Journal of Hazardous Materials 192 (2011) 986–994

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Removal of phenols from aqueous solutions by emulsion liquid membranes

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ARTICLE INFO

*Article history:*
Received 3 March 2011
Received in revised form 26 May 2011
Accepted 27 May 2011
Available online 6 June 2011

*Keywords:*
Phenols removal
Emulsion liquid membranes
Tyrosol
*p*-Coumaric acid
Phenols mixture

ABSTRACT

The present study deals with the extraction of phenols from aqueous solutions by using the emulsion liquid membranes technique. Besides phenol, two derivatives of phenol, i.e., tyrosol (2-(4-hydroxyphenyl)ethanol) and *p*-coumaric acid (4-hydroxycinnamic acid), which are typical components of the effluents produced in olive oil plants, were selected as the target solutes. The effect of the composition of the organic phase on the removal of solutes was examined. The influence of pH of feed phase on the extraction of tyrosol and *p*-coumaric was tested for the membrane with Cyanex 923 as an extractant. The use of 2% Cyanex 923 allowed obtaining a very high extraction of phenols (97–99%) in 5–6 min of contact time for either single solute solutions or for their mixtures. The removal efficiency of phenol and *p*-coumaric acid attained equivalent values by using the system with 2% isodecanol, but the removal rate of tyrosol was found greatly reduced. The extraction of tyrosol and *p*-coumaric acid from their binary mixture was also analysed for different operating conditions like the volume ratio of feed phase to stripping phase (sodium hydroxide), the temperature and the initial concentration of solute in the feed phase.



## 1. Introduction

Phenol and its derivatives are often present in wastewaters from many industrial sources, such as coal gasification, petrochemical, wood products, paint, paper and agro-industries [1]. Phenols are very difficult to degrade biologically because they are toxic for microorganisms. Therefore, the discharge of any phenolic effluent into aquatic or land environment must be prohibited. For instance, olive mill wastewater (OMW), generated by the oil extraction industry, represents a severe environmental problem to Mediterranean countries due to its highly polluting organic load arising from phenols content. However, OMW is also regarded as a potent source of natural antioxidants, like tyrosol, hydroxityrosol and phenolic acids, the recovery of such compounds being a benefit [2].

The chemical composition of OMW is not constant, depending on the kind of the olive, its level of maturation and especially the extraction process of the olive oil. OMW contains water, 83–96%, organics, 3.5–15%, and minerals, 0.5–2% [3]. The organic material in OMW includes lipids, sugars, organic acids, amino acids and phenolic compounds (acids, alcohols and tannins). Phenolic acids are mainly syringic acid, *p*-hydroxyphenylacetic acid, vanillic acid, veratric acid, caffeic acid, protocathechuic acid, *p*-coumaric acid and cinnamic acid. Phenolic alcohols include tyrosol and hydroxityrosol. The concentration of these phenols in the OMW usually exceeds 10 g/L whereas the content of tannins is in the range of 8–16 g/L and lipids can reach 50 g/L [4].

The aim of the present work was to study the removal of phenols, i.e., phenol (as the reference compound), tyrosol (2-(4-hydroxyphenyl)ethanol) and *p*-coumaric acid (4-hydroxycinnamic acid), from aqueous solutions by using emulsion liquid membranes. These phenol derivatives were selected because they are typical components of the OMW and also can be beneficial to health due to their antioxidant properties [5]. Furthermore, these phenolic compounds were found chemically stable under basic medium, which allows the use of sodium hydroxide as the stripping reagent for their recovery [6].

The effluents containing phenols can be treated using physical–chemical processes [7–10], biological processes [11–13] or by electrochemical oxidation [14,15]. However, when the phenol content in the effluent is above 50 mg/L, solvent extraction is the most economic non-destructive process [16]. For instance, solvent extraction has been applied with good results for recovering phenol from industrial effluents [17–19]. Also, the emulsion liquid membrane (ELM) technique has been tested as an alternative to the conventional solvent extraction due to its specific advantages. In this technique, the extraction and the stripping steps occur in a single contactor and the carrier that is an expensive reagent can be used in small quantities. Besides, the interfacial area of mass

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doi:10.1016/j.jhazmat.2011.05.092

**Nomenclature**

| | |
|---|---|
| $A$ | surface area of emulsion globules ($m^2$) |
| $c$ | concentration of solute (mg/L) |
| $N_{extr.}$ | extraction rate per unit area of interface (g/($m^2$ s)) |
| $V$ | volume of phase (L) |

*Subscripts*

| | |
|---|---|
| I | denotes internal stripping phase (phase I) |
| II | denotes organic membrane phase (phase II) |
| III | denotes external feed phase (phase III) |
| 0 | denotes initial value |

transfer is very high and the kinetics of stripping is particularly favoured because of the small size of the internal droplets of receiving phase.

ELM is a liquid membrane based process initially proposed by Norman Li [20], where a primary emulsion is dispersed in the feed phase to be treated. In the actual case, it is necessary to prepare a water-in-oil emulsion. Thus, the emulsion consists of an aqueous receiving phase (i.e., sodium hydroxide solution), which is encapsulated in the organic phase (membrane phase). The membrane phase consists of a diluent and a surfactant to stabilize the emulsion, besides other possible additives such as a carrier reagent (extractant) and a modifier. After permeation, the emulsion is separated from the raffinate and is broken up for separating the enriched internal phase (i.e., with phenolates) from the membrane phase, which can be reused for successive extractions.

In the literature, there are several studies on the extraction of phenolic compounds from aqueous phases by using ELM [21–31]. All these works revealed that such process is very efficient, but they simply deal with single solute solutions. Regarding the permeation of phenol and its derivatives using mixtures of compounds, the information is already scarce. Luan and Plasier [32] applied the ELM technique to remove nitro, dinitro and trinitrophenols from a real wastewater. They showed that under the suitable operating conditions (concentration of surfactant in the membrane, concentration of NaOH in the internal phase, pH and phase ratios) it was possible to reduce the concentration of nitrophenols from 1005 mg/L to less than 1 mg/L and from 6700 mg/L to 2.2 mg/L. Park et al. [33] studied the permeation of phenols by ELM using a Taylor vortex column instead of a conventional mixing reactor to minimize the rupture phenomena [34]. The process was found to be highly efficient (over 96%) for either single solute or their mixtures (chlorophenols, nitrophenols), nevertheless the tests with the mixtures showed a slight retardation in the mass transfer rate due to the competition between the solutes.

In this study the performance of the ELM process was also evaluated for the mixtures of target compounds under various operating conditions. The success of this process will allow the recovery of valuable antioxidants from a relatively cheap raw-material, i.e. the OMW, and the research will provide important data for the treatment of phenolic wastewaters.

## 2. Experimental

The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50) at 7000 rpm during 900 s. A 0.2 M NaOH solution was used as internal stripping phase in most experiments. A predetermined volume ratio of 1.5:1 was maintained for the organic phase to the internal stripping phase. The organic phase included a isoparaffinic hydrocarbon solvent with an aromatic content lower than 0.1% (ShellSol T, Shell Chemical Ltd.) and 2 wt.% of a non-ionic surfactant (polyamine ECA 4360J, Essochem Europe Inc.). In some experiments, 2 wt.% of a modifier (isodecanol, Riedel-de-Haën) and/or 2 wt.% of an extractant were added to the organic phase. The extractants tested were the tertiary amines, Hostarex A327 (Clariant Chemical Co.) and Alamine 336 (Cognis), the quaternary ammonium salt Aliquat 336 (Cognis) and Cyanex 923 (Cytec), which is a mixture of four trialkylphosphine oxides. The diluent, surfactant and extractant reagents were used as supplied.

The emulsion was dispersed in 800 mL of the external aqueous phase, which contained the phenols to be extracted. The solutes used were of high purity analytical grade (Merck). In some experiments, the pH of the external phase was adjusted by adding $H_2SO_4$ or NaOH. The three-phase dispersion was stirred for 360–1200s with a stainless steel paddle (45 mm × 45 mm × 1 mm) in a baffled glass reactor with 84 mm internal diameter and 1 L capacity, immersed in a water bath with temperature control. The stirring speed was kept at 300 rpm, which was previously optimized to achieve complete dispersion and minimize the breakage of the emulsion.

During permeation, samples were periodically taken for analysis. Also, several photographs were taken for measuring the Sauter mean diameter of the emulsion globules under the operating conditions tested. A Nikon F90X camera attached to a Nikon PB-6 and to a micro Nikkor 60 mm f/2.8D lens was used for this purpose. A Nikon SB-26 flash was used as light source. The size of the emulsion globules was obtained by using the KS100 image analysis software (Kontron Elektronik GmbH) after the digitalization of the negatives (Epson FilmScan200).

After permeation, the phases were settled and the emulsion was broken in a coaxial electrocoalescer. Demulsification was performed by applying a 2 kV and 3–6 kHz electric field. The concentration of each phenolic compound in both the aqueous phases was measured in a Dionex HPLC system including a Chromeleon software and equipped with a GINA$^{50}$ Autosampler, a P580 PUMP, a UVD340S UV–visible diode array detector and a LiChrospher 100RP18 (5 μm) column. The HPLC analyses were performed using an aqueous solution with 1% (v/v) *o*-phosphoric acid and 40% (v/v) acetonitrile as the mobile phase, with a flow rate of 0.7 mL/min. The column employed (RP18 Reverse Phase) was maintained at 25 °C. The usual channels 254, 280, 320 and 360 nm were tested. All the reagents used in the analysis had a high purity. In the case of simple solutions, containing a single phenolic compound, a double-beam visible-UV spectrophotometer Hitachi U2000 was used to measure the concentration in the aqueous phases. The analyses of phenol, tyrosol and *p*-coumaric acid were performed at 270, 275 and 308 nm, respectively, under acidic medium.

Distribution data were obtained by contacting the external aqueous phase with the organic phase (with 0–2 wt.% of surfactant) for at least 16 h. The agitation of the phases was kept at a low level (i.e., 70–90 rpm) and was performed by an orbital shaker with temperature control.

## 3. Results and discussion

### 3.1. Effect of membrane composition

The extraction of phenol from aqueous effluents was found to be easily accomplished using emulsion systems with membranes containing only an aliphatic diluent and an emulsifying agent [25,31,35]. Therefore, the same approach was tried to check the removal of tyrosol and *p*-coumaric acid from aqueous solution. The results obtained are presented in Fig. 1. As can be observed, these compounds showed a different behaviour from the one exhibited by phenol. In contrast to phenol, the extraction of tyrosol and

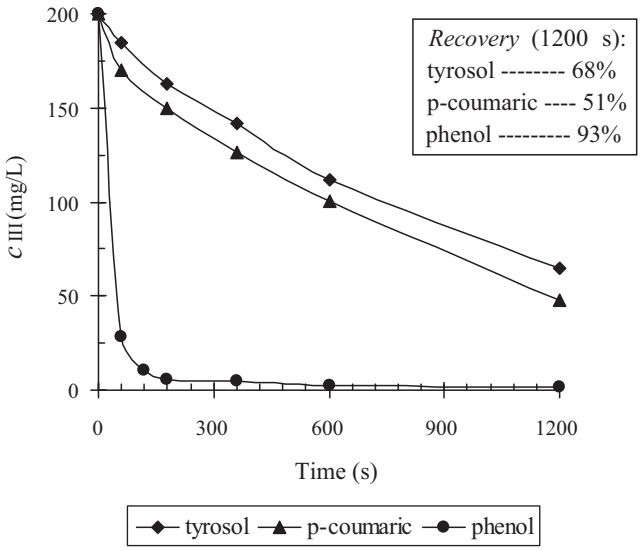


**Fig. 1.** Removal of phenols by ELM. Feed phase: 200 mg/L of solute, natural pH (phenol: 6.1, tyrosol: 6.5, *p*-coumaric acid: 3.7); organic phase: ShellSol T, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

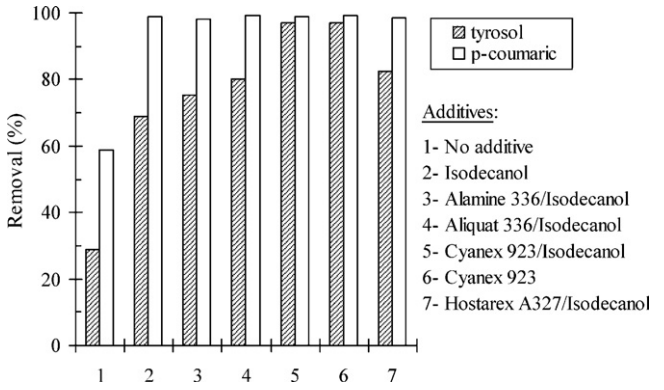


**Fig. 2.** Effect of additives (2 wt.%) in the organic phase on the percentage removal of tyrosol and *p*-coumaric acid. Feed phase: 200 mg/L of solute, natural pH (tyrosol: 6.5, *p*-coumaric acid: 3.7); internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C. Permeation time: 360 s.

