Emulsion liquid membrane extraction of polyphenols compound from palm oil mill effluent

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Polyphenols possess many health attributes, as they are powerful antioxidants. Recovery of value-added compounds from industrial waste is a new approach in order to promote sustainability. In this study, the extraction of polyphenols from palm oil mill sterilization condensate by emulsion liquid membrane (ELM) process is proposed. The sterilization condensate was first characterized to determine the total phenolic content (TPC) in the sample. For the extraction, liquid membrane was formulated to choose the best diluent, carrier, and stripping agent. Once the formulation was successfully attempted, the extraction of polyphenols to recover polyphenols was performed. The results show that 2627.3 mg GAE/L of TPC was obtained in the condensate. During the liquid membrane formulation, palm oil was chosen as a green diluent, TBP and n-Octanol were selected as the most appropriate carriers for synergize in a composition of 8:2 by volume, while sodium hydroxide was selected as the most appropriate stripping agents to best facilitate the extraction process. The extraction and recovery performance of polyphenols showed performance of 96.5% and 31%, respectively. The findings of this study show that ELM is a potential technology to extract and recover polyphenols from palm oil mill sterilization condensate.

Keywords: Polyphenols, extraction, emulsion liquid membrane, palm oil mill effluent, sterilization condensate

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INTRODUCTION

Malaysia is renowned as the largest manufacturer and exporter of palm oil. Palm oil processing in Malaysia is executed in palm oil mills where oil is extracted from a palm oil fruit bunch. In this process, large amounts of water are used for the extraction of crude palm oil from the fresh palm oil fruit bunch and about 50% of the water ends up in palm oil mill effluent (POME). POME consists of thick brownish liquid that contains elevated amounts of total solids (40,500 mg/L), COD (50,000 mg/L) and BOD (25,000 mg/L), and oil and grease (4000 mg/L) [1]. In a conventional palm oil mill, POME consists of mainly three types of waste, that is, the sterilization waste, separator sludge, and hydrocyclone waste. POME is also regarded as a potent source of natural antioxidants due to its rich content of phenolic compounds. Since sterilization is the first step in palm oil processing that uses steam to soften the fruits and increase oil yield, it is unquestionably one of the critical operations, ensuring the success of subsequent stages. After the operation, the condensate carries oil residue and dissolved organics, which can be considered as a potential source of polyphenols.

Polyphenols are a type of chemical substance that occur naturally in plants. Plant phenolics can be classified as flavonoids or phenolic acid. Flavonoids are some of the most potent free radical scavengers and ion chelators while phenolics act as free radical terminators. Flavonoids are claimed as more powerful than Alpha-tocopherol, Beta-carotene, and vitamin A as anti-oxidants [2-3]. As compared to the benefits of conventional vitamin, antioxidants, and carotenoids, the potential health attributes of dietary polyphenols have only been recognized and acknowledged relatively recent [4-6].

Prior to this, there have been methods used to extract polyphenols from various parts of a plant for their antioxidant properties. These methods including pressurized liquid extraction (PLE), enzyme assisted extraction (EAE), microwave assisted extraction (MAE), pulsed electric field extraction (PEF), ultrasound assisted extraction (UAE), and supercritical fluid extraction (SFE) [7]. When it comes to the wastewater extraction of polyphenols, the method commonly used is the solvent extraction technique [8]. However, the aforementioned methods are known to have certain drawbacks [7,9]. An alternative approach is known as emulsion liquid membrane (ELM) where this extraction technique uses both membrane and solvent extraction method.

The ELM extraction process is one of the potential methods to extract polyphenols. The ELM process have shown substantial potential in the vast application of industrial separations such as in the removal of many chemicals, biomolecules, metal ions, pollutants, and organic compounds [10]. Among other types of liquid membranes, ELM is the most attractive type due to the higher mass transfer area and lower diffusional resistance. ELM processes are of fast extraction and is applicable for extraction of small amounts of solutes. These features
are the result of high interfacial area for mass transfer in the extraction step and high driving force for the stripping step [11].

Hence, while existing studies suggest extraction of polyphenols from POME, there is none that suggests extraction from the palm oil sterilization steam condensate, which has lower total solids and no mixed effluents unlike that of POME. Therefore, recovery of polyphenols compound from the sterilization steam condensate of palm oil mills is significant for it is a very valuable compound for human health. This study, therefore, aims to develop an extraction process for polyphenols using ELM process. The total phenolic content (TPC) in sterilization condensate was first determined, followed by formulation of emulsion liquid membrane by component screening, and ELM extraction and recovery performance of polyphenols from sterilization condensate.

