Phenol removal from aqueous media by pertraction using vegetable oil as a liquid membrane

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HIGHLIGHTS

- This work deals with the removal of phenol from aqueous media.
- The process uses liquid membrane.
- The use of material is reduced: the liquid membrane is continuously regenerated.
- Vegetable oil is used as an alternative to hazardous conventional solvents.
- The process allows the concentration of phenol by semi-continuous pertraction.

ARTICLE INFO

ABSTRACT

The removal of phenol from aqueous media such as wastewater, using pertraction in rotating discs cont-actor is investigated. Preliminary equilibrium extraction study with several organic solvents show that vegetable oils (rapeseed and sunflower oils) can substitute classically volatile organic solvents used as phenol extracting agents. Rapeseed oil allows very efficient removal of phenol from acid aqueous solutions (feed phase) to basic aqueous solution (receiving phase) during batch pertraction studies. In order to optimize operating conditions, the influence of parameters, such as rotating discs speed and initial phenol concentration in the feed phase, on phenol mass transfer is studied. The transport rate of phenol increases with increasing the rotating discs speed. The increase of feed phase phenol concentration has not influence on its transport rate. Semi-continuous pertraction process allows the concentration of phenol.

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1. Introduction

In recent decades there has been considerable interest in treating polluted water generated by industrial processes. Water pollution due to phenol from petroleum refineries, coal conversion processes as well as the production of phenolic resins, dyes and pesticides has been a major cause of concern for chemists and environmental engineers, because phenol is one of the most toxic elements to be discharged to the environment because it is classed by the European Union like mutagen category number 3 [1]. Different technologies have been developed and are available to remove phenol from wastewater for many industrial processes, preventing the pollution of the environment [2]. The treatment of phenol effluents has been reported by several methods, such as adsorption [3], electrochemical reduction [4], photocatalytic degradation [5]. But these methods need high capital cost and expenses such as chemicals. In present work an alternative method of phenol treatment using liquid membrane process is investigated.

The science of liquid membranes has been developed very rapidly after the first patent on liquid membrane published in 1968 [6]. Liquid membrane techniques have received considerable attention due to the potential advantages of combining liquid–liquid extraction and stripping operations in a single unit operation called pertraction, regenerating continuously the membrane, reducing investment and operating costs due to the low capital

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and operating costs (low energy consumption) [7]. The extraction chemistry of liquid membrane process is similar to that found in classical liquid–liquid extraction. In a pertraction system the liquid membrane phase (usually organic solution) separates two other liquid phases (feed and stripping phase) with which it is immiscible (usually aqueous solutions). There are several types of liquid membranes. The most used are Bulk Liquid Membranes (BLM), Supported Liquid Membranes (SLM) and Emulsion Liquid Membranes (ELM) [7]. Bulk liquid membrane is one of the simplest designs for performing liquid membrane processes. Pertraction in a rotating discs contactor is a BLM technique which offers a constant and known surface area, a stability of the membrane, and no volume emulsion formation in the water phase [8]. This technique was successfully used for the removal or separation of heavy metal ions like zinc [9], nickel [10], chromium [11] and selective recovery of biomolecules like tylosin [12], glaucine [13] and surfactin [14].

In order to remove phenol using liquid membrane process, suitable organic phase and aqueous stripping solution have to be chosen. The processes of phenol extraction from aqueous media are finding wide applications, because of the toxicity and widespread occurrence of phenol. At present, for phenol removal from aqueous media volatile organic solvents such as benzene, 1-octanol [15], methyl-isobutyl ketone [16], diisopropyl ether [17] and organic solutions of reactive extractants with low solubility in the aqueous phase like Cyanex 923 [18], N$_{503}$ [19] were used. These components are categorized as hazardous chemicals. As an alternative to these conventional extracting agents, the use of less hazardous chemicals such as vegetable oils could be developed [20,21]. Having very low vapour pressure, they could replace the volatile conventional organic solvents. Moreover, they are naturally occurring, cheap, easily available, non toxic and renewable source.

One of the objectives of this work is to study the extraction of phenol by vegetable oils. Preliminary equilibrium studies goal to estimate the ability of vegetable oil to remove phenol by pertraction process. These results would furthermore allow the investigation of phenol transport in the three-liquid-phases system during pertraction in a rotating discs contactor.

