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Extraction of endocrine disrupting compound propylparaben from water by emulsion liquid membrane using trioctylphosphine oxide as carrier

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ABSTRACT

The extraction of endocrine disrupting compound propylpraben (PP) from aqueous solution by emulsion liquid membrane was investigated. The ELM contains trioctylphosphine oxide (TOPO) as extractant, *n*-hexane as solvent and Span 80 as surfactant. Na_2CO_3 was used as internal aqueous phase. The effects of operating parameters for the ELM process were examined. It was possible to perfectly remove all of PP molecules from the external feed solution by using the best experimental conditions. ELM treatment process represents an efficient advanced separation technique for the removal of PP even from complex matrices such as natural water, seawater and sewage water effluent.

Introduction

The development of society modernization leads to the extensive use of pharmaceuticals and personal care products (PPCPs). A large variety of PPCPs and metabolites thereof are continually introduced into the environment through human wastes by excretion, washings and manufacturing. PPCPs have recently been detected in sewage effluents [1–4], surface and ground water [3–6] and even drinking water [3,7].

Parabens, alkyl esters of *p*-hydroxybenzoic acid, are the most commonly used preservatives and bactericides in the foods, beverages, pharmaceuticals and cosmetic industries. These compounds are considered endocrine disrupting chemicals, because of their endocrine activity [8,9], and have been detected in human tissues, including breast tumors [10,11]. Moreover, parabens are continuously released in urban wastewater at relatively high levels and, despite being considerably removed during conventional sewage treatments, they have been still detected in river water samples [12]. Therefore, the U.S. Environmental Protection Agency (USEPA) has classified parabens as emerging environmental pollutants [13].

To avoid undesired accumulation of parabens in aquatic environments, development of powerful treatment techniques is underway to remove these compounds from water. From this point of view, emulsion liquid membrane (ELM) has gained much attention as an advanced extraction process for the removal of contaminants present in wastewater. Compared to conventional processes, the main advantages of ELM techniques are:

(a) simple operation, high extraction efficiency and scope of continuous operation;
(b) high interfacial area resulting in enhancement of mass transfer rate, especially at the inner membrane–water interface, due to the small size of the aqueous phase droplets;
(c) simultaneous performance of extraction (at the outer interface) and stripping (at the inner interface) in the same system, which implies that in practice there would be no need to construct separate circuits for stripping and extraction;
(d) capability of treating a variety of elements and compounds in industrial setting at a greater speed and with and a high degree of effectiveness, with varying contaminant concentrations and volume requirements;
(e) relatively low cost and energy conservation due to its cycling usage and non-dependence on heating consideration;

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(f) requirement of expensive extractant and organic solvent, necessary to form an oil membrane, in small quantities.

ELM processes are those involving a selective liquid membrane phase in which simultaneous extraction/stripping occurs. Separation is achieved by permeation of solute through this liquid phase from a feed phase to a receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. An ELM can be considered as a double emulsion consisting of three phases: the external, membrane and internal phases. Receiving phase is emulsified in an immiscible liquid membrane with the use of surfactants and high-speed agitation. Emulsion droplets range from 1 to 3 μm in diameter, thus providing good stability [14]. The emulsion is then dispersed in the feed solution with constant agitation and mass transfer from the feed to the internal receiving phase takes place. Once dispersed in the continuous phase, globules of the emulsion of a diameter of 100–2000 μm form [14]. Hence, the liquid membrane serves a dual purpose of permitting selective transfer of one or more components through it from external phase to internal droplets and vice versa and preventing mixing of external and internal phases. After the desired separation, the emulsion and the continuous phase are separated in a settling step. The final step in the ELM process involves breaking the emulsion, whereby the internal phase is then recovered and the membrane phase can be reused.

To the best of our knowledge, none of the earlier studies has evaluated the extraction of parabens from aqueous phase by ELM. Additionally, it is of considerable practical interest to examine the removal of parabens from complex matrices such as natural water, seawater and sewage water effluent. Therefore, the present investigation aims to the development of an ELM system for the extraction of PP from aqueous solutions. The influence of operating parameters such as surfactant and extractant concentrations, emulsification time, sodium sulfate concentration in external phase, salt type in external phase, internal phase concentration, type of internal phase, stirring speed, volume ratio of internal phase to membrane phase, treatment ratio, diluent type and PP initial concentration on the extraction of PP by ELM was evaluated. In addition, removal of PP by ELM from pure water, natural water, seawater and sewage water effluent was examined. The effect of internal phase concentration on the stripping of PP was studied.

