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Extraction of 2-(4-hydroxyphenyl)ethanol from aqueous solution by emulsion liquid membranes

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Abstract

The extraction of 2-(4-hydroxyphenyl)ethanol (a phenolic alcohol, common in olive mill wastewater) from aqueous solution by emulsion liquid membranes was studied. The effect of the presence of additives in the membrane phase on solute permeation was tested. Two systems were selected to examine physical and reactive extraction of 2-(4-hydroxyphenyl)ethanol. The modelling of solute extraction was done by taking into account the mass transfer in the external phase and globule, and the reaction between the diffusing component and the stripping reagent. The batch extraction with, and without extractant in the membrane phase was carried out under various experimental conditions. The agreement between the calculated results and the experimental data was found satisfactory.

Keywords: Emulsion liquid membranes; 2-(4-Hydroxyphenyl)ethanol; Tyrosol; Phenols extraction; Modelling

1. Introduction

Almost all plants in the nature produce polyphenols, which are present in several foods, like olive oils, red wine and some fruits, and in the wastewater streams from industrial processes that use plants as raw material. In very low levels, the polyphenols are beneficial for the health due to their antioxidative properties. In higher levels, however, the polyphenols have toxic characteristics, and the wastewaters containing these pollutants must be treated. When the phenols content is less than 50 ppm, biological, chemical, or electrochemical oxidation processes can be used for their treatment. However, liquid–liquid extraction is the most economical non-destructive process at higher concentrations [1].

This work aims to study the extraction of one of the common polyphenols, 2-(4-hydroxyphenyl)ethanol, from aqueous solution by using emulsion liquid membranes. This phenolic alcohol, also known as tyrosol, and its derivative hydroxytyrosol, are the most important polyphenols in the olive oil, because of their antioxidative properties [2–5]. These compounds are two of the most significant polyphenols in olive mill wastewaters, whose treatment is a serious problem in Mediterranean countries.

Since the emulsion liquid membranes (ELM) were proposed by Li [6], this technology has demonstrated its potential for a variety of separation operations. Several studies have been published concerning the recovery and concentration of metals [7–10] and biochemical products [11–15] and the treatment of wastewaters containing metal ions and phenols [16–20].

ELM have been tried as an alternative to the conventional liquid–liquid extraction due to their advantages, such as large specific surface area for extraction, simultaneous separation and concentration in a single step. ELM is a three-phase dispersion system, where a primary emulsion is dispersed in a continuous phase, which is the phase to be treated. The liquid membrane separates the external continuous from the encapsulated phase. The solutes are transported through the membrane from the external phase and are concentrated in the internal phase droplets. After permeation, the emulsion is separated from the continuous phase and the splitting of the emulsion is usually done by applying high voltage.

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The liquid membrane consists of a diluent, a surfactant to stabilise the emulsion, and a carrier reagent (extractant) in the case of separation of solutes by chemical reaction. Thus, the solute is able to diffuse through the membrane phase due to its solubility (type I facilitated transport) or it reacts with the extractant molecule giving a solute–carrier complex that is carried from the external phase to the inner interface (type II facilitated transport).

The extraction of phenol with ELM is usually performed using membranes with aliphatic diluents. Besides the natural affinity to the organic solutes, these diluents exhibit a negligible solubility in the aqueous phase. However, the distribution ratio between the feed phase and the organic phase is not very high. Moreover, the distribution ratios between tyrosol (and other similar polyphenols) and aliphatic solvents are expected to be lower than in the case of phenol. Therefore, the presence of additives such as extractants in the membrane phase can be regarded as an important tool to enhance the extraction. Despite the work of Dobre et al. [21] reporting the extraction of phenol and *o*-cresol using sulphuric acid salts of trioctylamine as carrier, there is a lack in the literature concerning this subject. In the present work, it is thus intended to study the extraction of tyrosol using emulsion liquid membranes with, and without, extractant. The modelling of mass transfer is also an aim in this study.

2. Theory

Since the ELM technique was proposed, much attention has been paid to the modelling of the mass transfer. Cahn and Li [22] were the first researchers to propose a rough and simple model for phenol permeation. Matulevicius and Li [23] established a more realistic model, the spherical shell or hollow sphere model. However, the consumption rate of the internal reagent is not taken into account, because the diffusion path of phenol inside the emulsion globule increases as the internal reagent is consumed. Kopp et al. [24] adopted a more complex approach to model such behaviour. They assumed that conceptually there was an interface inside the emulsion globule that advanced towards the centre as the internal reagent was consumed. This model was the basis for the advancing front model proposed by Ho et al. [25]. These authors formulated the problem of mass transfer within an emulsion globule based on the advancing front approach that included both the spherical geometry and the depletion of solute in the external phase. Fales and Stroeve [26] and Stroeve and Varanasi [27] extended the advancing front model to include external resistance of mass transfer. In addition to external mass transfer resistance, Teramoto et al. [28] and Bunge and Noble [29] considered the reaction reversibility between the solute and the internal reagent. Yan et al. [30] adopted the improved advancing front model and developed a model for type I facilitated transport that also takes into account the reaction between the diffusing component and the internal reagent in the globules. Yan [31] proposed a model with a similar approach to describe the transport in MLE systems in which an extractant is incorporated into the membrane. This author assumed pseudo-first-order reactions, forward and stripping, since the concentration of carrier and internal reagent are in excess in most cases.

The extraction of phenols with membranes without carriers has been interpreted with satisfactory results by using advancing front models and reversible models [19]. However, further work is necessary concerning the reactive extraction of phenols with ELM, as stated above. In this work, a model of mass transfer that allows to predict the extraction for both type I and type II facilitated transports is presented. The present model is based on the improved advancing front model and takes into account the stripping reaction. The assumptions are the following ones.

1. The size distribution of emulsion globules and internal droplets are uniform and can be described by Sauter mean diameter.
2. No coalescence and redispersion occur between all emulsion globules.
3. There is no internal circulation and coalescence within the emulsion globule.
4. The diffusion in the emulsion globule can be described by the use of effective diffusivity. There is no transport resistance in the internal phase.
5. Emulsion breakage and swelling can be neglected.
6. At the globule surface, the concentrations in the membrane and external phases are in equilibrium.
7. Since far excess of internal reagent (sodium hydroxide) is used in most experiments, its concentration remains approximately constant for each run. Assuming a first order with respect to the membrane reagent, the stripping reaction rate per unit of internal interface is therefore given as

$$r_s = k'_s c_{II} \tag{1}$$

where c_{II} is the concentration of the solute in the membrane phase for type I transport, or the concentration of the organic solute–carrier complex for type II transport, and k'_s is an apparent rate constant given as

$$k'_s = k_s\, c^n_{NaOH(I)} \tag{2}$$

where k_s is the stripping reaction rate constant.

In the case of type II transport, the stoichiometry of the extraction of phenolic solute A with the extractant B is assumed to be expressed as

$$aA + bB \leftrightarrow C \tag{3}$$

where C is the organic solute–carrier complex, K_{ex} being the equilibrium constant given as

$$K_{ex} = \frac{c_C}{c^a_A c^b_B} \tag{4}$$

The set of equations describing the mass transfer for a batch-type process of ELM is presented as follows: