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Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process☆

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ABSTRACT

Phenol is considered as pollutant due to its toxicity and carcinogenic effect. Thus, variety of innovative methods for separation and recovery of phenolic compounds is developed in order to remove the unwanted phenol from wastewater and obtain valuable phenolic compound. One of potential method is extraction using green based liquid organic solvent. Therefore, the feasibility of using palm oil was investigated. In this research, palm oil based organic phase was used as diluents to treat a simulated wastewater containing 300×10^{-6} of phenol solution using emulsion liquid membrane process (ELM). The stability of water-in-oil (W/O) emulsion on diluent composition and the parameters affecting the phenol removal efficiency and stability of the emulsion; such as emulsification speed, emulsification time, agitation speed, surfactant concentration, pH of external phase, contact time, stripping agent concentration and treat ratio were carried out. The results of ELM study showed that at ratio 7 to 3 of palm oil to kerosene, 5 min and 1300 $r \cdot min^{-1}$ of emulsification process the stabile primary emulsion were formed. Also, no carrier is needed to facilitate the phenol extraction. In experimental conditions of 500 $r \cdot min^{-1}$ of agitation speed, 3% Span 80, pH 8 of external phase, 5 min of contact time, 0.1 $mol \cdot L^{-1}$ NaOH as stripping agent and 1:10 of treat ratio, the ELM process was very promising for removing the phenol from the wastewater. The extraction performance at about 83% of phenol was removed for simulated wastewater and an enrichment of phenol in recovery phase as phenolate compound was around 11 times.

1. Introduction

Phenol is a major pollutant in wastewater due to its presence in the effluent of major processing and refining plant. It will cause severe effects on human being [1]. According to Mohammadi *et al.* [2], the concentration of phenols present in the wastewater from the industries is 6–500 $mg \cdot L^{-1}$ for refineries, 28–3900 $mg \cdot L^{-1}$ for coal processing and 2.8–1220 $mg \cdot L^{-1}$ for petrochemical plants. Pharmaceuticals, plastics, wood products, paints, pulp and paper industries contain 0.1–1600 $mg \cdot L^{-1}$ phenols. The Environment Protection Agency (EPA) has included phenol as one of primary pollutants that abide to specific regulations in order to protect the environment and human being as their toxicity is high [3]. It is essential to remove phenol from wastewater as much as possible so that the environment and human being are not exposed to it. On the other hand, the recovery of phenol from effluent can benefit to many industries, such as in the application as precursors to plastics and in production of adhesive, dyes, germicides, and chemical intermediate [4].

There are various methods of phenol removal and the methods can be classified into two main groups, which are traditional and advanced techniques. The traditional technologies include steam distillation, liquid–liquid extraction (LLE), adsorption, chemical oxidation and biodegradation, while advanced technologies include photo oxidation processes and membrane separation technologies [2]. A comparison had been made among the membrane separation technologies, ultrafiltration, supported liquid membrane (SLM) and emulsion liquid membrane (ELM) which are categorized in Table 1. Among them, the ELM shows very promising in removal of phenol. Although the instability of ELM such as swelling and leakage are the major problems, the stability of ELM can be minimized by optimizing the experimental conditions.

Previously, most of the emulsion liquid membrane technique used petroleum based diluents as an organic liquid membrane [16,17]. However, this petroleum based diluents such as kerosene, *n*-heptane and dicholoro-ethane have the properties of toxicity, non-renewable, non-biodegradable, flammable and volatile in nature. This will give

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Table 1
Comparison of phenol removal methods

	Mechanism	Removal efficiency	Advantages	References
Ultrafiltration process	Separation is based on the size of the molecules whereby the size of molecules can be enhanced by adding surfactant	27%–44.6%	Separation and recovery of surfactants and organic matters or metal ions is easy and economical	[5–7]
Supported liquid membrane (SLM)	Separation is based on the diffusion of solutes pass through the supported liquid membrane whereby liquid is immobilize in the pores of thin microporous solid support	67%–92.5%	– Simple operation and easy to scale up – Low capital investment and operating cost – Low energy consumption – Minimal loss of extractant – Low liquid membrane (LM) requirement	[8–10]
Emulsion liquid membrane (ELM)	Separation is based on the diffusion of solutes pass through a liquid membrane where the membrane is an organic phase.	More than 98%	– Simple operation – High efficiency – Extraction and stripping in one stage – Larger interfacial area – Scope of continuous operation	[11–15]

high impact to the environment if they are discharged to the environment. Thus, it is a must to replace the petroleum-based diluents with properties of renewable sources and non-toxic to become a green liquid membrane. The suggested environmental and green materials are vegetable oils such as coconut oil and palm oil [18,19]. Therefore, the use of vegetable palm oil based for emulsion liquid membrane is studied in order to prevent the production of secondary pollutant to the environment.