Materials and methods

Materials

Analytically pure PP ($C_{10}H_{12}O_3$, Propyl 4-hydroxybenzoate) was purchased from Fluka and has been used as received. Stock solutions of PP were prepared by dissolving appropriate amount of compound in distilled water. PP feed solutions from a known amount of PP stock solution were diluted with distilled water to a given concentration. Though PP occur in concentrations ranging from ng/L up to μg/L in water, we chose higher concentrations to check the feasibility of the ELM process.

Trioctylphosphine oxide (TOPO) used as extractant in this work was of analytical grade and procured from Sigma-Aldrich.

All other chemicals used in this work were of the highest available purity and were purchased from Sigma-Aldrich.

Internal aqueous standard solutions were prepared by taking the required amount of alkaline solution (Na_2CO_3, NaOH or NH_4OH) in distilled water. The organic membrane phase was prepared by dissolving the appropriate amount of Span 80 as a surfactant in hexane under a gentle mixing by a magnetic stirrer. The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a high-speed disperser (Ultra-Turrax IKA T18) for a fixed mixing time. The volume ratio of internal aqueous phase to organic phase was changed from 1/2 to 2/1.

Extraction

The extraction of PP using emulsion liquid membrane involves three steps namely preparation of liquid membrane emulsion, extraction of the solute from feed by contacting the emulsion and separation of liquid emulsion from the external phase by settling.

The three-phase dispersion (W/O/W) was stirred with a mechanic stirrer (Junke & Kunkel RW20) at 300 rpm (except when the effect of stirring speed was studied). The agitator used was a 45° pitch four blades down pumping impeller (diameter 5 cm). A volume of the prepared W/O emulsion was added to 250 mL of external aqueous solution in a cylindrical thermostated vessel that was attached to an overhead mechanical stirrer. The content of the vessel was stirred in order to disperse the W/O emulsion in the external phase at variable speeds for different contact times to make the W/O/W double emulsions. The external phase solution was periodically sampled at various time intervals. The concentration of pollutant in the solutions was determined by a UV–vis spectrophotometer set at the wavelength corresponding to maximum absorbance of the studied pollutant. Each experiment was performed twice at least and the mean values were presented. The maximum standard deviation was 2%.

Extraction efficiency was calculated using the following equation:

$$\text{Extraction efficiency } (\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of pollutant in the external phase (mg/L) and C is the concentration of pollutant in the external phase at any time (mg/L).

Stripping

The double emulsion (W/O/W) is allowed to be spontaneously separated by gravity and the demulsification of W/O emulsion was achieved by adding 10 mL of 2-methyl-2-propanol (*tert*-butyl alcohol). The mixture (W/O emulsion and *tert*-butanol) was stirred and poured in a separating funnel. The membrane phase and the internal phase receiving the extracted PP were separated by gravity in the separating funnel. The concentration of PP in the internal aqueous phase was determined by using a UV–vis spectrophotometer.

Stripping efficiency was calculated using Eq. (2) determined by mass balance:

$$\text{Stripping efficiency } (\%) = \frac{C_{\text{Fint}} V_{\text{Fint}}}{C_{0\ \text{ext}} V_{0\ \text{ext}} - C_{\text{Fext}} V_{\text{Fext}}} \times 100 \quad (2)$$

where C_{Fint} is the final concentration of PP in the internal phase (mg/L), $C_{0\text{ext}}$ is the initial concentration of PP in the external phase (mg/L), C_{Fext} is the final concentration of PP in the external phase (mg/L), V_{Fint} is the final volume of the internal phase (mL), $V_{0\text{ext}}$ is the initial volume of the external phase (mL) and V_{Fext} is the final volume of the external phase (mL).

Results and discussion

Extraction mechanism

In a simple transport, solute passes through due to its solubility in liquid membrane. Permeation stops when concentration equilibrium is reached. The solute does not react chemically with liquid membrane and is supposed to be in the same form in the feed, membrane, and receiving phases.