**EXPERIMENTAL**

**Materials**

Sterilization condensate was obtained from palm oil mill at Kulai, Johor. Gallic acid (97.5 % purity), Folin-Ciocalteu reagent, tributylphosphate (TBP, 99 % purity), n-Octanol (99 % purity), Trioctylphosphine oxide (TOPO), kerosene (78 % purity), and sorbitan monooleate (Span 80, ≥80 % oleic acid) were purchased from Sigma Aldrich. Sodium carbonate (Na2CO3, 99 % purity) and dodecane (99 % purity) were procured from Merck. Sodium hydroxide (NaOH, 98 % purity) and palm oil were supplied from J.T. Baker and Lam Soon Edible Oils. All of these materials were of analytical grade and used directly as received without further purification.

**Characterization of palm oil mill sterilization condensate**

For characterization, pretreatment via centrifugation of feed solution (100 mL condensate diluted in 100 mL distilled water) was carried out. The clear supernatant formed from 5 to 8 minutes of centrifugation at 4000 rpm was separated by a separating funnel to obtain aqueous solution. This solution was re-centrifuged under the same conditions and the clear supernatant formed was separated using centrifuge. The collected liquid from the separating process was then diluted 5 times and filtered via vacuum filtration and stored at -18 °C. The supernatants obtained from pretreatment, separation, and filtration methods were used in the determination of total phenolic content (TPC) in the palm oil sterilization condensate by using the Folin-Ciocalteu method and UV-Visible spectrophotometer to detect the TPC. pH of the solutions was determined using a pH meter (Mettler Toledo model FE20).

**Liquid membrane component selection**

The formulation was initiated with the screening of liquid membrane components, which consists of diluent and carriers using solvent extraction method. Firstly, diluent screening was attempted by mixing 10 mL of organic solution (1 M carrier in diluent) with an equal volume of palm oil sterilization steam condensate (10 mL). The diluents used were green diluent (palm oil), conventional kerosene, and dodecane, a hydrocarbon. The solution was shaken using a mechanical shaker at 320 rpm for 18 hours. The duration provided for the extraction process is sufficient for the phases to reach equilibrium [12]. Once the solution settles to equilibrium phases, it was separated using a separating funnel. The external phase at the bottom of the funnel was demulsified by ultrasonic vibration (LIR Biotech 020S) at a frequency of 40 kHz for 10 minutes. The internal phase separated from the emulsion phase were collected for TPC determination using the Folin-Ciocalteu method and UV-Visible spectrophotometer to detect the TPC. pH of the solutions was determined using a pH meter (Mettler Toledo model FE20).

Next, a similar procedure was carried out for carrier screening. An equal volume of palm oil steam condensate was mixed with 10 mL of organic solution which encompasses of the chosen diluent and carrier which is the neutral n-Octanol, solvating TBP, and TOPO in three 50 mL conical flasks, respectively. Next, in order to obtain higher carrier transfer rate, the effect of two synergized carriers was attempted with the synergized carrier of TBP and TOPO, TBP and n-Octanol, followed by n-Octanol and TOPO. The highest synergized carriers will then be used for studying the extraction performance by varying compositions.

Once the most suitable carrier was determined, it was used for screening stripping agents such as basic sodium bicarbonate (Na2CO3) and sodium hydroxide (NaOH). This method is also known as back extraction. The organic residue separated from extraction process was used in reaction with equal amounts (10 mL) of Na2CO3 and NaOH in separate flasks. The following equations were used to calculate the percentage of extraction and stripping:

\[
\text{Extraction(\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{2.1}
\]

\[
\text{Stripping(\%)} = \frac{C_{\text{strip}}}{(C_i - C_f)} \times 100 \tag{2.2}
\]

where \(C_i\) is the initial concentration of polyphenols in the feed phase before extraction, \(C_f\) is the final concentration of polyphenols in the feed phase after extraction process, and \(C_{\text{strip}}\) is the concentration of polyphenols in the aqueous stripping phase from back extraction. The overall liquid membrane component screening is as shown in Fig. 1.

**ELM extraction and recovery**

Based on results obtained from the LM formulation and parameter study of carrier concentration and stripping agent concentration, the chosen favorable condition was adopted to study the ELM extraction of polyphenols compound.

The LM (synergized carrier in palm oil and Span 80 as a surfactant) was homogenized with the stripping agent, NaOH using a motor-driven homogenizer (Heidolph Silent Crusher M, 12000 rpm, 5 minutes) to form primary emulsion. The stripping agents and carriers used in this study have a concentration of 1 M. The extraction process was initiated by dispersing the primary emulsion in the external feed phase of sterilization condensate. The extraction process was conducted for 3 minutes with a treat ratio of 1:5. After the dispersion, the solution was allowed to settle in a separation funnel. The external phase at the bottom of the funnel was collected for TPC determination using the calorimetric Folin-Ciocalteu method. For recovery purpose, emulsion at the top of the separation funnel were demulsified by ultrasonic vibration (LIR Biotech 020S) at a frequency of 40 kHz for 10 minutes. The internal phase separated from the emulsion phase were collected for TPC determination. To evaluate the ELM performance, Equation 2.1 was used for extraction, while the percentage of recovery and enrichment were determined using Equation 2.3 and 2.4, respectively.

\[
\text{Recovery(\%)} = \frac{C_{\text{internal}}}{(C_i \times 2 \times TR)} \times 100 \tag{2.3}
\]

\[
\text{Enrichment} = \frac{C_{\text{internal}}}{C_i} \tag{2.4}
\]
where $C_i$ is the initial concentration of polyphenols in the feed phase before extraction and $C_{\text{internal}}$ is the concentration of polyphenols in the internal phase.

**Analytical procedure**

To obtain TPC, the Folin-Ciocalteu phenol reagent technique with Gallic acid as the standard reference phenolic compound was used. A UV-Vis Spectrophotometer (Jenway 7305) at 760 nm was utilized to measure the absorbance of the samples and was converted into TPC using a Gallic acid calibration curve. The calibration curve was prepared using different concentrations of Gallic acid, ranging from 0 to 50 mg/L. In this study, an equation of $Y=0.0011X$ was obtained, where $Y$ represents absorbance and $X$ represents Gallic acid concentration (mg/L). TPC was expressed as milligrams per liter of sample (mg GAE/L).

**RESULTS AND DISCUSSION**

**Characterization of palm oil mill sterilization condensate**

Characterization to determine the total phenolic compound (TPC) in the palm oil sterilization steam condensate shows that 2627.3 mg GAE/L of TPC was obtained. TPC in the sample obtained from palm oil sterilization steam condensate are possibly water-soluble polyphenols. According to the literature, POME contains oil sterilization steam condensate are possibly water-soluble GAE/L of TPC was obtained. TPC in the sample obtained from palm oil sterilization steam condensate are possibly water-soluble polyphenols. According to Manna et al. [14], this is a favorable condition for polyphenols extraction, which is in the range of pH 4–6.

**Emulsion liquid membrane formulation**

**Diluent selection**

Diluents play an important role in the ELM process. In order to incorporate a green ELM system, which is more nature-friendly and non-toxic, the commonly used petroleum-based diluents are attempted to be replaced by using renewable and non-toxic diluents. Hence, three types of diluent, consisting of green vegetable-based diluent and conventional petroleum-based diluent were screened in this study. The results obtained are as shown in Fig. 2.

![Fig. 2 Percentage of polyphenols extraction from diluent screening (feed): 262.73 mg GAE/L; carrier: TBP, 1M; agitation speed: 320 rpm; extraction time: 18 hours).](image)

The highest polyphenols was extracted using palm oil (52 %), followed by dodecane (48 %), and kerosene (37 %). Palm oil (83.2 mPa.s) has higher viscosity than kerosene (2.2 mPa.s) and dodecane (1.36 mPa.s) [14]. Dodecane performed better extraction than kerosene due to its lower viscosity compared to kerosene, which creates a lower resistance in mass transport. This result is in agreement with other studies which have mentioned that diluents are desired to be of low viscosity in order to achieve higher extraction performances [15, 16].

Despite having a higher viscosity which may increase resistance to mass transport, palm oil shows higher extraction than the two petroleum-based diluents with lower viscosity. This is because palm oil can act as a co-carrier for the transportation of polyphenols. Palm oil contains triglycerides, which can react with polyphenols by forming hydrogen bonding or intermolecular interactions between them. Meanwhile, dodecane and kerosene contain mainly aliphatic hydrocarbon structure and could not form any chemical reaction with polyphenols. This finding is consistent with Othman et al. [16] who reported palm oil has the ability to dissolve phenolic substances. Rosly et al. [17] also indicate that the transportation of solute is better using palm oil compared to aliphatic hydrocarbons. Hence, palm oil that possesses a non-polar nature and triglycerides acts as a good diluent as well as co-carrier for TBP.

