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SELECTIVE RECOVERY OF PHENOLIC DERIVATIVES THROUGH THE TECHNIQUE OF LIQUID MEMBRANES

Ioana Diaconu^{1*}, Cristina Monica Mirea^{1,2}, Elena Ruse¹, Gheorghe Nechifor¹

¹University Politehnica Bucharest, Faculty of Applied Chemistry and Materials Science,
Department of Analytical Chemistry and Environmental Engineering, 011061 Bucharest, Romania

²Arcuda Laboratory, Water Quality Service, Joita, Giurgiu, Romania

Abstract

In the present paper we studied the competitive transport of p-nitrophenol (pNP) and 2,4-dinitrophenol (2,4-dNP) from aqueous media using the technique of liquid membranes. This technique is very efficient, economic and selective when compared to other removal techniques of phenolic derivatives. The paper presents the influence of the sodium carbonate concentration from the stripping phase, the influence of the concentration ratio $[2,4\text{-dNP}]/[pNP]$ upon the selectivity of the transport process and some kinetic aspects of the transport of 2,4-dNP in the presence of pNP through bulk liquid membranes.

Key words: 2,4-dinitrophenol, kinetics, membrane separation, p-nitrophenol

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1. Introduction

Phenolic compounds, especially those with – nitro groups, are toxic compounds that have harmful effects upon human beings and other terrestrial and aquatic creatures (Arsene et al., 2013; Berhanu et al., 2006; Chelba et al., 2014). For example, prolonged exposure to p-nitrophenol can cause blood disorder, methemoglobin formation, liver and kidney disease as well as eye and skin irritations (ATSDR, 1992; Zheng et al., 2009).

The carcinogenic effect of 2,4-dNP is well known, cellular growth is inhibited at a concentration of 1 ppm (Bagal et al., 2013; Cao and Shiraishi, 2010). This is why United States Environmental Protection Agency (US EPA) included these two nitrophenol compounds on the 126 proprietary pollutants list (U.S.EPA, 2009). The admitted limit for phenolic compounds is under 10 mg/L (Busca et al., 2008; Diaconu et al., 2009b), and in order the water to be drinkable the European Directive EU/440/75 has established the maximum range of

phenolic compounds at 1-10 µg/L (EC Directive, 1975).

Nitrophenols are frequently encountered in residual wastewaters from industries such as explosive manufacture, pharmaceuticals, wood preservatives, pesticides, fungicides, pigments, dyes and rubber industry where they are used as intermediary products (Chand and Shiraishi, 2013; Diaconu et al., 2011; 2010a; 2010b; Szczepański and Diaconu, 2012). These compounds can be formed as a result of the reaction of phenolic compounds in the atmosphere in aqueous or gaseous phase (Harrison et al., 2005; Lezamiz and Jönsson, 2007). Thus these compounds need to be removed from the environment.

There are several methods to remove nitrophenols such as: adsorption (Barreca et al., 2014; Jia et al., 2014), microbiological degradation (Diaconu et al., 2010a), catalytic oxidation (Das et al., 2006), electrochemical treatment (Jiang et al., 2010) and membrane separation (Diaconu et al., 2009a; 2009b). The disadvantage of certain

* Author to whom all correspondence should be addressed: e-mail: diaconuioana12@yahoo.com

techniques such as adsorption is that they have high costs and extremely selective and cheap methods must be found. An alternative is represented by the technique of liquid membrane. These technique is easy to use, low energy consumption, inexpensive and with high transport efficiency (Blaga et al., 2006; Cascaval et al., 2004; Diaconu et al., 2012; Galaction and Cascaval, 2004; Olteanu et al., 2013; Zaharia et al., 2012a, 2012b, 2013).

In the present paper a selective recovery and separation of two extremely toxic nitro-derivatives, pNP and 2,4-dNP, through the technique of liquid membranes is realized, as well as kinetic aspects of the transport of 2,4-dNP through a bulk liquid membrane.

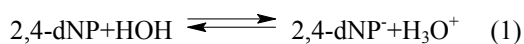
2. Material and method

All the reagents used were analytically grade and were used without further purification. pNP was purchased from Loba Chemie Wein Fischamend and 2,4- dNP was purchased from Merck (Germany). Chloroform used as organic membrane was previously saturated with distilled water. Chloroform was purchased from Flucka. HCl and Na₂CO₃, purchased from Merck (Germany) were used to prepare the feed phase and the stripping phase, respectively. The distilled water used to prepare the aqueous phases was previously saturated with chloroform. The transport cell used was a tube in tube transport cell presented in previous papers (Diaconu et al. 2009a, 2011). The experiments were realized with an acid feed phase, pH = 2 obtained with HCl 10⁻² mol/L. The transport time was 3h and stirring speed was of 180 rot/vit.

