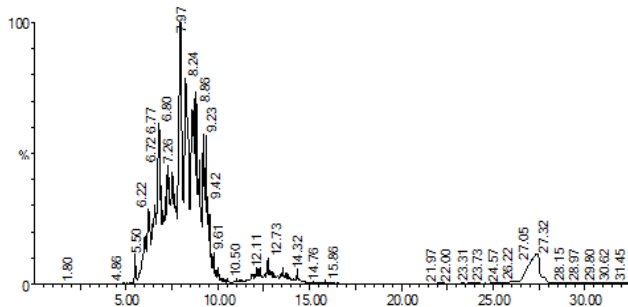


Figure 5 Demulsification efficiency (Total ion chromatogram of demulsification process at 2000 rpm)

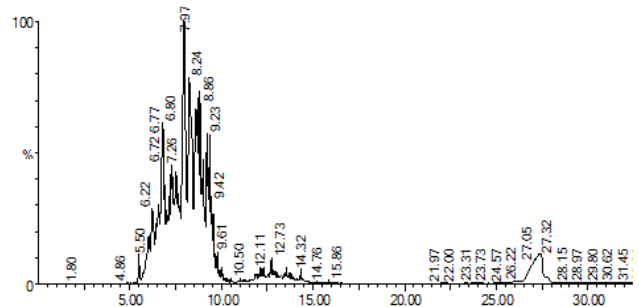


Figure 6 Demulsification efficiency (Total ion chromatogram of demulsification process at 2500 rpm)

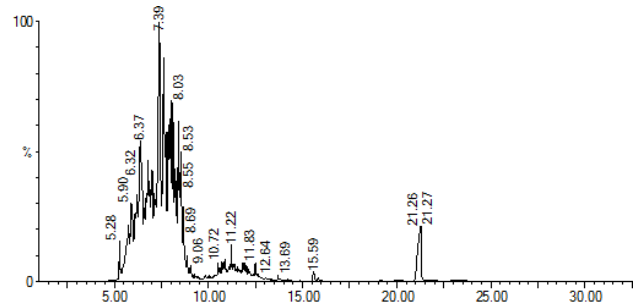


Figure 7 Demulsification efficiency (Total ion chromatogram of demulsification process at 3000 rpm)

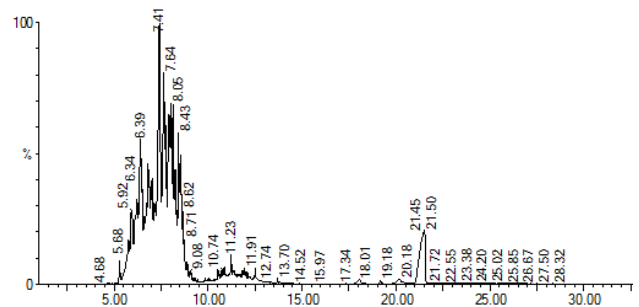


Figure 8 Demulsification efficiency (Total ion chromatogram of demulsification process at 3500 rpm)

The increase of centrifugation speed from 2000 rpm to 3500 rpm enabled the system to demulsify and to recover almost all of kerosene and TOA. It was indicated from total ion chromatogram report that demulsification process was able to recover about 99% and 98.7% of TOA and kerosene in organic membrane phase for 3500 rpm and 3000 rpm, respectively. Whereas at 2000 rpm, less than 90% of kerosene and TOA was able to be recovered while at 2500 rpm, more kerosene and TOA of about 97% was recovered.

3.4 Demulsification and Energy Consumption Assessment

Demulsification processes done by microwave, ultrasound, and centrifuge have been completed. Comparison of each process is described in Figure 9. It is seen that demulsification efficiency was in the order of ultrasound > microwave > centrifuge. However, there was no significant difference of demulsification efficiency of each mode. In term of energy consumption, there was tremendous difference of each demulsification tool. Microwave provided the most energy efficient demulsification process. In this case, microwave demulsification only used 16.875 kJ of energy or about 117 times lower than that of centrifuge. While ultrasound, required energy of about 600 kJ, was higher than that used of microwave. The highest energy of 1980 kJ was applied in centrifuge demulsification. It is therefore, microwave demulsification is the most recommended process.

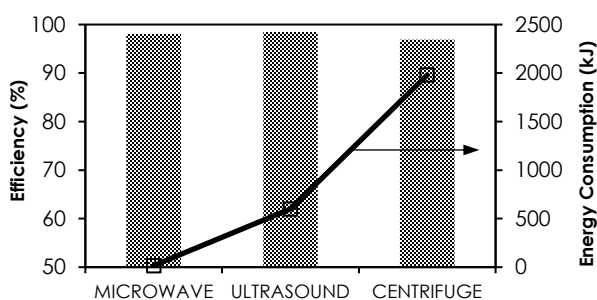


Figure 8 Comparison of demulsification efficiency and energy consumption for each demulsification equipment

4.0 CONCLUSION

Laboratory experiment showed the application of microwave, ultrasonic probe, and centrifuge for emulsion breaking. All the demulsification tools were successfully applied to break the used emulsion based on their specific operation condition. In general, demulsification efficiencies of above 97% were obtained. It was found that the order of demulsification efficiency was centrifuge < microwave < ultrasound. Although ultrasound provided the highest demulsification efficiency, it consumed more energy. Among the demulsification tools, microwave demulsification involved the lowest energy consumption. The significant difference of energy consumption was also supported by almost the same demulsification efficiency. So that, considering the economics of overall emulsion liquid membrane process, microwave irradiation is highly recommended for breaking the used emulsion.

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[JT] Editor Decision

From: Professor Dr. Rosli Md Illias (r-rosli@utm.my) To:

adhi_kusumastuti@yahoo.com

Cc: journal_utm@utm.my

Date: Thursday, 05 March 2020 at 11:05 am GMT+7

Dr Adhi Kusumastuti:

We have reached a decision regarding your submission to Jurnal Teknologi, "EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY".

Our decision is to: RESUBMIT FOR REVIEW

2. Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider my decision.

3. For your guidance, reviewers' comments are attached. Please refer to the attachment and kindly rework & rewrite your article. YOU SHOULD ALSO ATTACH THE LIST OF CORRECTIONS BEING DONE.

4. Please upload your revised article in the system for our further action and alert us through email : journal_utm@utm.my.

THANK YOU.

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GENERAL COMMENT

In general, the manuscript submitted highlight an important issue of emulsion breaking from emulsion liquid membrane system. Few major issues and comments should be clarified and corrected by the author before the manuscript can be publish in this journal.

The discussion not organized properly. It should be discussed separate for each parameters study.

Abstract – First sentence of the abstract should be revised for more specific in term of textile wastewater concentration.

Section 1.0

The discussion about the drawbacks of used organic phase and the methods used for emulsion breaking need to revised for consistency with many statements in the manuscript. Focus to what methods used in this study.

The Introduction should be re-phrased for better explanation.

Section 2

The methodology needs to re-organize. List all the material and reagents used in detail in separate section. Then the experimental procedures should be organized properly for better explanation.

Section 3

Need to re-organized and re-submitted for review.

Should be divided the discussion based on the parameter studied.

All the procedures should be explained in the section 2.

27 March 2020

Professor Dr. Rosli Md Illias

Editor

Jurnal Teknologi

Dear Professor Dr. Rosli Md Illias,

Re: Ms. "EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY"

Thank you very much for comments of the above manuscript. We have revised the manuscript in line with the comments and submitting for your kind attention.

The manuscript has been resubmitted to your journal. We look forward to your positive response. I hope that you will find our revised manuscript in order and suitable for publication.

Thank you once again and with regards.

Sincerely yours

(Dr. Adhi Kusumastuti)

Email: adhi_kusumastuti@mail.unnes.ac.id

The details of the revision are listed point by point as follow:

No	Comment	Revision
1.	In general, the manuscript submitted highlight an important issue of emulsion breaking from emulsion liquid membrane system. Few major issues and comments should be clarified and corrected by the author before the manuscript can be publish in this journal.	Thank you for the positive response.
2.	The discussion not organized properly. It should be discussed separate for each parameters study.	We have revised the discussion and organized it properly based on the parameter study.
3.	Abstract – First sentence of the abstract should be revised for more specific in term of textile wastewater concentration.	The first sentence of the abstract has been changed to make it more concise.
4.	Section 1.0 The discussion about the drawbacks of used organic phase and the methods used for emulsion breaking need to revised for consistency with many statements in the manuscript. Focus to what methods used in this study. The Introduction should be re-phrased for better explanation.	We have revised the manuscript and the discussion of methods in this section has only focused on the methods used in this work, as given in paragraph 5 and 6.
5.	Section 2 The methodology needs to re-organize. List all the material and reagents used in detail in separate section. Then the experimental procedures should be organized properly for better explanation.	The methodology has been reorganized, start from material to experimental procedures as given in Section 2.
6.	Section 3 Need to re-organized and re-submitted for review. Should be divided the discussion based on the parameter studied. All the procedures should be explained in the section 2.	We have revised the manuscript. Section 3 has been prepared and described according to parameter studied.

EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY

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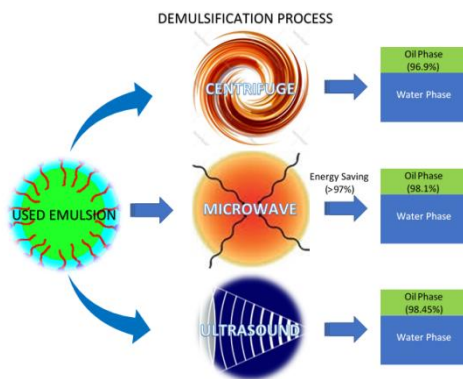
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Graphical abstract



Abstract

Emulsion liquid membrane (ELM) method has been widely applied in the separation process as the alternative of liquid/liquid extraction. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification. The results showed that the use of microwave to break the used emulsion provided demulsification efficiency of 98.10%, while application of ultrasonic probe was able to break emulsion at efficiency of 98.45%. In the meantime, demulsification efficiency of almost 97% was achieved when employing centrifuge at centrifugation speed of 3000 rpm. Considering the energy consumption, it is recommended to apply microwave irradiation for emulsion breaking. It could save energy up to 97% and 99% compared to that of ultrasonic probe and centrifuge, respectively.