*p*-coumaric acid with ShellSol T was very slow. The removal of phenol from a feed solution with 200 mg/L solute achieved 99% after 600 s and was 97% after 180 s. On the other hand, the removal of tyrosol and *p*-coumaric acid merely attained 68 and 76%, respectively, after 1200s of permeation. These results might be related to the hydrophobicity of these substituted phenols, which should be lower than that of phenol. In fact, the measurement of the partition coefficients for the system octanol/water indicated the following values for the extraction of phenol, tyrosol and *p*-coumaric acid: 30, 4.2, and 20, respectively. These data support the low extraction rate of tyrosol but the relatively high partition coefficient of *p*-coumaric acid does not corroborate the results depicted in Fig. 1. Regarding the recovery obtained, which was calculated from the concentration ratio $c_{I,final}/c_{III,0}$ multiplied by the volume ratio $V_I/V_{III}$, it indicates that some accumulation of solute occurred in the membrane. In particular, the recovery of *p*-coumaric acid was quite lesser than the corresponding removal, which can be ascribed to an additional resistance due to stripping.

The results obtained with the simple organic phase, constituted by the diluent and the surfactant, led us to the introduction of additional reagents with the purpose of improving the extraction kinetics of phenols, like tyrosol and *p*-coumaric acid. The effect of the presence of the modifier isodecanol and/or a reagent as an extractant in the organic phase on the removal of phenols is presented in Fig. 2. The partition data were also obtained to examine the affinity of the target compounds for the different organic phases tested. The results are listed in Table 1.

As shown in Fig. 2, the addition of isodecanol and/or an extractant in the membrane increased significantly the percentage removal of phenols, particularly in the case of the *p*-coumaric acid. In fact, the simple introduction of isodecanol in the membrane allowed achieving a very high removal of this substituted phenol, which was equivalent to the one attained with the extractant Cyanex 923 (i.e., 99%). It should be also emphasized that a decrease of 30–40% in the size of the emulsion globules was noticed for the extraction of phenols, when the alcohol was added to the membrane with diluent and surfactant, which increased the interfacial area of mass transfer.

Regarding the partition data, the system with Cyanex 923 was the most favourable for the extraction of *p*-coumaric acid and tyrosol, which supports the high removal of these compounds. It should be emphasized that the distribution ratio of *p*-coumaric acid with the diluent and the surfactant is also relatively large. As stated in a previous study [26], the acidic character of this substituted phenol seems to be recognized by the surfactant ECA 4360J, which may act as an extractant. Therefore, the slow kinetics of *p*-coumaric acid extraction displayed in Fig. 1 was not expected. The addition of isodecanol to the membrane did not influence the equilibrium but was found to enhance the kinetics of extraction with the polyamine. Other authors also pointed out the similar effect of isodecanol on the extraction kinetics of citric acid with trioctylamine [36].

Besides the magnitude of mass transfer and kinetics, there are other factors to be considered for selecting the most adequate membrane phase of the ELM system, namely the demulsification time and the occurrence of non-ideal phenomena, such as water transport and break-up, which must be minimized. The system with Cyanex 923 was found the most attractive while taking into account all these aspects. It is noteworthy to mention that some breakage of the emulsion was observed, but it was kept below 5%.

**Table 1**
Effect of additives (2 wt.%) in the organic phase on the distribution ratio of tyrosol and *p*-coumaric acid.

| Additives | Tyrosol Without ECA 4360J | Tyrosol With ECA 4360J | *p*-Coumaric acid Without ECA 4360J | *p*-Coumaric acid With ECA 4360J |
|---|---|---|---|---|
| – | <0.005[b] | 0.010 | 0.022[a] | 10[a] |
| Isodecanol | 0.007 | 0.010[b] | 0.056[a] | 10[a] |
| Alamine 336 + isodecanol | <0.005 | 0.005 | 0.40 | 3.7 |
| Aliquat 336 + isodecanol | 0.20 | 0.26 | 6.7 | 23 |
| Cyanex 923 + isodecanol | 0.10 | 0.12 | 6.4 | 18 |
| Cyanex 923 | 0.45 | 0.43 | 70 | 22 |
| Hostarex A327 + isodecanol | <0.005 | <0.005 | 0.20 | 3.6 |

Aqueous phase: 200 mg/L of solute, natural pH; A/O = 1:1; 25 °C.
[a] From [26].
[b] From [27].

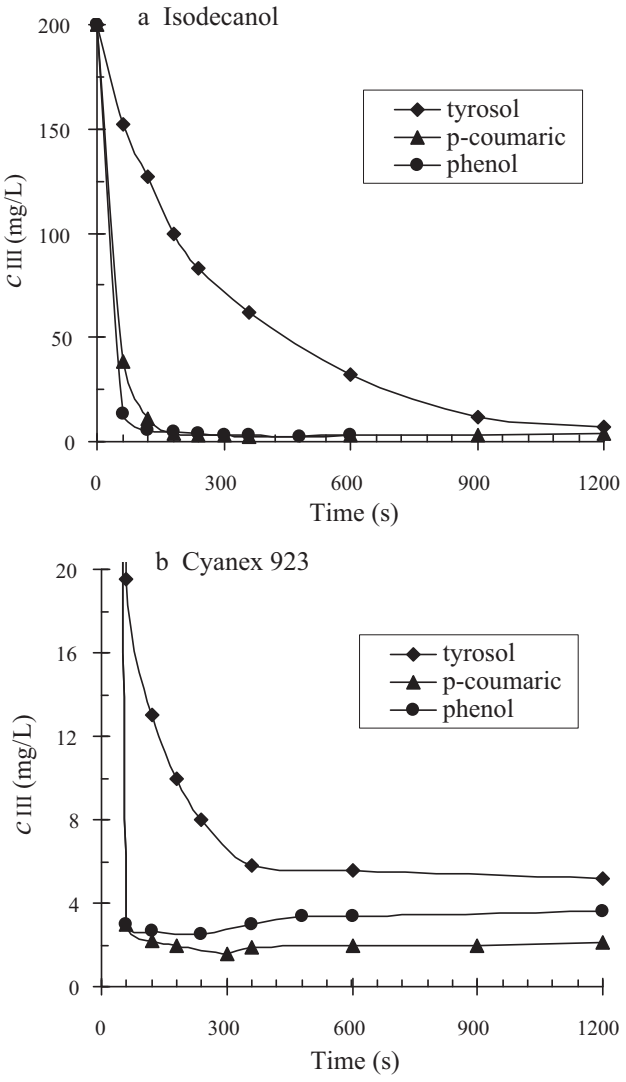


**Fig. 3.** Effect of permeation time on the removal of phenols for the organic systems: (a) 2 wt.% isodecanol, 2 wt.% ECA 4360J and (b) 2 wt.% Cyanex 923, 2 wt.% ECA 4360J. Feed phase: 200 mg/L of solute, natural pH; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