**Carrier selection**

Since this study incorporates Type II ELM process, carrier selection is conducted via solvent extraction. Three types of extractants were screened in terms of their capability on extracting polyphenols compounds from palm oil sterilization steam condensate. The effect of carrier types is as shown in Fig. 3.

![Fig. 3 Percentage of polyphenols extraction from carrier screening (feed): 262.73 mg GAE/L; diluent: palm Oil; [carriers]: 1M; agitation speed: 320 rpm; extraction time: 18 hours).](image)

The result depicts that the highest polyphenols extraction was achieved by using TBP, which is 52 %, followed by TOPO (47 %) and n-Octanol (33 %). TBP is the most efficient extractant as it has the highest extraction percentage. This is possibly due to TBP being able to react with the electron acceptor part of polyphenols, thus providing good selectivity for efficient extraction. This outcome is in accordance to a study by Yim et al. [18].

TOPO and n-Octanol have lower extraction rates than TBP. This is possibly due to these carriers having lower selectivity towards polyphenols, hence the efficiency in extracting polyphenols is lower. TOPO has better selectivity towards polyphenols as compared to n-Octanol, which is why TOPO shows better extraction result in contrary to n-Octanol. This finding is consistent with the study by Rahman et al. [19] which shows neutral extractant TOPO having a higher extraction capability as compared to n-Octanol.

**Effect of synergized carrier**

Synergism occurs on the basis of combination of carriers to increase the possibilities of bonding of solute to the carrier, thus enabling a more efficient solute transfer process followed by a higher extraction percentage. In this study of synergized carriers, combination of neutral extractants have been conducted in a binary extractant system and the results are as shown in Fig. 4.

The highest polyphenols extraction was by using TBP-n-Octanol synergist (49 %), followed by TOPO-n-Octanol synergist (45 %) and TBO-TOPO synergist (41 %). TBP and n-Octanol shows slightly higher synergistic performance compared to TBP and TOPO or n-Octanol and TOPO. The extraction of polyphenols using mixture n-Octanol-TBP compared to single n-Octanol carrier has improved from...
Synergism of n-Octanol-TOPO compared to single n-Octanol has shown increment from 33 % to 45 %, respectively. This shows that using synergism for n-Octanol increases the extraction percentage due to the possibilities of bonding to occur with polyphenols. This finding is in line with Sarkar et al. [20] whereby synergism enables cooperation or alteration to the molecules.

As compared to single TOPO, synergized TOPO with TBP and n-Octanol do not show improvement and the same can be observed for single TBP extractant as compared to synergized TBP extractants with TBP and TOPO, respectively. Synergism may not be able to be observed due to certain factors. In this case of synergized TOPO and synergized TBP, the distribution ratio of the binary extractant system has possibly been lower than that of the single carrier system. This finding is as pointed out by previous studies, whereby the carrier synergism is established only when the distribution ratio of the carrier mixture system is greater than the single carrier system whereas the opposite effect occurs if the situation was reversed [21]. Therefore, an overall desired synergistic reaction was unable to be observed with the given composition rate or ratio of extractants used in this screening process. This carrier screening experiment result was based on extraction composition with a ratio of 1:1. Hence, the synergized extractant with highest percentage polyphenols extraction, TBP and n-Octanol, was chosen to be synergized under different compositions in order to study its effect.

**Effect of synergist carrier composition**

Synergistic carriers can be synergized under varying compositions in order to obtain a more desirable or higher percentage of solute extraction. Compositions or ratio of two extractants in the binary extractant system are significant in enabling maximum synergy of two extractants [20]. In this experiment, TBP and n-Octanol have been assorted under different compositions. The results can be viewed in Table 1.

The trend shows that TBP-n-Octanol composition has an increment in extraction percentage from TBP-n-Octanol ratio of 10:0 to TBP-n-Octanol 8:2 by 52.0 % to 56.4 %, respectively. This indicates the cooperation of synergized carriers in efficiently extracting more polyphenols. When more n-Octanol was added into the composition or when the ratio of n-Octanol was increased and that of TBP was decreased, the extraction percentage has shown a reduction from 56.4 % to 49.8 %. The trend becomes relatively plateau with more addition of n-Octanol and starts to decline notably when more than 80% of the synergized composition of TBP-n-Octanol was dominated by n-Octanol.