Keywords: emulsion liquid membrane; heavy metals; removal; emulsion breaking; demulsification

Abstrak

Kaedah membran cecair emulsi (ELM) telah digunakan secara meluas dalam proses pemisahan sebagai alternatif kepada penyarian cecair-cecair. Kajian ini membandingkan aplikasi gelombang mikro, kuar ultrasonik, dan emparan untuk memecahkan emulsi yang telah digunakan. Kecekapan pengemulsian diselidiki dari segi kandungan air dalam larutan fasa membran sebelum dan selepas demulsifikasi. Keputusan menunjukkan bahawa penggunaan gelombang mikro untuk memecahkan emulsi yang digunakan mencapai kecekapan demulsifikasi 98.10%, manakala penggunaan kuar ultrasonik telah memecahkan emulsi pada kecekapan 98.45%. Sementara itu, kecekapan demulsifikasi hampir 97% dicapai apabila menggunakan emparan pada kelajuan 3000 rpm. Kaedah gelombang mikro adalah disyorkan untuk memecahkan emulsi disebabkan penggunaan tenaga yang kurang. Penjimatan tenaga untuk demulsifikasi adalah sehingga 97% bagi kaedah kuar ultrasonik dan 99% bagi kaedah emparan.

Kata kunci: membran cecair emulsi; logam berat; penyingkiran; pecah emulsi; demulsifikasi

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1.0 INTRODUCTION

Emulsion liquid membrane (ELM) is an established technology as a modification of liquid/liquid extraction. In ELM method, extraction and stripping processes occur in a single step thus make the method economically feasible. ELM involves the mixing of double emulsions, either water in oil in water or oil in water in oil. External phase contains impurities to be extracted. Membrane phase composed of organic solution act as a barrier of external and internal phases. The solute is transferred through the membrane phase towards internal phase [1, 2]

ELM system involves three main processes, i.e. emulsification, extraction, and demulsification. Emulsion could be produced using blender [3, 4], homogenizer [5, 6], ultrasonic probe [7, 8], and stirrer [9]. Those researches characterised the produced emulsion in term of emulsion diameter, membrane breakage, and emulsion swelling. The emulsion performance was also tested in the extractions of various impurities.

The ELM method has been widely applied in the separation process. Heavy metal removals using ELM have been intensively studied by many researchers. Cadmium recoveries under ELM system have been investigated by Ahmad, et.al. [10], Kumbasar [11], and Mortaheb, et.al. [12]. Other researchers conducted experiments on copper removal by ELM [8, 13, 14]. Chromium extractions have been studied by some other researchers [15-17].

The last process in ELM system is demulsification. The used emulsion must be broken that the entrapped solutes could be recovered for further necessities. The liquid membrane and internal phase solution could be reused in the following emulsification process. Emulsion breaking occurs through three steps, i.e. flocculation, coagulation and coalescence. In the first step, flocculation of the dispersed droplets of internal phase occurs, forming some larger groups. Furthermore, the drops in groups coalesce into a large group, leads to the decrease of drops numbers. Finally, due to gravity effect, the large internal drops sink in the interface of membrane and internal phase, coagulate with the water phase, and generate the emulsion breaking [18].

There are several methods of demulsification [19], i.e. chemical demulsification [20, 21], gravity or centrifugal settling [22], pH adjustment, filtration, heating treatment, electrostatic demulsification [23, 24], and membrane technique [25]. Demulsification process based on the gravity effect occurs in a centrifuge. Centrifugation accelerates sedimentation of an immiscible mixture. Moreover, in the mixtures of solutions in similar densities, gravity separations might take hours. The use of centrifuge could minimise the separation time to be few minutes. Centripetal force

could separate greater and lesser density solutions leading to emulsion breaking [22].

Heating has also been used in demulsification, but it is energy-intensive. Emulsion breaking is achieved by applying heat. It has been known that surfactant induces the formation of micelle by interactions of polar hydrophilic head and non-polar hydrophobic tail groups in the mixture. The applied heat interrupts the micelle interactions leading to micelles breakdown and liquids separation. Euston, et.al [26] investigated destabilization of oil in water emulsion by heat induction. They found that large increase of emulsion breakdown occurred at degree of hydrolysis > 27%. Electric field methods have been used to demulsify water-in-oil emulsions [18]. It promotes an irreversible rupturing of the stabilizing emulsions and the droplets coalesce if the external field exceeds a certain critical value. However, it is ineffective for the water-in-oil emulsion having high water content or a swelling. It can produce a "sponge" phase which contains abundant internal aqueous phase in the interface of oil and aqueous phase, so that demulsification efficiency is seriously affected. Another demulsification method is microwave irradiation. This process has similar mechanism with that of dielectric heating. Internal heating occurs when emulsion exposed to electromagnetic field of microwave resulting in molecular rotation and ionic conduction. It is therefore accelerated the emulsion separation process. Chan and Chen [27] investigated the performance of microwave in breaking water in oil emulsion by microwave irradiation by testing the effects of emulsion conditions and microwave operating conditions on the demulsification rate and the separation efficiency of W/O emulsion.

In spite of the available reports of emulsion breaking processes through many methods, there is limited articles reveals the comprehensive studies of demulsification in ELM system. Whereas ELM performance also determined by successful demulsification process. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification. The used membrane phase solution was then used in the next emulsification process and the emulsion performance in cadmium extraction was tested.

2.0 METHODOLOGY

2.1 MATERIALS

The aqueous copper solutions were prepared by dissolving copper nitrate (Merck) in deionised water.

HCl (Merck) was added to the feed solution to adjust the pH. Trioctylamine (Merck) and Span 80 (Merck) were used as extractant and surfactant, respectively. Low odour kerosene purchased from Sigma Aldrich was used as diluent. Ammonia (Merck) was used as internal phase solution.

2.1 PROCEDURES

After the extraction process, the organic membrane phase was recovered for its diluents. The demulsification processes using physical treatment process were applied. The water content in the emulsion before demulsification and in the membrane phase after demulsification was measured. The demulsification efficiency (Br) was calculated as:

$$Br = \frac{\theta_0 - \theta_1}{\theta_0 \times (1 - \theta_1)} \times 100\% \quad (1)$$

Br refers to demulsification efficiency, θ_0 is the fraction of water content in the emulsion before demulsification, and θ_1 is the fraction of water content in the membrane phase after demulsification. Energy consumption (E_c) for emulsion breaking was determined as:

$$E_c = P_{in} \times t \quad (2)$$

where P_{in} is the power consumed (J/s) and t is the demulsification time (s).

2.1.1 Microwave Demulsification

A beaker glass was used to collect used emulsion. It was then placed in defined position in the microwave (domestic microwave oven, Panasonic, NN-SM330 M) thus every experiment got the same heating irradiation. Experiments were done at irradiation power of 50 W, 380 W, 540 W, and 700 W for 8 s, 10 s, 12 s, and 15 s irradiation time. The irradiated sample was settled down until 15 minutes and then collected for water content analysis.

2.1.2 Ultrasound Demulsification

Used emulsion was placed in a beaker glass. The 22.5 kHz ultrasonic irradiation (ultrasonic USG-150) equipped with a titanium horn (3 mm diameter) was mounted at the top of the cylindrical glass cell. The emulsion was treated for 2, 4, 8, and 10 minutes at a frequency of 20 kHz in different intensities of about 20%, 60%, and 80%. Water content analysis was also done to the demulsified samples.

2.1.3 Centrifuge Demulsification

Certain volume of the used emulsion was put in the centrifuge bottle. The demulsifying method was conducted in a centrifuge (Kubota 5220) that accelerates the sedimentation at 2500-3500 rpm. The centrifugation time was varied from 5 to 15 minutes with interval of 5 minutes. After centrifugation

process, the organic sample on the top layer of the solution is collected for water content analysis.

GC-MS analysis by using a Perkin Elmer GC Clarus 680 MS Clarus SQ 8T was also applied to quantify the organic membrane phase after demulsification. The length of column is 30 m with 250 μ m of diameter. Maximum temperature of oven was set at about 300°C. Helium was used as carrier gas with 0.8 ml/min of flow rate. The sample was filtered by using a filter paper before injected into the GC at one μ l.

3.0 RESULTS AND DISCUSSION

3.1. Microwave Demulsification

The used emulsion needs to be broken so that membrane component can be reused for further emulsification process. After demulsification, the clear upper layer was sampled; pure kerosene indicated the success of demulsification process. The water content was then tested and the efficiency was calculated using Equation 1. Study of Henry [28] found that microwave irradiation was effective in reducing emulsion stability at relatively high water separation efficiency. It was also revealed that at equal irradiation exposure time and power, emulsion with higher water content achieved better demulsification efficiency. This is due to the nature properties of water, in which energy absorption of water is higher than that of oil. Figure 1 shows the effects of both microwave irradiation and settling time on demulsification efficiency. It is seen that demulsification efficiency increase with the increase of irradiation and settling time. Right after separation at irradiation time of 8 s, almost no separation of water and oil phase occurred thus resulted in very low demulsification efficiency. Significant increase of demulsification efficiency was seen after prolonging settling times. Increment of demulsification rate by the increase of microwave irradiation time is affected by dielectric heating properties that able to separate water-in-oil emulsions. The highest demulsification efficiency of 82.45% was achieved by applying irradiation time of 15 s and settling time of 15 min.

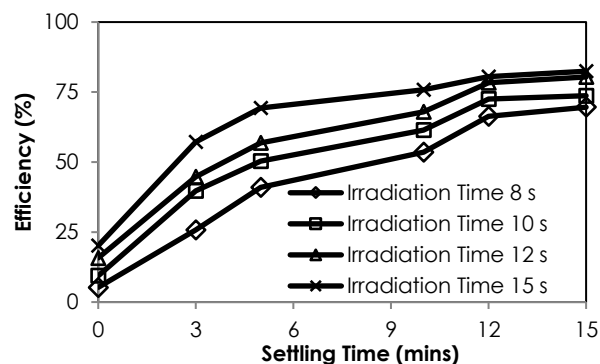


Figure 1 Demulsification efficiency (Microwave power 540 W; Irradiation time: 8, 10, 12, and 15 s; settling time: 0, 3, 5, 10, 12, 15 mins)

Figure 2 reveals that very small amount of aqueous phase can be separated with a 50 W power output. Even with power output above 380 W, a critical settling time greater than 5 min was necessary to give significant raise in demulsification rate. Along with settling time, demulsification rate increases with the increase of microwave power. The increase of microwave irradiation power resulted in higher separation efficiency as well as sample temperature. Improvement of microwave irradiation power from 50 W to 380 W gave insignificant effect of demulsification efficiency. Neither did further improvement to 540 W. Mohammed and Mohammed [29] found that this phenomenon was triggered by the increase of wavelength and penetration depth as the increase of microwave power.