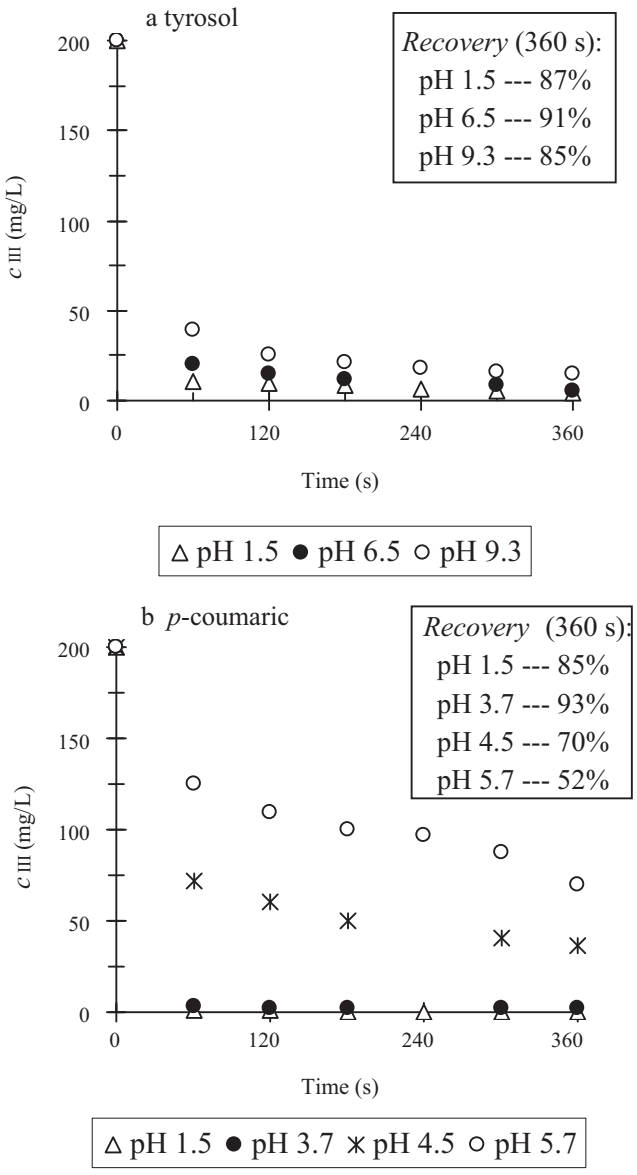


**Fig. 4.** Effect of pH of the feed phase on the extraction of tyrosol (a) and *p*-coumaric acid (b). Feed phase: 200 mg/L of solute (tyrosol: natural pH 6.5; *p*-coumaric acid: natural pH 3.7); organic phase: 2 wt.% Cyanex 923, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

Thus, the two organic systems were chosen to pursue the present study, i.e., the membrane with Cyanex 923 and the membrane with isodecanol because of its simplicity.

Fig. 3 shows the depletion of tyrosol, *p*-coumaric acid and phenol along with the permeation time for the selected organic systems. Like phenol, the extraction rate of *p*-coumaric acid was very high in the earliest stage of permeation for both systems. The maximum efficiency of *p*-coumaric acid removal (i.e., ~99%) was achieved at 300–360 s with isodecanol and with Cyanex 923. The removal of phenol also reached 99% after 360 s with isodecanol, whereas 60–120 s of contact time allowed attaining a similar extraction using Cyanex 923. Regarding tyrosol, which is very less hydrophobic, its removal was 97% at 360 s for the system with Cyanex 923 and no significant improvement was noticed with the increase in the permeation time. On the other hand, the removal of this phenolic alcohol with isodecanol reached 96% only at the end of 1200s.

### 3.2. Effect of pH of feed phase

The compounds tyrosol and *p*-coumaric acid differ essentially in their acidity. Tyrosol is an alcohol and its acidity is similar to that of phenol ($pK_a \approx 10$); *p*-coumaric acid is much more acidic ($pK_{a1} \approx 4.5$). Therefore, the effect of pH of the feed phase on the extraction of these phenols using single solute solutions was examined. The results obtained are illustrated in Fig. 4. Fig. 5 displays the distribution ratio for both phenols against the equilibrium pH. As can be observed, the pertraction of tyrosol and *p*-coumaric acid with Cyanex 923 was affected by the pH of the external aqueous phase, the effect being particularly pronounced for the acidic phenol. In terms of equilibrium, the extraction of tyrosol with Cyanex 923 is strongly decreased for pH above 8 (see Fig. 5) reflecting the growing dissociation of this compound. Similar behaviour is exhibited by phenol [28]. So, the worst results achieved at pH 9.3 are easily explained. On the other hand, the decrease in pH from natural pH 6.5 to pH 1.5 was found to increase the extraction rate of tyrosol with Cyanex 923. Also, the extraction rate of *p*-coumaric acid increased for natural pH 3.7 to pH 1.5. Above natural pH, the extraction rate was significantly reduced due to the rise in the concentration of the anionic species, with a lesser affinity for the extractant.

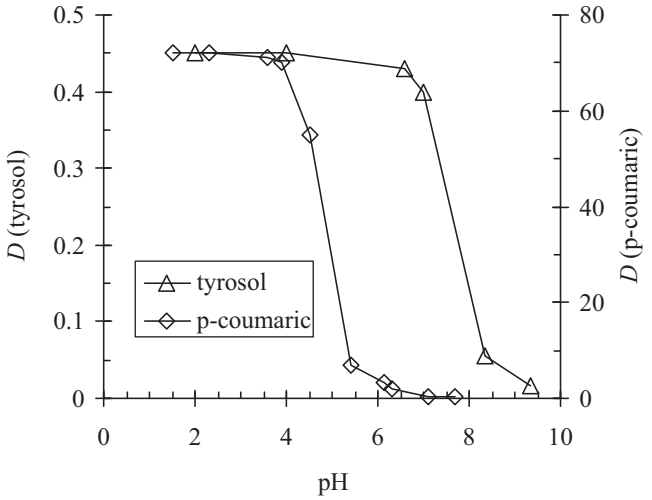


**Fig. 5.** Effect of the equilibrium pH on the distribution ratio $D$ of tyrosol and $p$-coumaric acid. Aqueous phase: 200 mg/L solute; organic phase: 2 wt.% Cyanex 923 (0.04 M); A/O = 1:1; 25 °C.

The enhancement in the extraction kinetics at pH 1.5 should be related to the increase in the interfacial area of mass transfer. Table 2 presents the values of the Sauter mean diameter of the emulsion globules for the experiments conducted at different pHs. It was found that the globules diameter was reduced to about the half when the pH of the natural solution (deionized water plus solute) was adjusted to 1.5 by adding $H_2SO_4$. The adjustment of pH with NaOH also caused a decrease in the size of globules, although quite small. In the particular case of low pH, the small size of globules should be caused by a possible interaction between sulphuric acid and the surfactant polyamine, which led to the decrease in the interfacial tension. A similar effect was noticed using the system isodecanol/ECA 4360J/ShellSol T for the extraction of tyrosol at pH lower than the natural pH [27]. On the other hand, the decrease in the size of the globules at pH 1.5 favoured the occurrence of non-ideal phenomena, leading to the dilution of the internal phase with the consequent loss of solute recovery.