The trend of result obtained suggests that TBP-n-Octanol of 8:2 has the best distribution ratio as n-Octanol occupies the empty or available sites for bonding of TBP, thus enabling larger mass transfer of polyphenols solutes. However, at a certain limit, in this case at the composition of synergized TBP-n-Octanol of 6:4, no more sites are available for bonding and n-Octanol may tend to bond among themselves. This leads to the decline in extraction of polyphenols. The behavior described is known as antagonism that occurs due to a combination of some reagents in certain composition, that causes a decrease in extraction performance.

**Stripping agent selection**

The function of a stripping agent is to re-extract the solute from the organic phase specifically from the stripping-organic interface of the ELM system. In this experimental study, two types of potential stripping agents for the extraction of polyphenols have been screened. The effect of stripping agent types in component selection is as depicted in Fig. 5.

From the result, the highest polyphenols stripping was by using sodium hydroxide (NaOH, 96.3 %), followed by sodium bicarbonate (Na2CO3, 73 %). Since polyphenols is naturally acidic, the pH difference between the receiving phase and organic phase will serve as the driving force for this stripping process. This is due to the basic stripping agent solutions such as that of NaOH or Na2CO3 would dissociate in water to form a strong base which provided a high pH difference for efficient stripping. NaOH shows better extraction performance than Na2CO3 despite both being strong bases. Since the trend of basicity is as follows: Na2CO3 < NaOH, the strongest base (NaOH) is able to create higher chemical potential among the organic and aqueous stripping phase. This is in line with a study by Rahman et al. [22] where stripping performance increases proportionally with the basicity of stripping agents.

**ELM extraction and recovery**

The ELM performance of polyphenols extraction and recovery is as shown in Table 2. This result indicates that high extraction of polyphenols was achieved (96.5 %). This result can be attributed mainly to the high selectivity of polyphenols that was achieved through the ELM system. This finding is similar to previous studies which have attributed high extraction performance due extraction and stripping steps that take place simultaneously as well as for high selectivity of solute [23-25].
Meera Sheriffa Begum and Jusoh of polyphenols and the conditions of ELM was possibly not optimal for feed phase as characterized, has high amounts be easily saturated, hence contributing to a low recovery. This may have been sufficient to strip polyphenols. Othman et al. acknowledged that 3 minutes was inadequate for high extraction to be obtained. Also, palm oil as a diluent, synergized carriers TBP-n-Octanol (1M, ratio 8:2 by volume), and NaOH as a stripping agent were selected as the ELM formulation for this study. Lastly, using formulated components as stated and emulsion conditions of 1:5 treat ratio, 300 rpm rotational speed with 3 minutes agitation time, extraction of 96.5 %, recovery of 31 %, and 3.1 times enrichment was obtained.

A few comparisons of the high extraction of polyphenols achieved by ELM in contrast to other techniques are presented in Table 3. As compared to previous studies done in the extraction of palm phenolics, it shows that application of other techniques such as combination of extraction techniques consumes time, expensive equipment and meticulous use of equipment to achieve a high extraction rate as obtained in this experiment [26]. Moreover, studies show that commonly used solvent extraction techniques in polyphenols extraction from tea leaves have relatively low extraction performance [27]. Meanwhile, a comparatively high extraction was obtained from a study of polyphenols extraction from simulated Gallic acid solution using solvent extraction and ELM. It was also reported that a lower volume of organic solution with lower carrier concentration is required in ELM compared to solvent extraction [18]. Therefore, this result suggests that using ELM, a cost-efficient method with minimal use of chemicals is able to result in high extraction performance.

| Method          | Extraction (%) | Recovery (%) | Enrichment | Reference |
|-----------------|----------------|--------------|------------|-----------|
| ELM (real waste) | 96.5           | 31           | 3.1        | This study |
| MAE             | 22             | N/A          | N/A        | [26]      |
| Solvent extraction | 19.33         | N/A          | N/A        | [27]      |
| Solvent extraction | 75            | 75           | 1          | [18]      |
| ELM (Gallic acid) | 92             | N/A          | 12         | [18]      |

*N/A: Not available

### Table 2

| Internal concentration (mg GAE/L) | Final external concentration (mg GAE/L) | Extraction (%) | Recovery (%) | Enrichment |
|----------------------------------|----------------------------------------|----------------|--------------|------------|
| 813.64                           | 9.1                                    | 96.5           | 31           | 3.1        |

### Table 3

Comparison of polyphenols extraction and recovery performance using different methods.

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