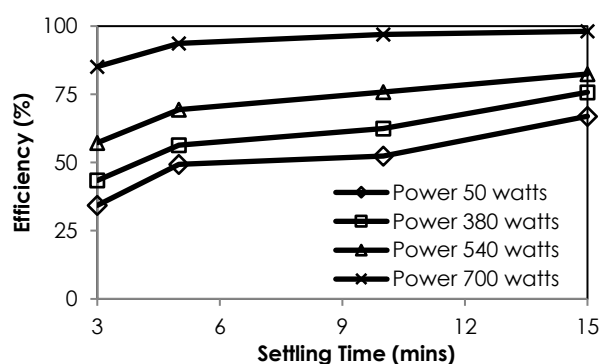


Figure 2 Demulsification efficiency (Irradiation time: 15 s; Microwave power 50, 380, 540, and 700 W)

3.2 Ultrasound Demulsification

Among the important factors affecting emulsions breaking is sound intensity. In which, energy level is varied depend on the sound intensities given to emulsions. Dehydration process of emulsions is only determined by mechanical effects of ultrasound. It was revealed that the increment of sound intensity resulted in the lower emulsion water content [30]. They found that the lowest water content was achieved at sound intensity of 0.66 W/cm², further increase in sound intensity actually increased water content. This also applies in this study, where sound intensity of 60% resulted in the best demulsification efficiency, shown in Figure 3. This is due to higher sound intensity triggered the reduction of water-oil interface tension leading to emulsion breaking. However, further increment of sound intensity to be 80% leading to the decrease of demulsification efficiency. This is because excessive sound intensity caused re-emulsification phenomenon [30].

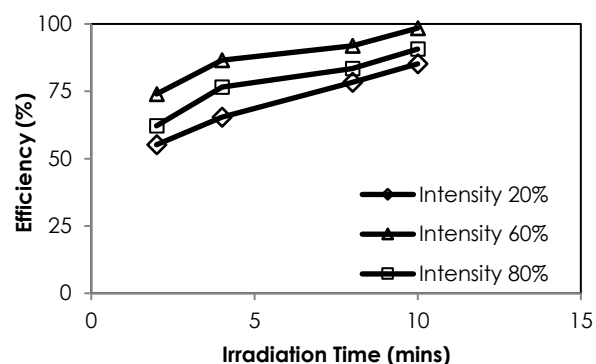


Figure 3 Demulsification efficiency (Intensity: 20%, 60%, and 80%; Irradiation time: 2, 4, 8, 10 min)

3.3 Centrifuge Demulsification

Demulsification under centrifuge force was investigated in terms of time and speed. To see the compounds, some of the samples were tested using GC-MS. The demulsification results are presented in Figure 4.

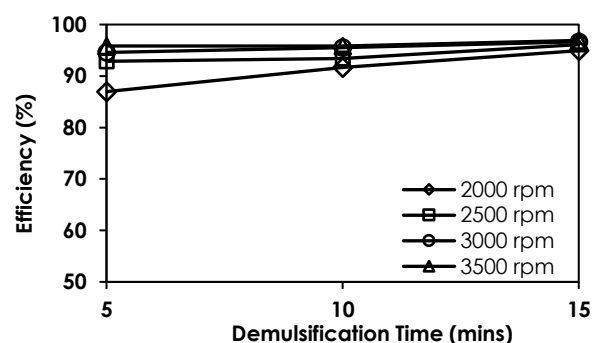


Figure 4 Demulsification efficiency (centrifugation speed: 2000, 2500, 3000, and 3500 rpm; centrifugation time: 5, 10, and 15 min)

It is revealed in Figure 4 that due to the principles of gravity separation, increasing centrifugation speed could enhance demulsification efficiency. Each phase is separated due to the density difference between each phase. Higher centrifugation speed as well as longer centrifugation time is able to accelerate the separation process. The graph also shows that at centrifugation speed of 2000 rpm, efficiency was governed by time. At 5 min, efficiency was only about 86%, it gradually increased to be 90% at 10 min, and at the end of the process it succeeded to reach 92%. On the contrary, at high centrifugation speed of 3500 rpm, there was no significant increase in efficiency with the time extension. At 5, 10, and 15 min of demulsification process, the efficiencies were about 96%. It is also seen that at 15 min, demulsification efficiency increased from 95% at 2000 rpm to be 97% at 3500 rpm.

GC-MS testing was done to qualitatively describe 20 major compounds of total ion chromatogram

(TIC) detected from the organic membrane phase sample. GC-MS result for each centrifugation speed was revealed in Figures 5-8. The figures define that in retention time of 5-15 min, kerosene compounds were exclusively detected. TOA was detected at around 21 min and after 25 min of retention time for centrifugation speeds above and below 3000 rpm, respectively.

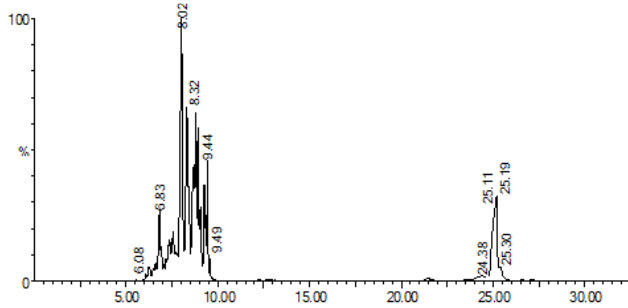


Figure 5 Demulsification efficiency (Total ion chromatogram of demulsification process at 2000 rpm)

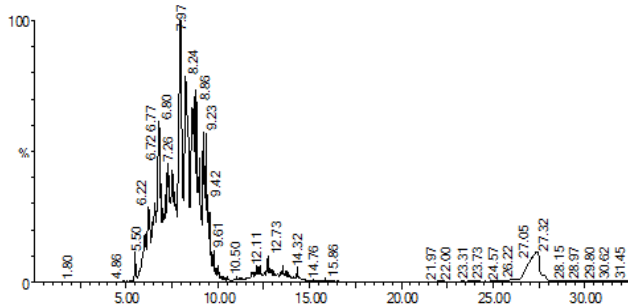


Figure 6 Demulsification efficiency (Total ion chromatogram of demulsification process at 2500 rpm)

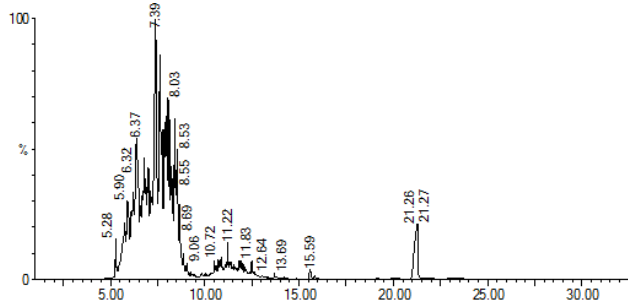


Figure 7 Demulsification efficiency (Total ion chromatogram of demulsification process at 3000 rpm)

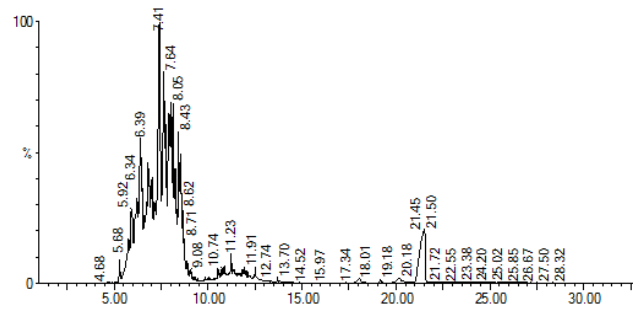


Figure 8 Demulsification efficiency (Total ion chromatogram of demulsification process at 3500 rpm)

The increase of centrifugation speed from 2000 rpm to 3500 rpm enabled the system to demulsify and to recover almost all of kerosene and TOA. It was indicated from total ion chromatogram report that demulsification process was able to recover about 99% and 98.7% of TOA and kerosene in organic membrane phase for 3500 rpm and 3000 rpm, respectively. Whereas at 2000 rpm, less than 90% of kerosene and TOA was able to be recovered while at 2500 rpm, more kerosene and TOA of about 97% was recovered.

3.4 Demulsification and Energy Consumption Assessment

Demulsification processes done by microwave, ultrasound, and centrifuge have been completed. Comparison of each process is described in Figure 9. It is seen that demulsification efficiency was in the order of ultrasound > microwave > centrifuge. However, there was no significant difference of demulsification efficiency of each mode. In term of energy consumption, there was tremendous difference of each demulsification tool. Microwave provided the most energy efficient demulsification process. In this case, microwave demulsification only used 16.875 kJ of energy or about 117 times lower than that of centrifuge. While ultrasound, required energy of about 600 kJ, was higher than that used of microwave. The highest energy of 1980 kJ was applied in centrifuge demulsification. It is therefore, microwave demulsification is the most recommended process.

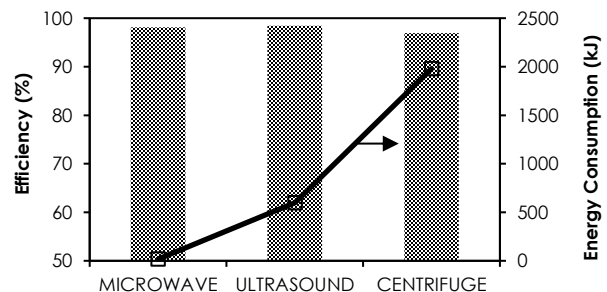


Figure 9 Comparison of demulsification efficiency and energy consumption for each demulsification equipment

4.0 CONCLUSION

Laboratory experiment showed the application of microwave, ultrasonic probe, and centrifuge for emulsion breaking. All the demulsification tools were successfully applied to break the used emulsion based on their specific operation condition. In general, demulsification efficiencies of above 97% were obtained. It was found that the order of demulsification efficiency was centrifuge < microwave < ultrasound. Although ultrasound provided the highest demulsification efficiency, it consumed more energy. Among the demulsification tools, microwave demulsification involved the lowest energy consumption. The significant difference of energy consumption was also supported by almost the same demulsification efficiency. So that, considering the economics of overall emulsion liquid membrane process, microwave irradiation is highly recommended for breaking the used emulsion.

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DOI: <https://doi.org/10.1080/15567036.2011.551921>

Review Form Response

Review Form 1

Article Title

EMULSION LIQUID MEMBRANE FOR HEAVY METALS

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- JT (Science and Engineering)
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Referee's comments

This manuscript explains the emulsion liquid membrane (ELM) technology for heavy metal separation. The last part of ELM is demulsification which can be divided into three approaches (microwave, ultrasonic and centrifuge). In this study, authors compared these three approaches in term of its efficiency. The results provided is promising, however, very limited to convince readers. Therefore, some minor comments are provided below:

1. What type of heavy metal authors used to separate in this study? Based on the materials section, is it copper? Please state the disadvantage of copper in the introduction that need to be separated.
2. Why authors used ELM instead of polymeric membrane?
3. Can authors add a figure to describe ELM in detail.
4. Based on the conclusion made, microwave demulsification is the most suitable in term of economic value. However, microwave still used heat energy. Any comment?
5. Why GS-MC testing was done towards centrifuge demulsification only?