**Table 2**
Effect of pH of the feed phase on the Sauter mean diameter of globules (see operating conditions of ELM experiments in Fig. 4); (tyrosol: natural pH 6.5; $p$-coumaric acid: natural pH 3.7).

| Compound | Sauter mean diameter, $d_{32} \times 10^4$ m | | | | | |
|---|---|---|---|---|---|---|
| | pH 1.5 | pH 3.7 | pH 4.5 | pH 5.7 | pH 6.5 | pH 9.3 |
| Tyrosol | 2.33 | – | – | – | 4.36 | 3.86 |
| $p$-Coumaric acid | 2.36 | 4.90 | 4.80 | 4.50 | – | – |

### 3.3. Single solute solutions vs mixtures of phenols

The performance of the liquid membrane process was evaluated using single solute solutions with phenol, tyrosol and $p$-coumaric

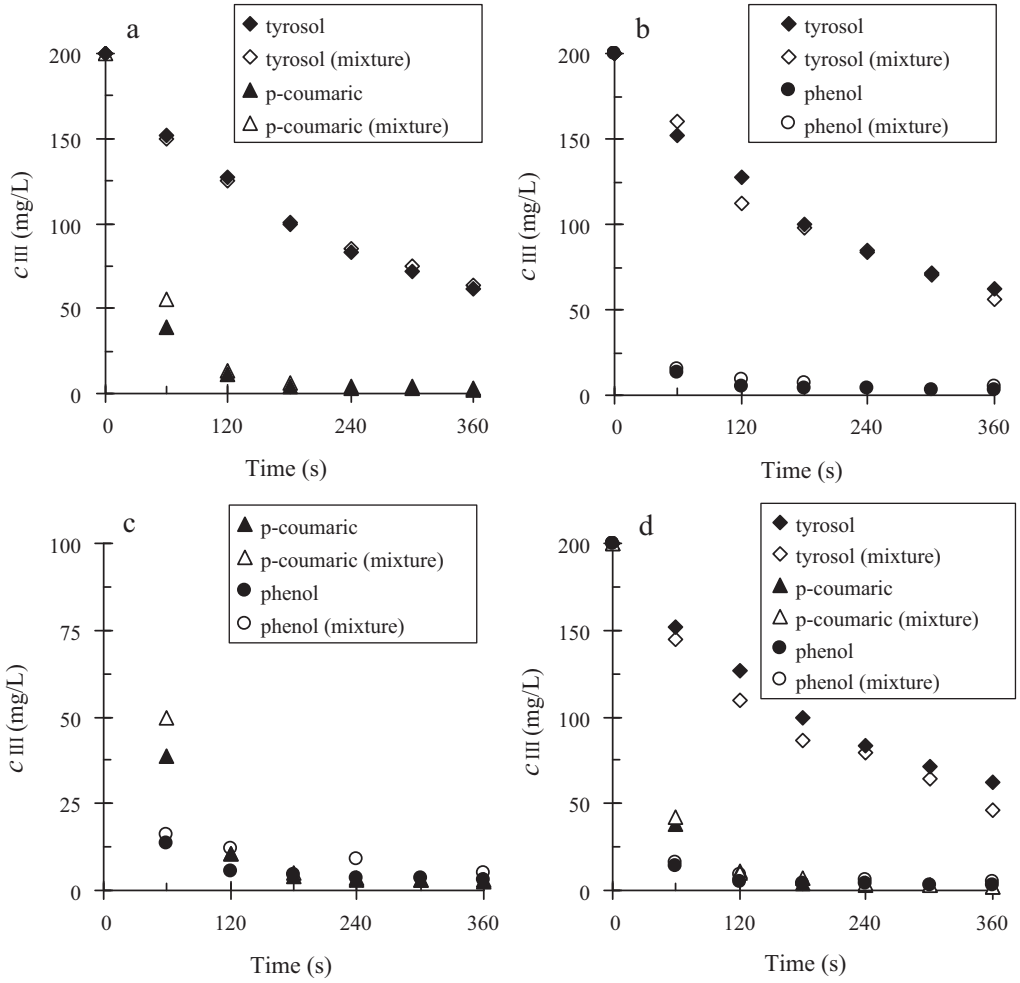


**Fig. 6.** Extraction of phenols from single solute solutions and mixtures: (a), (b), (c) binary mixtures; (d) ternary mixture. Feed phase: 200 mg/L of each solute, natural pH; organic phase: 2 wt.% isodecanol, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