2. Material and methods

2.1. Reagents

All chemicals used were of analytical grade reagents and purchased from VWR, Alfa Aesar or Across. Rapeseed and sunflower oils were purchased from retail stores. Properties of used organic solvents are mentioned in Table 1. Phenol was used without further purification. The feed solutions of various compositions used in the experiments were prepared by dissolving a pre-determinated amount of phenol in buffer solutions. Phenol existing in two forms in the aqueous phase, it was decided to prepare acid, neutral and basic solutions. To adjust the pH of initial phenol solutions, buffer solutions of pH 2, 7, 10, 12 and 13 were prepared using potassium phosphate and hydrochloric acid according to [22]. Demineralised water was used for all prepared solutions.

2.2. Analytical methods

A pH meter Nichipet EX was used for pH measurements. The total phenolic content of the aqueous solutions was determined with the Folin–Ciocalteu assay. It was based on the method reported in [23,24]. 100 μL of solution was added to a flask containing 1.5 mL of solvent, having the same pH of the solution. 100 μL of the Folin–Ciocalteu's phenol reagent was added to the mixture and shaken. After three minutes 300 μL of 20% sodium carbonate was added to the mixture. After incubation for 120 min at room temperature the phenol-Folin–Ciocalteu complex was formed. The absorbance was determined by a thermospectronic heλios α UV–visible spectrophotometer with matched 10 mm quartz cells at 765 nm. The system obeying Beer's law in the studied concentration range (40–300 mg L^{-1}) determination of phenol concentration in aqueous phases was carried. The error of the analysis was found to be less than 5%. The phenol concentration in the organic phase was calculated from the mass balance.

2.3. Extraction equilibrium studies

In order to study phenol recovery from aqueous media, extraction equilibrium experiments were are carried out in closed tubes. The extraction equilibrium isotherms were determined for initial phenol concentrations of 100 mg L^{-1}. As organic phase kerosene, 1-octanol, di-isopropyl ether, rapeseed oil or sunflower oil were used. Equal volumes of aqueous and organic phases were prepared, mixed moderately and kept in contact for 24 h at 20 °C before the separation of aqueous and organic phases. The effect of initial pH on the distribution of phenol was investigated. Extraction efficiency E was calculated from the experimental data, according to the following equation:

$$E = \frac{C_F(t=0) - C_{aq}^*}{C_F(t=0)} = \frac{C_{org}^*}{C_F(t=0)} \tag{1}$$

where C_{aq}^* and C_{org}^* are respectively the equilibrium phenol concentrations in the aqueous and organic phases, and $C_F(t=0)$ is the initial phenol concentration in the aqueous solution.

2.4. Kinetic studies of phenol recovery and concentration by pertraction

Kinetic studies were carried out in a laboratory-scale pertraction system described in details elsewhere [25]. The scheme of the rotating discs contactor used in these studies is shown in Fig. 1. Phenol solutions of pH 2 and concentrations of 100 or 300 mg.L^{-1} were used as a feed phase. The pH of the feed solution was adjusted with potassium chloride and hydrochloric acid according to [20]. The stripping phase was a potassium buffer solution pH 12. Equal volume (160 mL) of feed phase and stripping phase were placed in the corresponding compartments of the pertraction device. The bulk liquid membrane phase (350 mL) of rapeseed oil was laid above these aqueous phases. All three phases were agitated by the rotating discs. Appropriate rotation speeds were applied avoiding mixture of the feed and stripping solutions

Table 1
Some properties of the solvents used.

Solvent used	Kinematic viscosity (m^2 s^{-1})	Density (kg m^{-3})	Solubility in water (kg m^{-3})
Diisopropyl ether		725 (20 °C)	1.2 (25 °C)
Kerosene	1.48 · 10^{-6} (40 °C)	800 (15 °C)	Immiscible
1-Octanol		824 (25 °C)	0.54 (25 °C)
Rapeseed oil	4.71 · 10^{-6}	921 (15 °C)	0.03
Sunflower oil	31.7 · 10^{-6} (40 °C)	923 (15 °C)	