A. Evaluations

Please evaluate the paper according to the following criteria:

1. The topic is important and relevant for publication *

- Yes
- No

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2. The work presented in the manuscript is original *

- Yes
- No

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3. The manuscript uses sufficient references *

- Yes
- No

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4. The manuscript uses appropriate language and styles *

- Yes
- No

Comment

5. The title of the manuscript is appropriate *

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- No

Comment

6. The order of presentation is satisfactory *

- Yes
- No

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7. The abstract adequately summarizes the content of the manuscript *

- Yes
- No

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8. The introduction is adequately developed *

- Yes
 No

Comment

Need some minor revision.

9. The problem described in the manuscript is clearly stated *

- Yes
 No

Comment

The heavy metal used for separation is not discussed in introduction

10. The adopted methodology described in the manuscript is sound *

- Yes
 No

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11. The findings of this manuscript are correctly interpreted *

- Yes
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13. The quality of figures and illustrations is acceptable for publications *

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B. Suggestions to the author(s)

What can the author(s) do to improve the quality of this paper?

*

A schematic diagram describing the mechanism of the process can be added in the manuscript.

C. Recommendations to the editors

The manuscript should be:

*

- Published as it is
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 Returned to the writer to be completely reworked and rewritten
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Close

* Denotes required field

10 July 2020

Assoc. Prof. Dr. Mohd Hafiz Dzarfan Othman

Editor

Jurnal Teknologi

Dear Assoc. Prof. Dr. Mohd Hafiz Dzarfan Othman,

Re: Ms. "EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY"

Thank you very much for comments of the above manuscript. We have revised the manuscript in line with the comments and submitting for your kind attention. The revised parts are highlighted in yellow colour.

The manuscript has been resubmitted to your journal. We look forward to your positive response. I hope that you will find our revised manuscript in order and suitable for publication.

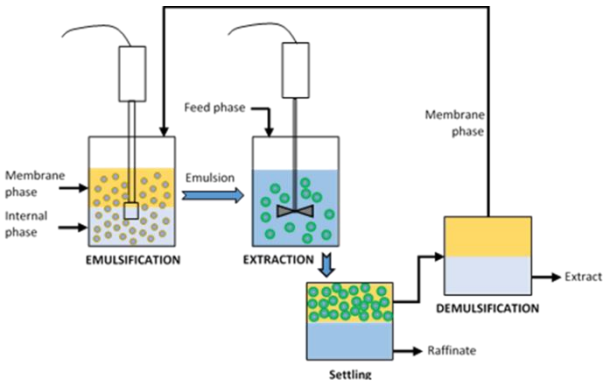
Thank you once again and with regards.

Sincerely yours

(Dr. Adhi Kusumastuti)

Email: adhi_kusumastuti@mail.unnes.ac.id

The details of the revision are listed point by point as follow:

No	Comment	Revision
1.	What type of heavy metal authors used to separate in this study? Based on the materials section, is it copper? Please state the disadvantage of copper in the introduction that need to be separated.	<p>The heavy metal separated in this study is copper as described in materials section.</p> <p>The disadvantage of copper has also stated in paragraph 3 of introduction section as follows:</p> <p>“High concentration of copper is mostly available in the wastewater of many industries such as metallurgy, steel, paper and pulp, fertiliser, and petroleum refining [20]. Beyond the maximum allowable concentration of 1.3 ppm, copper is considered as hazardous pollutant. Copper accumulation in animals and humans may cause several disorders of gastroenteritis, diarrhoea, anorexia, dehydration, and shock, while chronic copper poisoning contributes to Alzheimer’s, Memkes and Wilson’s diseases [21].”</p>
2.	Why authors used ELM instead of polymeric membrane?	<p>The reasons of use of ELM instead of polymeric membrane have been incorporated in the revised manuscript as stated in paragraph 1 of introduction section as follows:</p> <p>“ELM has been considered as one of the most attractive type of liquid membrane and more selective than polymer-based membranes [1]. Moreover, most molecules have higher diffusivity through liquids than that of through polymer membranes, leading to higher extraction efficiency [2].”</p>
3.	Can authors add a figure to describe ELM in detail?	<p>The figure ELM process has been provided in Figure 1 of the revised manuscript as follows:</p>  <p style="text-align: center;">Figure 1 Emulsion liquid membrane process</p>
4.	Based on the conclusion made, microwave demulsification is the most suitable in term of economic value. However, microwave still used heat energy. Any comment?	<p>We agreed that microwave used heat energy to demulsify the used emulsion. Thus, the irradiation time must be as short as possible.</p> <p>We have added the statement to the conclusion, as follows:</p> <p>“.....It should be noted that the water in the sample absorbs microwave energy, resulting in heating due to polarization of water molecules, leading to the acceleration of the demulsification process. In this study, 15 seconds of irradiation time was enough to break the emulsion at high efficiency.”</p>
5.	Why GC-MS testing was done towards centrifuge demulsification only?	<p>In this work, GC-MS testing was done and intended to verify the compounds in the organic membrane phase after demulsification process, <i>which consists of kerosene as a diluent and TOA as a carrier</i>. For this reason, the membrane phase obtained from centrifuge demulsification process was selected and used as the sample.</p> <p>The above statements have been included in the revised manuscript in paragraph 3 of section 3.3.</p>

EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY

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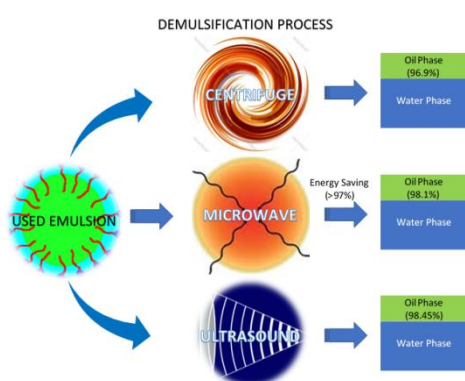
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Graphical abstract



Abstract

Emulsion liquid membrane (ELM) method has been widely applied in the separation process as the alternative of liquid/liquid extraction. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification. The results showed that the use of microwave to break the used emulsion provided demulsification efficiency of 98.10%, while application of ultrasonic probe was able to break emulsion at efficiency of 98.45%. In the meantime, demulsification efficiency of almost 97% was achieved when employing centrifuge at centrifugation speed of 3000 rpm. Considering the energy consumption, it is recommended to apply microwave irradiation for emulsion breaking. It could save energy up to 97% and 99% compared to that of ultrasonic probe and centrifuge, respectively.

Keywords: emulsion liquid membrane; heavy metals; removal; emulsion breaking; demulsification

Abstrak

Kaedah membran cecair emulsi (ELM) telah digunakan secara meluas dalam proses pemisahan sebagai alternatif kepada penyarian cecair-cecair. Kajian ini membandingkan aplikasi gelombang mikro, kuar ultrasonik, dan emparan untuk memecahkan emulsi yang telah digunakan. Kecekapan pengemulsian diselidiki dari segi kandungan air dalam larutan fasa membran sebelum dan selepas demulsifikasi. Keputusan menunjukkan bahawa penggunaan gelombang mikro untuk memecahkan emulsi yang digunakan mencapai kecekapan demulsifikasi 98.10%, manakala penggunaan kuar ultrasonik telah memecahkan emulsi pada kecekapan 98.45%. Sementara itu, kecekapan demulsifikasi hampir 97% dicapai apabila menggunakan emparan pada kelajuan 3000 rpm. Kaedah gelombang mikro adalah disyorkan untuk memecahkan emulsi disebabkan penggunaan tenaga yang kurang. Penjimatan tenaga untuk demulsifikasi adalah sehingga 97% bagi kaedah kuar ultrasonik dan 99% bagi kaedah emparan.

Kata kunci: membran cecair emulsi; logam berat; penyingkiran; pecah emulsi; demulsifikasi

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1.0 INTRODUCTION

Emulsion liquid membrane (ELM) is an established technology as a modification of liquid/liquid extraction. ELM has been considered as one of the most attractive type of liquid membrane and more selective than polymer-based membranes [1]. Moreover, most molecules have higher diffusivity through liquids than that of through polymer membranes, leading to higher extraction efficiency [2]. In ELM method, extraction and stripping processes occur in a single step thus make the method economically feasible. ELM involves the mixing of double emulsions, either water in oil in water or oil in water in oil. External phase contains impurities to be extracted. Membrane phase composed of organic solution act as a barrier of external and internal phases. The solute is transferred through the membrane phase towards internal phase [3, 4]

ELM system involves three main processes, i.e. emulsification, extraction, and demulsification as illustrated in Figure 1. Emulsion could be produced using blender [5, 6], homogenizer [7, 8], ultrasonic probe [9, 10], and stirrer [11]. Those researches characterised the produced emulsion in term of emulsion diameter, membrane breakage, and emulsion swelling. The emulsion performance was also tested in the extractions of various impurities.

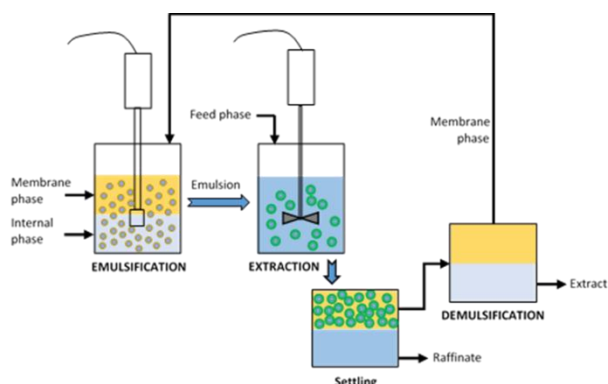


Figure 1 Emulsion liquid membrane process

The ELM method has been widely applied in the separation process. Heavy metal removals using ELM have been intensively studied by many researchers. Cadmium recoveries under ELM system have been investigated by Ahmad, et.al. [12], Kumbasar [13], and Mortaheb, et.al. [14]. Chromium extractions have been studied by some other researchers [15-17]. Other researchers conducted experiments on copper removal by ELM [10, 18, 19]. High concentration of copper is mostly available in the wastewater of many industries such as metallurgy, steel, paper and pulp, fertiliser, and petroleum refining [20]. Beyond the maximum allowable concentration of 1.3 ppm, copper is considered as hazardous pollutant. Copper accumulation in animals and humans may cause several disorders of gastroenteritis, diarrhoea, anorexia, dehydration, and

shock, while chronic copper poisoning contributes to Alzheimer's, Memkes and Wilson's diseases [21].

The last process in ELM system is demulsification. The used emulsion must be broken that the entrapped solutes could be recovered for further necessities. The liquid membrane and internal phase solution could be reused in the following emulsification process. Emulsion breaking occurs through three steps, i.e. flocculation, coagulation and coalescence. In the first step, flocculation of the dispersed droplets of internal phase occurs, forming some larger groups. Furthermore, the drops in groups coalesce into a large group, leads to the decrease of drops numbers. Finally, due to gravity effect, the large internal drops sink in the interface of membrane and internal phase, coagulate with the water phase, and generate the emulsion breaking [22].