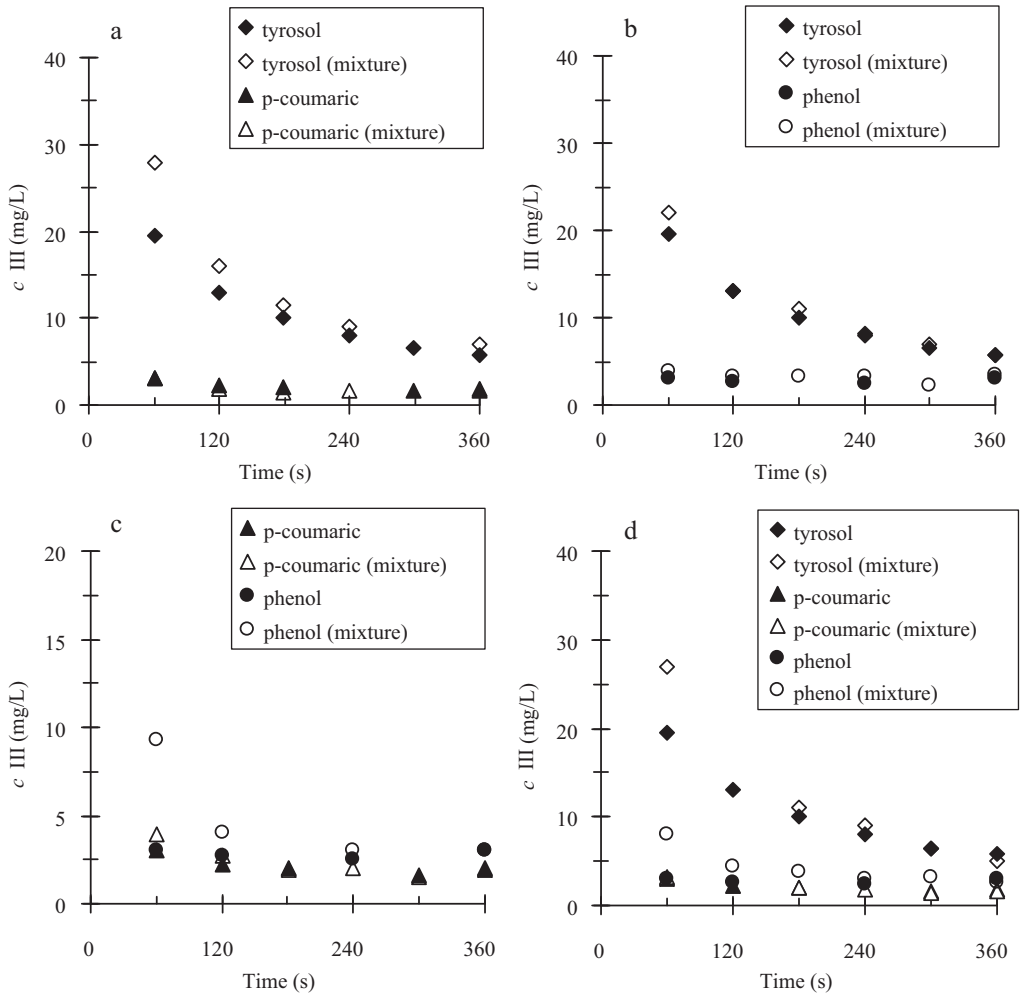


**Fig. 7.** Extraction of phenols from single solute solutions and mixtures: (a), (b), (c) binary mixtures; (d) ternary mixture. Feed phase: 200 mg/L of each solute, natural pH; organic phase: 2 wt.% Cyanex 923, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

acid and also using mixtures of the target compounds. Fig. 6 displays the comparison of the removal rates of these phenols when present individually in solution and when present in mixtures (binary and ternary) for the selected organic system with isodecanol. The equivalent results obtained with the extractant Cyanex 923 are presented in Fig. 7.

As shown, the depletion of the concentration for each solute in mixture followed the trend very similar to that obtained with the single solute solution. The main difference was the concentration of the first sample (i.e., 1 min), which was generally higher when the phenols were processed as a mixture. To discern this effect, the initial extraction rate was calculated from the experimental data and divided by the specific interfacial area (surface area of globules/feed phase volume). The values of the Sauter mean diameter of globules are listed in Table 3. The initial extraction rate per unit area of interface, $N_{extr.,0}$, is given in Table 4.

Regarding the system with isodecanol, the extraction of the less hydrophobic solute, tyrosol, was found to be retarded in the presence of the other phenols, which had higher affinity to the membrane phase. In fact, the initial flux of tyrosol entering in the membrane in the case of mixtures was about 70% of the one estimated for single solution. On the other hand, the values of $N_{extr.,0}$ for phenol and *p*-coumaric acid are quite similar, when mixtures are compared with single solute. Park et al. [33] also noticed the reduction of the initial extraction rate due to competitive effect of solutes on the mass transfer.

The use of the extractant Cyanex 923 against isodecanol made the initial extraction rate per unit area of interface higher for tyrosol and *p*-coumaric acid, whereas phenol was not significantly affected. It is worth mentioning that Cyanex 923 reacts with the target solutes facilitating the transport, but also interacts with the surfactant polyamine. On the other hand, this additive also acts as a

**Table 3**
Sauter mean diameter of the emulsion globules: single solute solutions and mixtures of phenols.

| System | Sauter mean diameter, $d_{32} \times 10^4$ m | | | | | | |
|---|---|---|---|---|---|---|---|
| | Tyrosol | *p*-Coumaric | Phenol | Tyrosol + *p*-coumaric | Tyrosol + phenol | *p*-Coumaric + phenol | Tyrosol + *p*-coumaric + phenol |
| Isodecanol | 6.90 | 4.32 | 5.20 | 4.44 | 5.90 | 4.65 | 4.60 |
| Cyanex 923 | 4.36 | 4.90 | 4.80 | 4.30 | 4.32 | 4.90 | 4.81 |

Feed phase: 200 mg/L of each solute, natural pH; $V_{III}/V_I = 10$; 25 °C; isodecanol system: $A/V_{III} = (2.2–3.4) \times 10^3$ m$^2$/m$^3$; Cyanex 923 system: $A/V_{III} = (3.1–3.5) \times 10^3$ m$^2$/m$^3$.

**Table 4**
Initial extraction rate per unit area of interface (operating conditions: see Figs. 6 and 7; data of Sauter mean diameter: see Table 3).

| System | Initial extraction rate/unit area of interface, $N_{extr.,0} \times 10^4$ g/(m$^2$ s) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Single | | | Tyrosol + *p*-coumaric | | Tyrosol + phenol | | *p*-Coumaric + phenol | | Tyrosol + *p*-coumaric + phenol | | |
| | Tyrosol | *p*-Coumaric | Phenol | Tyrosol | *p*-Coumaric | Tyrosol | Phenol | *p*-Coumaric | Phenol | Tyrosol | *p*-Coumaric | Phenol |
| Isodecanol | 3.7 | 7.8 | 11 | 2.5 | 7.2 | 2.6 | 12 | 7.8 | 9.5 | 2.8 | 8.1 | 9.4 |
| Cyanex 923 | 8.7 | 11 | 11 | 8.2 | 9.4 | 8.5 | 9.4 | 11 | 10 | 9.2 | 10 | 10 |

carrier of *p*-coumaric acid, which can support the high fluxes found for this solute.

The results showed that Cyanex 923 was a potential extractant for the removal of the target phenols from their mixtures. The removal of tyrosol was about 97% after 300–360 s of permeation, while the removal of *p*-coumaric acid and phenol achieved 99%. Also, *p*-coumaric acid and phenol were efficiently removed from mixtures (i.e., 98–99%) using the system with isodecanol. In the case of tyrosol, its removal was in the range of 68–77% after 360 s, but it might be higher with increasing permeation time.

The simple system with isodecanol was further exploited in examining several factors that can influence the performance of ELM. Therefore, several experiments were conducted to study the effects of the volume ratio of feed phase to stripping phase, the temperature and the initial concentration of solute on the removal of tyrosol and *p*-coumaric acid from binary mixture. The concentration of the stripping reagent was also tested in the range of 0.2–0.5 M, but was decided to be kept at 0.2 M to minimize the occurrence of non-ideal phenomena. The results are presented in the following sections.

### 3.4. Effect of the volume ratio of feed phase to stripping phase

The volume ratio of feed phase to stripping phase plays an important role in the treatment of effluents. As shown in Fig. 8, the extraction rate of tyrosol and *p*-coumaric acid decreased with the increase in the ratio $V_{III}/V_I$, which was caused by the reduction in the hold-up of the dispersed phase, i.e. the emulsion globules. This reduction decreases the interfacial area of mass transfer and decreases the capacity of the internal stripping phase for trapping solutes simultaneously. In fact, increasing the ratio $V_{III}/V_I$ from 10 to 40, decreased the Sauter mean diameter from 0.44 to 0.32 mm but the interfacial area per unit volume of feed phase decreased from $3.4 \times 10^3$ to $1.2 \times 10^3$ m$^2$/m$^3$.