Basically, ELM comprises of three phases that are organic phase, internal phase and external phase. The organic liquid phase consists of diluents, surfactants and carriers. External phase is the water that carries the metal or element of interest, while the internal phase is the liquid phase that will trap the recover solutes [16].

There are two types of mass transport in ELM that are Type 1 facilitation and Type 2 facilitation [20]. Removal of phenol was considered as Type 1 facilitation, where the mass transfer rate is increased by incorporating a stripping agent in the internal phase and the stripping agent will react with the solutes to form membrane insoluble product [11,13,21–23]. However, based on the previous study [12,14], the used of the carrier were also performed in the extraction of phenol. Hence, in this research, palm oil will be utilized as a novel, naturally occurring and green liquid membrane for the recovery of phenol from the aqueous solution. The feasibility of palm oil without the existing of carrier in the emulsion liquid membrane for phenol extraction and its stability were investigated. Furthermore, the effects of parameters which affect the extraction and recovery performance of phenol in ELM process are also presented in this paper.

2. Materials and Methods

2.1. Materials and equipment

Kerosene, sorbitan monooleate (Span 80) (more than 60% oleic acid composition) and phenol crystals (>99% assay) were obtained from Sigma-Aldrich, Buruh edible oil from Lam Soon Edible Oils Sdn. Bhd. Malaysia, and sodium hydroxide (NaOH) (98% assay) from J.T. Baker. The equipment used in this research includes a homogenizer Heidolph Silent Crusher M, a compact digital mixer system Cole-Parmer EW50006-00, quartz, an UV Spectrophotometer Jenway 7305, a magnetic stirrer with temperature controller IKA RCT basic Safety Control, a microscope Olympus CX31 RTSF and a rotational Programmable Viscometer Brookfield Model LDDV-II with LV spindle.

2.2. Liquid–liquid extraction

Phenol extraction experiment was designed to identify the type of diluent required to remove phenol from aqueous phase. The diluents such as palm oil and kerosene will be tested. The viscosity of each organic diluent was measured using Viscometer Brookfield Model LDDV-II with LV spindle. An equal volume (50 ml) of phenol (300×10^{-6}) was mixed with organic solution in a 100 ml conical flask. Then, it was shaken using a mechanical shaker (IKA KS 130 BASIC) with rotation of 320 $r \cdot min^{-1}$ for duration of 1 h. The bottom layer, which was the feed aqueous phase was taken and carefully separated from organic phase for absorbance measurement at various time intervals. The experiments were repeated with different diluents. The experiments were conducted at room temperature, (25 ± 1) °C.

2.3. Stability test of vegetable palm oil-based W/O emulsion

The main purpose of investigating the stability of emulsion was to evaluate the possibility of using palm oil as organic diluents for phenol removal. The stability of emulsion was tested on the different ratio of palm oil to kerosene composition (0:100, 30:70, 50:50, 70:30, 100:0). 12 ml of organic phase with 3% (w/v) of Span 80 and 4 ml of internal phase, 0.1 $mol \cdot L^{-1}$ NaOH (membrane: internal phase = 3:1) were mixed together at lower emulsification speed (1000 $r \cdot min^{-1}$) for 5 min. The stability of the white W/O emulsion was determined by transferring the emulsion into a measuring cylinder and left for phase separation. The time was recorded when the phase separation of water started to appear at the bottom of measuring cylinder where the emulsion start to break.

2.4. W/O emulsion preparation

The emulsion composition needed for W/O emulsion in the ELM system is organic phase (solvent/diluent, surfactants) and stripping agent. The solubility of the components in the organic phase was checked first and then the proper amount of diluent composition (kerosene to palm oil) that selected from Section 2.3 was prepared. 12 ml of solvent was then mixed with 3% of Span 80 using magnetic stirrer. The internal phase, NaOH solution at 0.1 $mol \cdot L^{-1}$ of concentration with 4 ml of volume (ratio solvent to internal phase; 3:1) was slowly added into the membrane phase during the emulsification process. It was continuously stirred at 1000 $r \cdot min^{-1}$ for 5 min. The white emulsion was then ready for the extraction study. The emulsion prepared must be fresh each time before the extraction process.

2.5. ELM extraction of phenol

The prepared W/O emulsion was then dispersed into the agitated vessel with 80 ml of the external solution and stirred with 400 $r \cdot min^{-1}$ for extraction time of 5 min. Several parameters are investigated such as emulsification time, homogenizer speed, agitation speed, surfactant concentration, feed pH, extraction time, strip phase concentration and treat ratio. All of the parameter range is presented in Table 2. One-factor-at-a-time method was applied. The samples were then introduced into a separating funnel and left for phase separation. The volume of emulsion was measured and recorded for membrane swelling and breakage calculation. The feed phase at the bottom