There are several methods of demulsification [23], i.e. chemical demulsification [24, 25], gravity or centrifugal settling [26], pH adjustment, filtration, heating treatment, electrostatic demulsification [27, 28], and membrane technique [29]. Demulsification process based on the gravity effect occurs in a centrifuge. Centrifugation accelerates sedimentation of an immiscible mixture. Moreover, in the mixtures of solutions in similar densities, gravity separations might take hours. The use of centrifuge could minimise the separation time to be few minutes. Centripetal force could separate greater and lesser density solutions leading to emulsion breaking [26].

Heating has also been used in demulsification, but it is energy-intensive. Emulsion breaking is achieved by applying heat. It has been known that surfactant induces the formation of micelle by interactions of polar hydrophilic head and non-polar hydrophobic tail groups in the mixture. The applied heat interrupts the micelle interactions leading to micelles breakdown and liquids separation. Euston, et.al [30] investigated destabilization of oil in water emulsion by heat induction. They found that large increase of emulsion breakdown occurred at degree of hydrolysis > 27%. Electric field methods have been used to demulsify water-in-oil emulsions [22]. It promotes an irreversible rupturing of the stabilizing emulsions and the droplets coalesce if the external field exceeds a certain critical value. However, it is ineffective for the water-in-oil emulsion having high water content or a swelling. It can produce a "sponge" phase which contains abundant internal aqueous phase in the interface of oil and aqueous phase, so that demulsification efficiency is seriously affected. Another demulsification method is microwave irradiation. This process has similar mechanism with that of dielectric heating. Internal heating occurs when emulsion exposed to electromagnetic field of microwave resulting in molecular rotation and ionic conduction. It is therefore accelerated the emulsion separation process. Chan and Chen [31] investigated the performance of microwave in breaking water in oil emulsion by microwave irradiation by testing the effects of emulsion conditions and microwave

operating conditions on the demulsification rate and the separation efficiency of W/O emulsion.

In spite of the available reports of emulsion breaking processes through many methods, there is limited articles reveals the comprehensive studies of demulsification in ELM system. Whereas ELM performance also determined by successful demulsification process. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification.

2.0 METHODOLOGY

2.1 MATERIALS

The aqueous copper solutions were prepared by dissolving copper nitrate (Merck) in deionised water. HCl (Merck) was added to the feed solution to adjust the pH. Trioctylamine (Merck) and Span 80 (Merck) were used as extractant and surfactant, respectively. Low odour kerosene purchased from Sigma Aldrich was used as diluent. Ammonia (Merck) was used as internal phase solution.

2.1 PROCEDURES

After the extraction process, the organic membrane phase was recovered for its diluents. The demulsification processes using physical treatment process were applied. The water content in the emulsion before demulsification and in the membrane phase after demulsification was measured. The demulsification efficiency (Br) was calculated as:

$$Br = \frac{\theta_0 - \theta_1}{\theta_0 \times (1 - \theta_1)} \times 100\% \quad (1)$$

Br refers to demulsification efficiency, θ_0 is the fraction of water content in the emulsion before demulsification, and θ_1 is the fraction of water content in the membrane phase after demulsification. Energy consumption (E_c) for emulsion breaking was determined as:

$$E_c = P_{in} \times t \quad (2)$$

where P_{in} is the power consumed (J/s) and t is the demulsification time (s).

2.1.1 Microwave Demulsification

A beaker glass was used to collect used emulsion. It was then placed in defined position in the microwave (domestic microwave oven, Panasonic, NN-SM330 M) thus every experiment got the same heating irradiation. Experiments were done at irradiation power of 50 W, 380 W, 540 W, and 700 W for 8 s, 10 s, 12 s, and 15 s irradiation time. The irradiated sample was settled down until 15 minutes and then collected for water content analysis.

2.1.2 Ultrasound Demulsification

Used emulsion was placed in a beaker glass. The 22.5 kHz ultrasonic irradiation (ultrasonic USG-150) equipped with a titanium horn (3 mm diameter) was mounted at the top of the cylindrical glass cell. The emulsion was treated for 2, 4, 8, and 10 minutes at a frequency of 20 kHz in different intensities of about 20%, 60%, and 80%. Water content analysis was also done to the demulsified samples.

2.1.3 Centrifuge Demulsification

Certain volume of the used emulsion was put in the centrifuge bottle. The demulsifying method was conducted in a centrifuge (Kubota 5220) that accelerates the sedimentation at 2500-3500 rpm. The centrifugation time was varied from 5 to 15 minutes with interval of 5 minutes. After centrifugation process, the organic sample on the top layer of the solution is collected for water content analysis.

GC-MS analysis by using a Perkin Elmer GC Clarus 680 MS Clarus SQ 8T was also applied to identify the organic membrane phase after demulsification. The length of column is 30 m with 250 μ m of diameter. Maximum temperature of oven was set at about 300°C. Helium was used as carrier gas with 0.8 ml/min of flow rate. The sample was filtered by using a filter paper before injected into the GC at one μ l.

3.0 RESULTS AND DISCUSSION

3.1. Microwave Demulsification

The used emulsion needs to be broken so that membrane component can be reused for further emulsification process. After demulsification, the clear upper layer was sampled; pure kerosene indicated the success of demulsification process. The water content was then tested and the efficiency was calculated using Equation 1. Study of Henry [32] found that microwave irradiation was effective in reducing emulsion stability at relatively high water separation efficiency. It was also revealed that at equal irradiation exposure time and power, emulsion with higher water content achieved better demulsification efficiency. This is due to the nature properties of water, in which energy absorption of water is higher than that of oil. Figure 1 shows the effects of both microwave irradiation and settling time on demulsification efficiency. It is seen that demulsification efficiency increase with the increase of irradiation and settling time. Right after separation at irradiation time of 8 s, almost no separation of water and oil phase occurred thus resulted in very low demulsification efficiency. Significant increase of demulsification efficiency was seen after prolonging settling times. Increment of demulsification rate by the increase of microwave irradiation time is affected by dielectric heating properties that able to separate

water-in-oil emulsions. The highest demulsification efficiency of 82.45% was achieved by applying irradiation time of 15 s and settling time of 15 min.

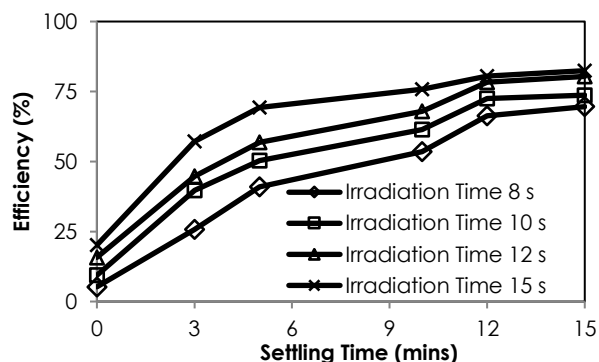


Figure 1 Demulsification efficiency (Microwave power 540 W; Irradiation time: 8, 10, 12, and 15 s; settling time: 0, 3, 5, 10, 12, 15 mins)

Figure 2 reveals that very small amount of aqueous phase can be separated with a 50 W power output. Even with power output above 380 W, a critical settling time greater than 5 min was necessary to give significant raise in demulsification rate. Along with settling time, demulsification rate increases with the increase of microwave power. The increase of microwave irradiation power resulted in higher separation efficiency as well as sample temperature. Improvement of microwave irradiation power from 50 W to 380 W gave insignificant effect of demulsification efficiency. Neither did further improvement to 540 W. Mohammed and Mohammed [33] found that this phenomenon was triggered by the increase of wavelength and penetration depth as the increase of microwave power.

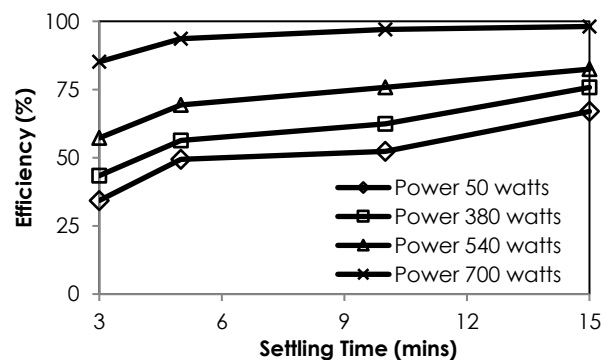


Figure 2 Demulsification efficiency (Irradiation time: 15 s; Microwave power 50, 380, 540, and 700 W)

3.2 Ultrasound Demulsification

Among the important factors affecting emulsions breaking is sound intensity. In which, energy level is varied depend on the sound intensities given to emulsions. Dehydration process of emulsions is only determined by mechanical effects of ultrasound. It was revealed that the increment of sound intensity resulted in the lower emulsion water content [34].

They found that the lowest water content was achieved at sound intensity of 0.66 W/cm², further increase in sound intensity actually increased water content. This also applies in this study, where sound intensity of 60% resulted in the best demulsification efficiency, shown in Figure 3. This is due to higher sound intensity triggered the reduction of water-oil interface tension leading to emulsion breaking. However, further increment of sound intensity to be 80% leading to the decrease of demulsification efficiency. This is because excessive sound intensity caused re-emulsification phenomenon [34].

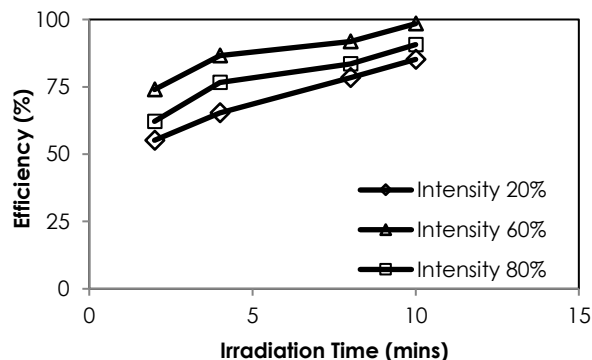


Figure 3 Demulsification efficiency (Intensity: 20%, 60%, and 80%; Irradiation time: 2, 4, 8, 10 min)

3.3 Centrifuge Demulsification

Demulsification under centrifuge force was investigated in terms of time and speed. To see the compounds, some of the samples were tested using GC-MS. The demulsification results are presented in Figure 4.