The initial extraction rates per unit area of interface were also estimated from the experimental data displayed in Fig. 8. It was found nearly constant (i.e., 1.7–2.5 $\times 10^{-4}$ g/(m$^2$ s)) for tyrosol under the conditions tested. In the case of *p*-coumaric acid, it varied from $7.2 \times 10^{-4}$ g/(m$^2$ s) at $V_{III}/V_I = 10$ to $1.1 \times 10^{-3}$ g/(m$^2$ s) at $V_{III}/V_I = 40$. The initial fluxes entering in the membrane were also determined using single solute solutions for comparison. The values were found to be in the range of 3.5–3.7 $\times 10^{-4}$ g/(m$^2$ s) for tyrosol and 7.8–9.7 $\times 10^{-4}$ g/(m$^2$ s) for *p*-coumaric acid. Thus, the depletion of solutes in mixture and single solution followed a similar trend against the treatment ratio $V_{III}/V_I$, but tyrosol was retarded in the presence of the other phenol, which corroborates the findings of the preceding section.

### 3.5. Effect of temperature

Fig. 9 depicts the effect of temperature on the removal of tyrosol and *p*-coumaric acid from binary mixture. As observed, increasing temperature in the range of 17–35 °C increased the extraction rate of each solute. The flux entering in the membrane was found to rise from $1.5 \times 10^{-4}$ to $2.8 \times 10^{-4}$ g/(m$^2$ s) for tyrosol, whereas it varied from $6.3 \times 10^{-4}$ to $8.3 \times 10^{-4}$ g/(m$^2$ s) for *p*-coumaric acid over the range of temperatures tested. It is worth noting that a similar trend was noticed when single solute solutions were processed. In the latter case, the flux entering in the membrane was $2.2 \times 10^{-4}$ and $6.7 \times 10^{-4}$ g/(m$^2$ s) for tyrosol and *p*-coumaric acid, respectively, at 17 °C, and augmented to $4.7 \times 10^{-4}$ and $8.4 \times 10^{-4}$ g/(m$^2$ s),

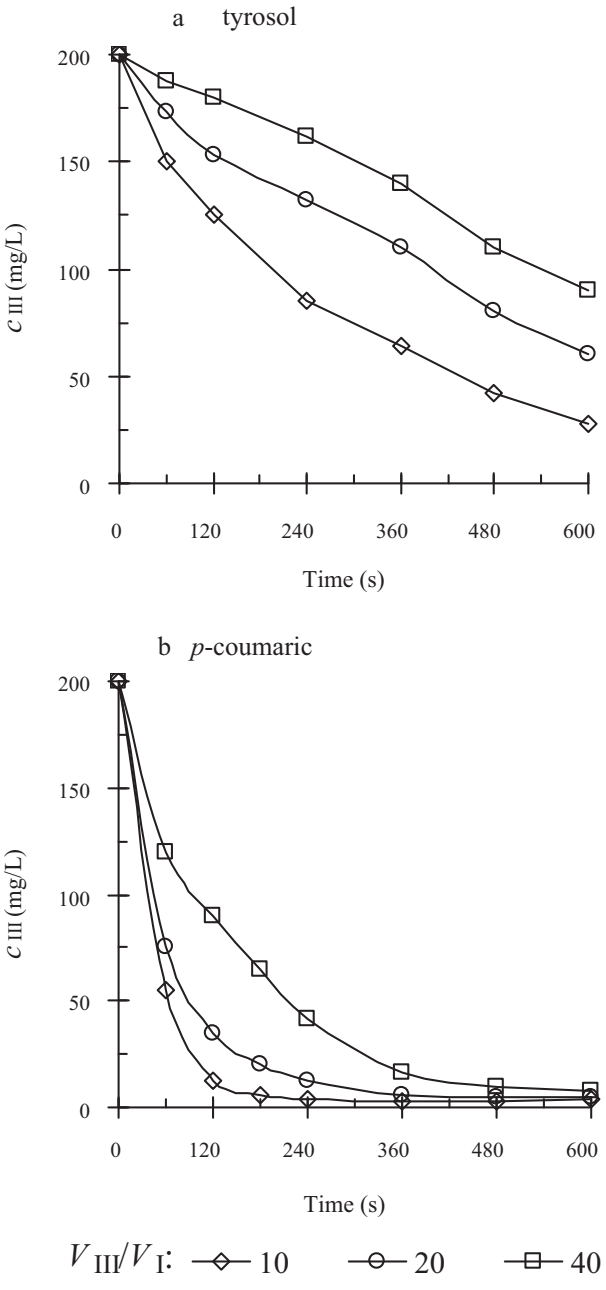


**Fig. 8.** Effect of the volume ratio of feed phase to stripping phase on the extraction of tyrosol and *p*-coumaric acid from binary mixture; (a) tyrosol, (b) *p*-coumaric acid. Feed phase: 200 mg/L of each solute, natural pH 3.7; organic phase: 2 wt.% isodecanol, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; 25 °C.

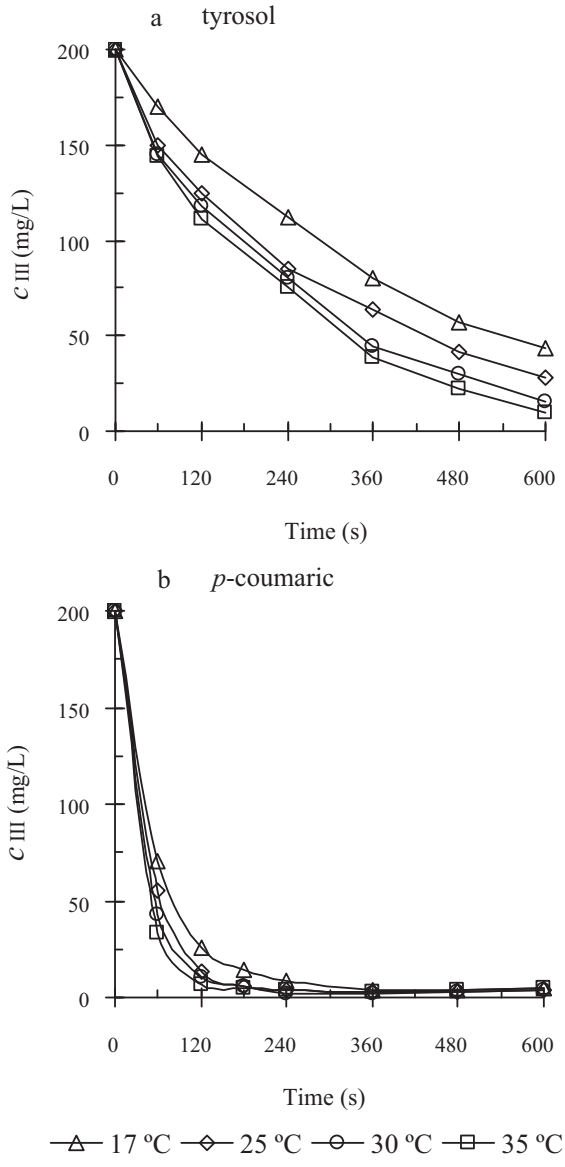


**Fig. 9.** Effect of temperature on the extraction of tyrosol and *p*-coumaric acid from binary mixture; (a) tyrosol, (b) *p*-coumaric acid. Feed phase: 200 mg/L of each solute, natural pH; organic phase: 2 wt.% isodecanol, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$.