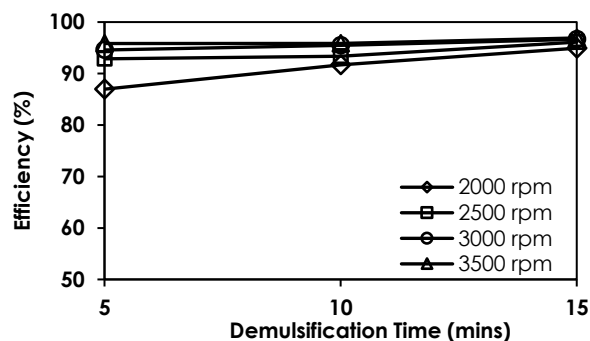


Figure 4 Demulsification efficiency (centrifugation speed: 2000, 2500, 3000, and 3500 rpm; centrifugation time: 5, 10, and 15 min)

It is revealed in Figure 4 that due to the principles of gravity separation, increasing centrifugation speed could enhance demulsification efficiency. Each phase is separated due to the density difference between each phase. Higher centrifugation speed as well as longer centrifugation time is able to accelerate the separation process. The graph also shows that at centrifugation speed of 2000 rpm,

efficiency was governed by time. At 5 min, efficiency was only about 86%, it gradually increased to be 90% at 10 min, and at the end of the process it succeeded to reach 92%. On the contrary, at high centrifugation speed of 3500 rpm, there was no significant increase in efficiency with the time extension. At 5, 10, and 15 min of demulsification process, the efficiencies were about 96%. It is also seen that at 15 min, demulsification efficiency increased from 95% at 2000 rpm to be 97% at 3500 rpm.

GC-MS testing was done and intended to verify the compounds in the organic membrane phase after demulsification process, which consists of kerosene as a diluent and TOA as a carrier. For this reason, the membrane phase obtained from centrifuge demulsification process was selected and used as the sample. In general, there were about 20 major compounds of total ion chromatogram (TIC) detected qualitatively from the organic membrane phase sample. GC-MS result for each centrifugation speed was revealed in Figures 5-8. The figures define that in retention time of 5-15 min, kerosene compounds were exclusively detected. TOA was detected at around 21 min and after 25 min of retention time for centrifugation speeds above and below 3000 rpm, respectively.

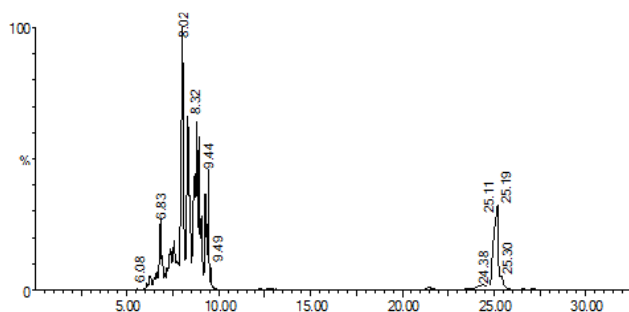


Figure 5 Demulsification efficiency (Total ion chromatogram of demulsification process at 2000 rpm)

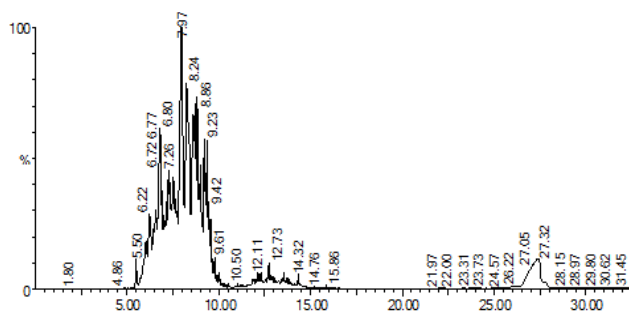


Figure 6 Demulsification efficiency (Total ion chromatogram of demulsification process at 2500 rpm)

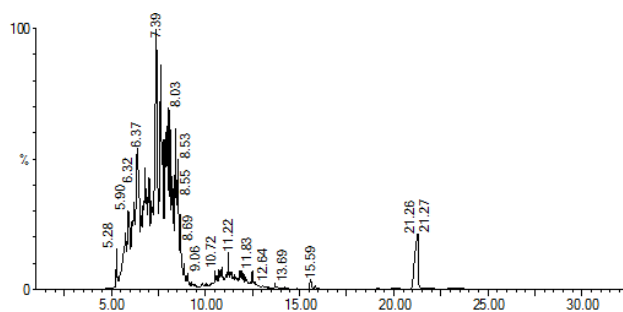


Figure 7 Demulsification efficiency (Total ion chromatogram of demulsification process at 3000 rpm)

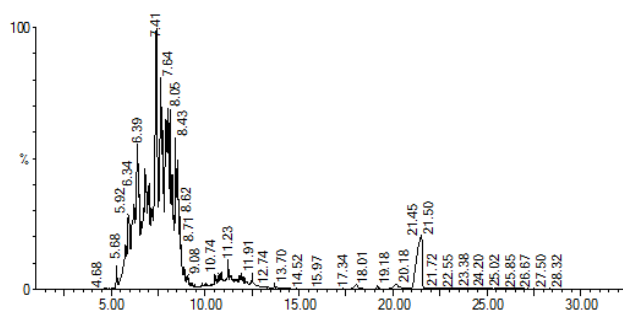


Figure 8 Demulsification efficiency (Total ion chromatogram of demulsification process at 3500 rpm)

The increase of centrifugation speed from 2000 rpm to 3500 rpm enabled the system to demulsify and to recover almost all of kerosene and TOA. It was indicated from total ion chromatogram report that demulsification process was able to recover about 99% and 98.7% of TOA and kerosene in organic membrane phase for 3500 rpm and 3000 rpm, respectively. Whereas at 2000 rpm, less than 90% of kerosene and TOA was able to be recovered while at 2500 rpm, more kerosene and TOA of about 97% was recovered.

3.4 Demulsification and Energy Consumption Assessment

Demulsification processes done by microwave, ultrasound, and centrifuge have been completed. Comparison of each process is described in Figure 9. It is seen that demulsification efficiency was in the order of ultrasound > microwave > centrifuge. However, there was no significant difference of demulsification efficiency of each mode. In term of energy consumption, there was tremendous difference of each demulsification tool. Microwave provided the most energy efficient demulsification process. In this case, microwave demulsification only used 16.875 kJ of energy or about 117 times lower than that of centrifuge. While ultrasound, required energy of about 600 kJ, was higher than that used of microwave. The highest energy of 1980 kJ was applied in centrifuge demulsification. It is therefore,

microwave demulsification is the most recommended process.

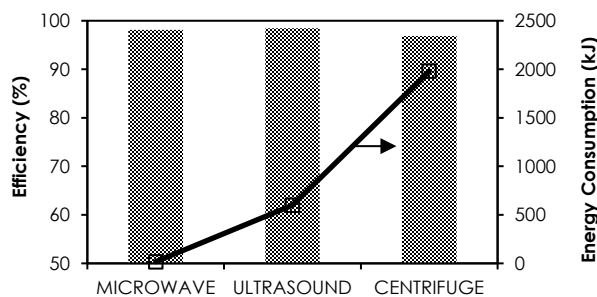


Figure 9 Comparison of demulsification efficiency and energy consumption for each demulsification equipment

4.0 CONCLUSION

Laboratory experiment showed the application of microwave, ultrasonic probe, and centrifuge for emulsion breaking. All the demulsification tools were successfully applied to break the used emulsion based on their specific operation condition. In general, demulsification efficiencies of above 97% were obtained. It was found that the order of demulsification efficiency was centrifuge < microwave < ultrasound. Although ultrasound provided the highest demulsification efficiency, it consumed more energy. Among the demulsification tools, microwave demulsification involved the lowest energy consumption. The significant difference of energy consumption was also supported by almost the same demulsification efficiency. So that, considering the economics of overall emulsion liquid membrane process, microwave irradiation is highly recommended for breaking the used emulsion. It should be noted that the water in the sample absorbs microwave energy, resulting in heating due to polarization of water molecules, leading to the acceleration of the demulsification process. In this study, 15 seconds of irradiation time was enough to break the emulsion at high efficiency.

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EMULSION LIQUID MEMBRANE FOR HEAVY METALS REMOVAL: EMULSION BREAKING STUDY

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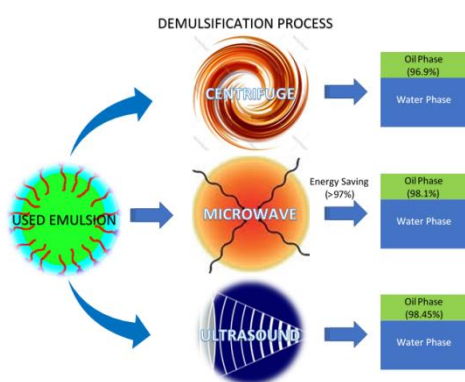
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Graphical abstract



Abstract

Emulsion liquid membrane (ELM) method has been widely applied in the separation process as the alternative of liquid/liquid extraction. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification. The results showed that the use of microwave to break the used emulsion provided demulsification efficiency of 98.10%, while application of ultrasonic probe was able to break emulsion at efficiency of 98.45%. In the meantime, demulsification efficiency of almost 97% was achieved when employing centrifuge at centrifugation speed of 3000 rpm. Considering the energy consumption, it is recommended to apply microwave irradiation for emulsion breaking. It could save energy up to 97% and 99% compared to that of ultrasonic probe and centrifuge, respectively.

Keywords: Emulsion liquid membrane, heavy metals, removal, emulsion breaking, demulsification

Abstrak

Kaedah membran cecair emulsi (ELM) telah digunakan secara meluas dalam proses pemisahan sebagai alternatif kepada penyarian cecair-cecair. Kajian ini membandingkan aplikasi gelombang mikro, kuar ultrasonik, dan emparan untuk memecahkan emulsi yang telah digunakan. Kecekapan pengemulsian diselidiki dari segi kandungan air dalam larutan fasa membran sebelum dan selepas demulsifikasi. Keputusan menunjukkan bahawa penggunaan gelombang mikro untuk memecahkan emulsi yang digunakan mencapai kecekapan demulsifikasi 98.10%, manakala penggunaan kuar ultrasonik telah memecahkan emulsi pada kecekapan 98.45%. Sementara itu, kecekapan demulsifikasi hampir 97% dicapai apabila menggunakan emparan pada kelajuan 3000 rpm. Kaedah gelombang mikro adalah disyorkan untuk memecahkan emulsi disebabkan penggunaan tenaga yang kurang. Penjimatan tenaga untuk demulsifikasi adalah sehingga 97% bagi kaedah kuar ultrasonik dan 99% bagi kaedah emparan.