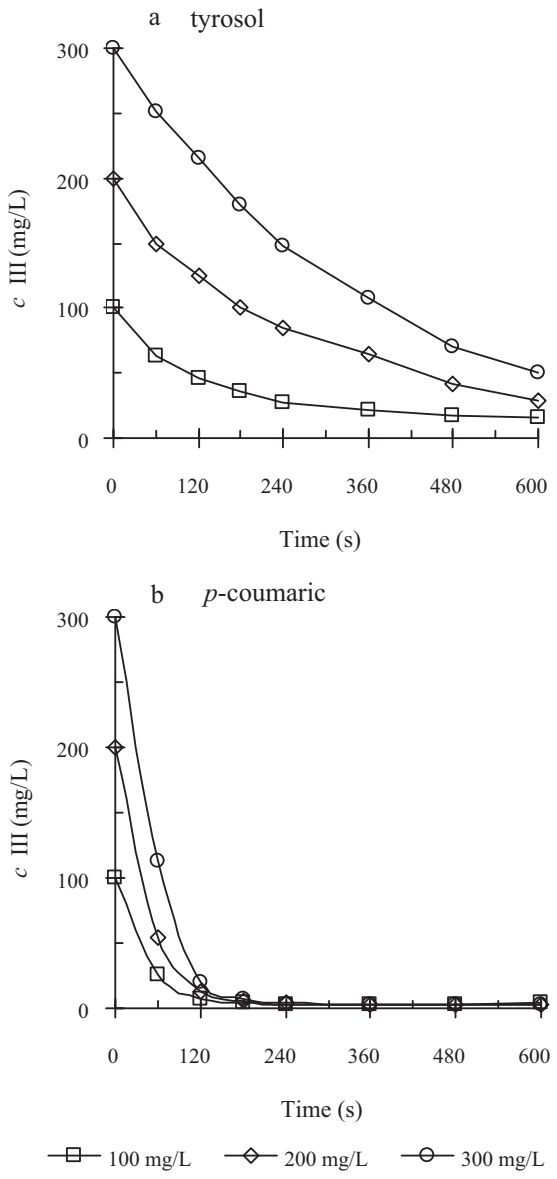


**Fig. 10.** Effect of the initial concentration of solute in the feed phase on the extraction of tyrosol and *p*-coumaric acid from binary mixture; (a) tyrosol, (b) *p*-coumaric acid. Feed phase: 100, 200 and 300 mg/L of each solute, natural pH; organic phase: 2 wt.% isodecanol, 2 wt.% ECA 4360J; internal phase: 0.2 M NaOH; $V_{III}/V_I = 10$; 25 °C.

respectively, when the temperature was 35 °C. Since the effect of temperature on the equilibrium was found to be negligible for these conditions and taking into account the results of modelling performed in previous studies [26,27] the increase in the extraction rate was attributed to the kinetics of stripping that was faster with increasing temperature. Also, the diffusivity of solute through the membrane increased with temperature.

### 3.6. Effect of solute concentration in the feed phase

The effect of the initial concentration of solute in the feed phase on the extraction of tyrosol and *p*-coumaric acid is illustrated in Fig. 10. It is observed that the extraction rate of tyrosol did not change significantly in the range of 100–300 mg/L solute, the degree of removal being decreased when the initial concentration increased. The initial extraction rate per unit interfacial area was evaluated to be $1.9–2.6 \times 10^{-4}$ g/(m$^2$ s) for tyrosol. On the other hand, the kinetics of extraction was found more dependent on the initial concentration of *p*-coumaric acid. The degree of solute removal from 100 to 200 mg/L solution was approximately constant in the earliest stage of permeation and was lowered when the initial concentration augmented to 300 mg/L. Regarding the initial extraction rate per unit interfacial area, it was determined to be $3.7 \times 10^{-4}$, $7.8 \times 10^{-4}$ and $9.8 \times 10^{-4}$ g/(m$^2$ s) for 100, 200 and 300 mg/L solute, respectively. When the concentration of solute increases, the length of the diffusional path through the emulsion globule increases, since the internal droplets in the peripheral region are saturated more rapidly. So, more strippant reagent is necessary to provide a larger capacity of the emulsion for extraction.

In addition, the effect of solute concentration in the feed phase was examined for the single component system. The initial extraction rate per unit interfacial area was found to be $2.0–4.8 \times 10^{-4}$ g/(m$^2$ s) for 100–300 mg/L tyrosol, whereas it was $4.0–12 \times 10^{-4}$ g/(m$^2$ s) for 100–300 mg/L *p*-coumaric acid. The results obtained corroborate the former statement related to the

retardation of mass transfer rate of tyrosol due to competitive transport.

## 4. Conclusions

The results obtained are quite promising for the application of the emulsion liquid membranes in the treatment of aqueous solutions containing phenol and its derivatives like tyrosol and *p*-coumaric acid. The process was found to be highly efficient for either single solute solutions or their mixtures. The use of 2% Cyanex 923 in the membrane allowed attaining 97–99% removal of phenols (200 mg/L of each solute) after 5–6 min of permeation. A similar performance regarding the removal of phenol and *p*-coumaric acid was obtained using a membrane with 2% isodecanol, while the removal of tyrosol was more difficult. The initial extraction rates per unit interfacial area were evaluated for both membrane systems and revealed that tyrosol was retarded in the presence of the other phenols when the membrane with isodecanol was used.

The simple system with the modifier isodecanol was exploited in examining the influence of several factors on the extraction rate of tyrosol and *p*-coumaric acid from binary mixture. The extraction rate of these phenols was found strongly dependent on the volume ratio of feed phase to stripping phase and was moderately enhanced by increasing temperature. The extraction rate of *p*-coumaric acid increased with the initial concentration of solute in the feed phase (100–300 mg/L) but the same variable had no significant effect on the removal of tyrosol. The initial fluxes data are also in agreement with the statement of the retardation of mass transfer rate of tyrosol.

## Acknowledgements

This work was conducted in the "Centro de Processos Químicos do IST" ("Centre for Chemical Processes"), Instituto Superior Técnico (IST), Technical University of Lisbon (UTL), Portugal. Financially, this work was supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal) with European Community (FEDER) and national funds, through the project POCTI/EQU/33207/2000.

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