Kata kunci: Membran cecair emulsi, logam berat, penyingkiran, pecah emulsi, demulsifikasi

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1.0 INTRODUCTION

Emulsion liquid membrane (ELM) is an established technology as a modification of liquid/liquid extraction. ELM has been considered as one of the most attractive type of liquid membrane and more selective than polymer-based membranes [1]. Moreover, most molecules have higher diffusivity through liquids than that of through polymer membranes, leading to higher extraction efficiency [2]. In ELM method, extraction and stripping processes occur in a single step thus make the method economically feasible. ELM involves the mixing of double emulsions, either water in oil in water or oil in water in oil. External phase contains impurities to be extracted. Membrane phase composed of organic solution act as a barrier of external and internal phases. The solute is transferred through the membrane phase towards internal phase [3, 4].

ELM system involves three main processes, i.e. emulsification, extraction, and demulsification as illustrated in Figure 1. Emulsion could be produced using blender [5, 6], homogenizer [7, 8], ultrasonic probe [9, 10], and stirrer [11]. Those researches characterised the produced emulsion in term of emulsion diameter, membrane breakage, and emulsion swelling. The emulsion performance was also tested in the extractions of various impurities.

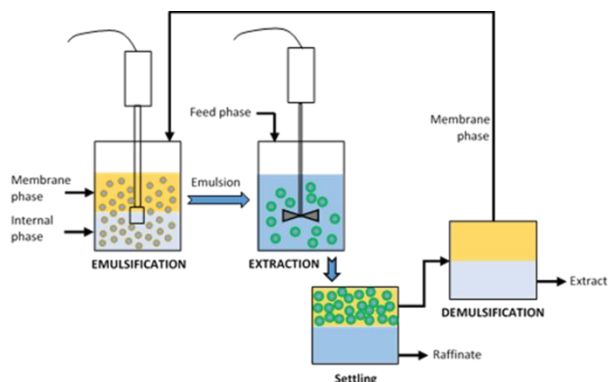


Figure 1 Emulsion liquid membrane process

The ELM method has been widely applied in the separation process. Heavy metal removals using ELM have been intensively studied by many researchers. Cadmium recoveries under ELM system have been investigated by Ahmad, *et al.* [12], Kumbasar [13], and Mortaheb, *et al.* [14]. Chromium extractions have been studied by some other researchers [15–17]. Other researchers conducted experiments on copper removal by ELM [10, 18, 19]. High concentration of copper is mostly available in the wastewater of many industries such as metallurgy, steel, paper and pulp, fertiliser, and petroleum refining [20]. Beyond the maximum allowable concentration of 1.3 ppm, copper is considered as hazardous pollutant. Copper accumulation in

animals and humans may cause several disorders of gastroenteritis, diarrhoea, anorexia, dehydration, and shock, while chronic copper poisoning contributes to Alzheimer's, Memkes and Wilson's diseases [21].

The last process in ELM system is demulsification. The used emulsion must be broken that the entrapped solutes could be recovered for further necessities. The liquid membrane and internal phase solution could be reused in the following emulsification process. Emulsion breaking occurs through three steps, i.e. flocculation, coagulation and coalescence. In the first step, flocculation of the dispersed droplets of internal phase occurs, forming some larger groups. Furthermore, the drops in groups coalesce into a large group, leads to the decrease of drops numbers. Finally, due to gravity effect, the large internal drops sink in the interface of membrane and internal phase, coagulate with the water phase, and generate the emulsion breaking [22].

There are several methods of demulsification [23], i.e. chemical demulsification [24, 25], gravity or centrifugal settling [26], pH adjustment, filtration, heating treatment, electrostatic demulsification [27, 28], and membrane technique [29]. Demulsification process based on the gravity effect occurs in a centrifuge. Centrifugation accelerates sedimentation of an immiscible mixture. Moreover, in the mixtures of solutions in similar densities, gravity separations might take hours. The use of centrifuge could minimise the separation time to be few minutes. Centripetal force could separate greater and lesser density solutions leading to emulsion breaking [26].

Heating has also been used in demulsification, but it is energy-intensive. Emulsion breaking is achieved by applying heat. It has been known that surfactant induces the formation of micelle by interactions of polar hydrophilic head and non-polar hydrophobic tail groups in the mixture. The applied heat interrupts the micelle interactions leading to micelles breakdown and liquids separation. Euston, *et al.* [30] investigated destabilization of oil in water emulsion by heat induction. They found that large increase of emulsion breakdown occurred at degree of hydrolysis > 27%. Electric field methods have been used to demulsify water-in-oil emulsions [22]. It promotes an irreversible rupturing of the stabilizing emulsions and the droplets coalesce if the external field exceeds a certain critical value. However, it is ineffective for the water-in-oil emulsion having high water content or a swelling. It can produce a "sponge" phase which contains abundant internal aqueous phase in the interface of oil and aqueous phase, so that demulsification efficiency is seriously affected. Another demulsification method is microwave irradiation. This process has similar mechanism with that of dielectric heating. Internal heating occurs when emulsion exposed to electromagnetic field of microwave resulting in molecular rotation and ionic conduction. It is therefore accelerated the emulsion separation process. Chan and Chen [31] investigated the performance of microwave in breaking water in oil

emulsion by microwave irradiation by testing the effects of emulsion conditions and microwave operating conditions on the demulsification rate and the separation efficiency of W/O emulsion.

In spite of the available reports of emulsion breaking processes through many methods, there is limited articles reveals the comprehensive studies of demulsification in ELM system. Whereas ELM performance also determined by successful demulsification process. This study compared the application of microwave, ultrasonic probe, and centrifuge in breaking the used emulsion. Demulsification efficiency was investigated in term of water content in the membrane phase solution before and after demulsification.

2.0 METHODOLOGY

2.1 Materials

The aqueous copper solutions were prepared by dissolving copper nitrate (Merck) in deionised water. HCl (Merck) was added to the feed solution to adjust the pH. Trioctylamine (Merck) and Span 80 (Merck) were used as extractant and surfactant, respectively. Low odour kerosene purchased from Sigma Aldrich was used as diluent. Ammonia (Merck) was used as internal phase solution.

2.2 Procedures

After the extraction process, the organic membrane phase was recovered for its diluents. The demulsification processes using physical treatment process were applied. The water content in the emulsion before demulsification and in the membrane phase after demulsification was measured. The demulsification efficiency (Br) was calculated as:

$$Br = \frac{\theta_0 - \theta_1}{\theta_0 \times (1 - \theta_1)} \times 100\% \quad (1)$$

Br refers to demulsification efficiency, θ_0 is the fraction of water content in the emulsion before demulsification, and θ_1 is the fraction of water content in the membrane phase after demulsification. Energy consumption (E_c) for emulsion breaking was determined as:

$$E_c = P_{in} \times t \quad (2)$$

where P_{in} is the power consumed (J/s) and t is the demulsification time (s).

2.1.1 Microwave Demulsification

A beaker glass was used to collect used emulsion. It was then placed in defined position in the microwave (domestic microwave oven, Panasonic, NN-SM330 M) thus every experiment got the same

heating irradiation. Experiments were done at irradiation power of 50 W, 380 W, 540 W, and 700 W for 8 s, 10 s, 12 s, and 15 s irradiation time. The irradiated sample was settled down until 15 minutes and then collected for water content analysis.

2.1.2 Ultrasound Demulsification

Used emulsion was placed in a beaker glass. The 22.5 kHz ultrasonic irradiation (ultrasonic USG-150) equipped with a titanium horn (3 mm diameter) was mounted at the top of the cylindrical glass cell. The emulsion was treated for 2, 4, 8, and 10 minutes at a frequency of 20 kHz in different intensities of about 20%, 60%, and 80%. Water content analysis was also done to the demulsified samples.

2.1.3 Centrifuge Demulsification

Certain volume of the used emulsion was put in the centrifuge bottle. The demulsifying method was conducted in a centrifuge (Kubota 5220) that accelerates the sedimentation at 2500-3500 rpm. The centrifugation time was varied from 5 to 15 minutes with interval of 5 minutes. After centrifugation process, the organic sample on the top layer of the solution is collected for water content analysis.

GC-MS analysis by using a Perkin Elmer GC Clarus 680 MS Clarus SQ 8T was also applied to identify the organic membrane phase after demulsification. The length of column is 30 m with 250 μ m of diameter. Maximum temperature of oven was set at about 300°C. Helium was used as carrier gas with 0.8 ml/min of flow rate. The sample was filtered by using a filter paper before injected into the GC at one μ l.

3.0 RESULTS AND DISCUSSION

3.1 Microwave Demulsification

The used emulsion needs to be broken so that membrane component can be reused for further emulsification process. After demulsification, the clear upper layer was sampled; pure kerosene indicated the success of demulsification process. The water content was then tested and the efficiency was calculated using Equation 1. Study of Henry [32] found that microwave irradiation was effective in reducing emulsion stability at relatively high water separation efficiency. It was also revealed that at equal irradiation exposure time and power, emulsion with higher water content achieved better demulsification efficiency. This is due to the nature properties of water, in which energy absorption of water is higher than that of oil. Figure 1 shows the effects of both microwave irradiation and settling time on demulsification efficiency. It is seen that demulsification efficiency increase with the increase of irradiation and settling time. Right after separation at irradiation time of 8 s, almost no separation of

water and oil phase occurred thus resulted in very low demulsification efficiency. Significant increase of demulsification efficiency was seen after prolonging settling times. Increment of demulsification rate by the increase of microwave irradiation time is affected by dielectric heating properties that able to separate water-in-oil emulsions. The highest demulsification efficiency of 82.45% was achieved by applying irradiation time of 15 s and settling time of 15 min.

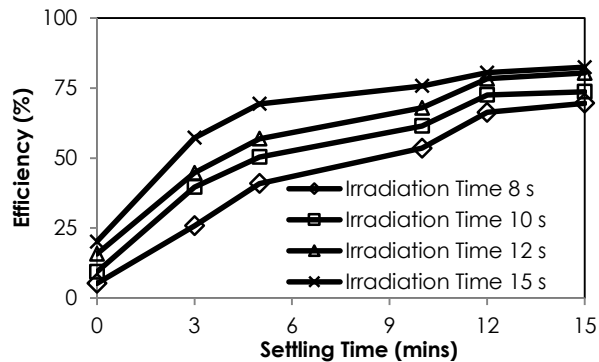


Figure 1 Demulsification efficiency (Microwave power 540 W; Irradiation time: 8, 10, 12, and 15 s; settling time: 0, 3, 5, 10, 12, 15 mins)

Figure 2 reveals that very small amount of aqueous phase can be separated with a 50 W power output. Even with power output above 380 W, a critical settling time greater than 5 min was necessary to give significant raise in demulsification rate. Along with settling time, demulsification rate increases with the increase of microwave power. The increase of microwave irradiation power resulted in higher separation efficiency as well as sample temperature. Improvement of microwave irradiation power from 50 W to 380 W gave insignificant effect of demulsification efficiency. Neither did further improvement to 540 W. Mohammed and Mohammed [33] found that this phenomenon was triggered by the increase of wavelength and penetration depth as the increase of microwave power.

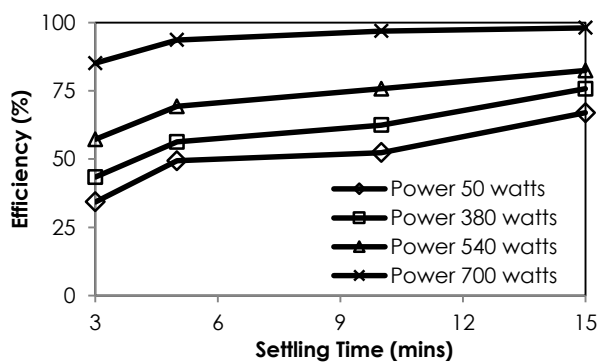


Figure 2 Demulsification efficiency (Irradiation time: 15 s; Microwave power 50, 380, 540, and 700 W)

3.2 Ultrasound Demulsification

Among the important factors affecting emulsions breaking is sound intensity. In which, energy level is varied depend on the sound intensities given to emulsions. Dehydration process of emulsions is only determined by mechanical effects of ultrasound. It was revealed that the increment of sound intensity resulted in the lower emulsion water content [34]. They found that the lowest water content was achieved at sound intensity of 0.66 W/cm², further increase in sound intensity actually increased water content. This also applies in this study, where sound intensity of 60% resulted in the best demulsification efficiency, shown in Figure 3. This is due to higher sound intensity triggered the reduction of water-oil interface tension leading to emulsion breaking. However, further increment of sound intensity to be 80% leading to the decrease of demulsification efficiency. This is because excessive sound intensity caused re-emulsification phenomenon [34].

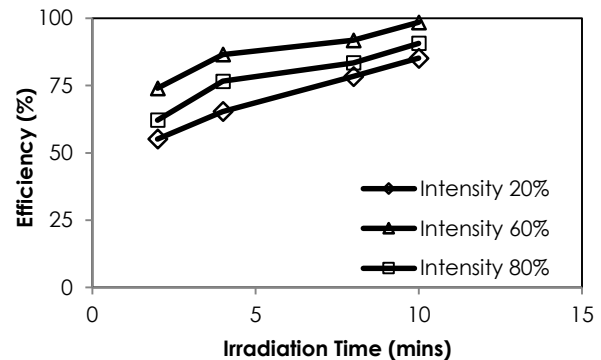


Figure 3 Demulsification efficiency (Intensity: 20%, 60%, and 80%; Irradiation time: 2, 4, 8, 10 min)

3.3 Centrifuge Demulsification

Demulsification under centrifuge force was investigated in terms of time and speed. To see the compounds, some of the samples were tested using GC-MS. The demulsification results are presented in Figure 4.

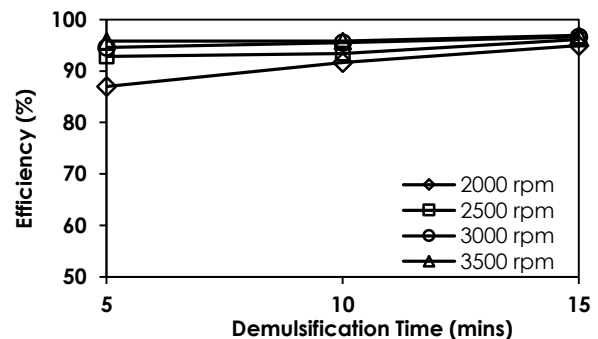


Figure 4 Demulsification efficiency (centrifugation speed: 2000, 2500, 3000, and 3500 rpm; centrifugation time: 5, 10, and 15 min)

It is revealed in Figure 4 that due to the principles of gravity separation, increasing centrifugation speed could enhance demulsification efficiency. Each phase is separated due to the density difference between each phase. Higher centrifugation speed as well as longer centrifugation time is able to accelerate the separation process. The graph also shows that at centrifugation speed of 2000 rpm, efficiency was governed by time. At 5 min, efficiency was only about 86%, it gradually increased to be 90% at 10 min, and at the end of the process it succeeded to reach 92%. On the contrary, at high centrifugation speed of 3500 rpm, there was no significant increase in efficiency with the time extension. At 5, 10, and 15 min of demulsification process, the efficiencies were about 96%. It is also seen that at 15 min, demulsification efficiency increased from 95% at 2000 rpm to be 97% at 3500 rpm.

GC-MS testing was done and intended to verify the compounds in the organic membrane phase after demulsification process, which consists of kerosene as a diluent and TOA as a carrier. For this reason, the membrane phase obtained from centrifuge demulsification process was selected and used as the sample. In general, there were about 20 major compounds of total ion chromatogram (TIC) detected qualitatively from the organic membrane phase sample. GC-MS result for each centrifugation speed was revealed in Figures 5-8. The figures define that in retention time of 5-15 min, kerosene compounds were exclusively detected. TOA was detected at around 21 min and after 25 min of retention time for centrifugation speeds above and below 3000 rpm, respectively.

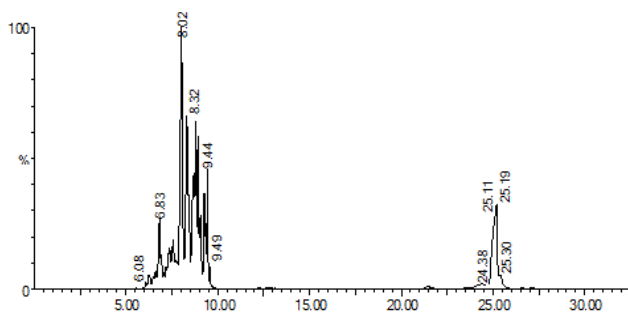


Figure 5 Demulsification efficiency (Total ion chromatogram of demulsification process at 2000 rpm)

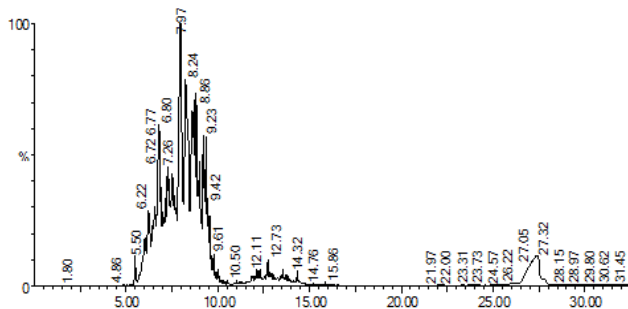


Figure 6 Demulsification efficiency (Total ion chromatogram of demulsification process at 2500 rpm)

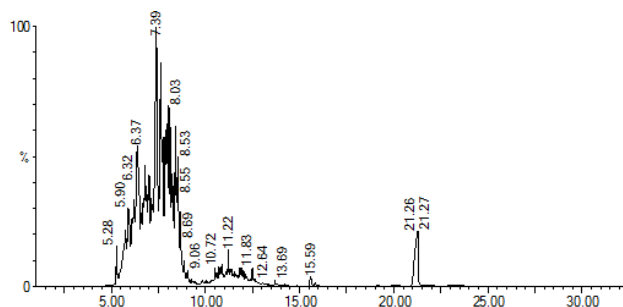


Figure 7 Demulsification efficiency (Total ion chromatogram of demulsification process at 3000 rpm)

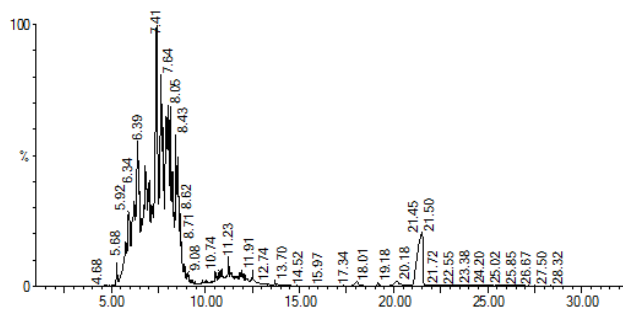


Figure 8 Demulsification efficiency (Total ion chromatogram of demulsification process at 3500 rpm)

The increase of centrifugation speed from 2000 rpm to 3500 rpm enabled the system to demulsify and to recover almost all of kerosene and TOA. It was indicated from total ion chromatogram report that demulsification process was able to recover about 99% and 98.7% of TOA and kerosene in organic membrane phase for 3500 rpm and 3000 rpm, respectively. Whereas at 2000 rpm, less than 90% of kerosene and TOA was able to be recovered while at 2500 rpm, more kerosene and TOA of about 97% was recovered.

3.4 Demulsification and Energy Consumption Assessment

Demulsification processes done by microwave, ultrasound, and centrifuge have been completed. Comparison of each process is described in Figure 9. It is seen that demulsification efficiency was in the order of ultrasound > microwave > centrifuge. However, there was no significant difference of demulsification efficiency of each mode. In term of energy consumption, there was tremendous difference of each demulsification tool. Microwave provided the most energy efficient demulsification process. In this case, microwave demulsification only used 16.875 kJ of energy or about 117 times lower than that of centrifuge. While ultrasound, required energy of about 600 kJ, was higher than that used of microwave. The highest energy of 1980 kJ was applied in centrifuge demulsification. It is therefore,

microwave demulsification is the most recommended process.

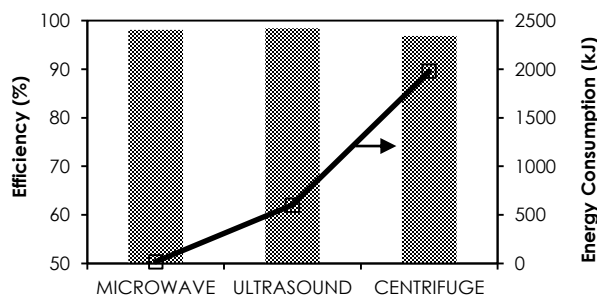


Figure 9 Comparison of demulsification efficiency and energy consumption for each demulsification equipment

4.0 CONCLUSION

Laboratory experiment showed the application of microwave, ultrasonic probe, and centrifuge for emulsion breaking. All the demulsification tools were successfully applied to break the used emulsion based on their specific operation condition. In general, demulsification efficiencies of above 97% were obtained. It was found that the order of demulsification efficiency was centrifuge < microwave < ultrasound. Although ultrasound provided the highest demulsification efficiency, it consumed more energy. Among the demulsification tools, microwave demulsification involved the lowest energy consumption. The significant difference of energy consumption was also supported by almost the same demulsification efficiency. So that, considering the economics of overall emulsion liquid membrane process, microwave irradiation is highly recommended for breaking the used emulsion. It should be noted that the water in the sample absorbs microwave energy, resulting in heating due to polarization of water molecules, leading to the acceleration of the demulsification process. In this study, 15 seconds of irradiation time was enough to break the emulsion at high efficiency.

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