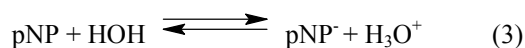
The analytical control was realized using a LAMDA UV-VIS-NIR (Perkin Elmer Life and Analytical Sciences) spectrophotometer at pNP specific wavelength: at 317 nm-for feed phase and 404 nm-for stripping phase and at 2,4-dNP specific wavelength: at 358 nm-for feed phase and 361 nm-for stripping phase.

3. Experimental

Previous studies (Diaconu et al., 2009a; 2009b; Szczepański and Diaconu, 2012) demonstrated that pNP and 2,4-dNP can cross through an organic membrane from an aqueous acid phase (feed phase) into an aqueous alkaline phase (strip phase). In the aqueous boundary layer of the stripping phase the neutralization reaction of the two compounds takes place based on the ionization equilibriums (Eqs. 1-4), where K_{a1} and K_{a2} are acidity constants.



$$K_{a1} = \frac{[2,4\text{-dNP}^-][\text{H}_3\text{O}^+]}{[2,4\text{-dNP}]} \quad (2)$$



$$K_{a2} = \frac{[\text{pNP}^-][\text{H}_3\text{O}^+]}{[\text{pNP}]} \quad (4)$$

Keeping in mind the expression of the acidity constants the hydrogen ion concentration in the diffusion boundary layer is obtained according to Eq. (5), which will result in Eq. (6).

$$[\text{H}_3\text{O}^+] = \frac{K_{a1}[2,4\text{-dNP}]}{[2,4\text{-dNP}^-]} = \frac{K_{a2}[\text{pNP}]}{[\text{pNP}^-]} \quad (5)$$

$$\frac{K_{a1}}{K_{a2}} = \frac{[\text{pNP}]}{[\text{pNP}^-]} \cdot \frac{[2,4\text{-dNP}]}{[2,4\text{-dNP}^-]} \quad (6)$$

If $K_{a1} \gg K_{a2}$ Eq. (7) will result, with the conditions: $[\text{pNP}] \gg [2,4\text{-dNP}]$ or $[\text{pNP}] \ll [2,4\text{-dNP}]$. Therefore, the sodium carbonate reacts firstly with 2,4-dNP and than pNP.

$$\frac{[\text{pNP}]}{[\text{pNP}^-]} \gg \frac{[2,4\text{-dNP}]}{[2,4\text{-dNP}^-]} \quad (7)$$

Depending on the concentration ratio of the two compounds $[2,4\text{-dNP}]/[\text{pNP}]$, the reaction of pNP with the sodium carbonate can start the neutralization before the total neutralization of 2,4-dNP. The influence of the concentration ratio of the two compounds in the diffusion boundary layer is expressed by Eq. (8) (Liteanu and Hopârtan, 1972).

$$\frac{K_{a1}}{K_{a2}} = \frac{10^2 \alpha - 10^2 \alpha r + \alpha^2 r}{10^4 r + 2 \times 10^2 \alpha r + \alpha^2 r} \quad (8)$$

where: $r = [2,4\text{-dNP}]/[\text{pNP}]$; α = neutralization degree of harder acid (2,4-dNP).

Given these considerations in the present paper the influence of the ratio $[2,4\text{-dNP}]/[\text{pNP}]$ upon the selectivity of the transport process was studied.

3.1. Influence of the sodium carbonate concentration from the stripping phase on membrane transport

It was studied the behavior at the membrane transport of a mixture formed from the two compounds, 2,4-dNP and pNP, at different concentrations of sodium carbonate in the stripping phase. The concentration range of sodium carbonate was between 10⁻²-1 mol/L.

The experimental data obtained showed that there is no major influence of the sodium carbonate from the stripping phase in the studied concentration range upon the efficiency of the transport of 2,4-dNP, respectively pNP at the concentration ratio of $[2,4\text{-dNP}]/[\text{pNP}] = 10^{-3}/10^{-4}$ in the feed phase. This can be also observed from Fig. 1.

3.2. Influence of the concentration ration $[2,4\text{-dNP}]/[p\text{NP}]$ from the feed phase upon the selectivity of the transport process

The influence of the concentration ratio of the two compounds in the feed source at the fallowing values: $[2,4\text{-dNP}]/[p\text{NP}] = 10^{-3}/10^{-3}$; $10^{-3}/5 \cdot 10^{-4}$; $10^{-3}/10^{-4}$

We can observe from Fig. 2 that the best results are obtained at the concentration ratio in the feed source of $[2,4\text{-dNP}]/[p\text{NP}] = 10^{-3}/10^{-4}$. Thus using a concentration ratio for the feed source of $[2,4\text{-dNP}]/[p\text{NP}] = 10^{-3}/10^{-4}$ at $\text{pH}=2$ obtained with HCl , a chloroform membrane and a Na_2CO_3 stripping phase at a concentration of 10^{-2} mol/L the two compounds can be separated obtaining a transport efficiency for 2,4-dNP that exceed 98%.

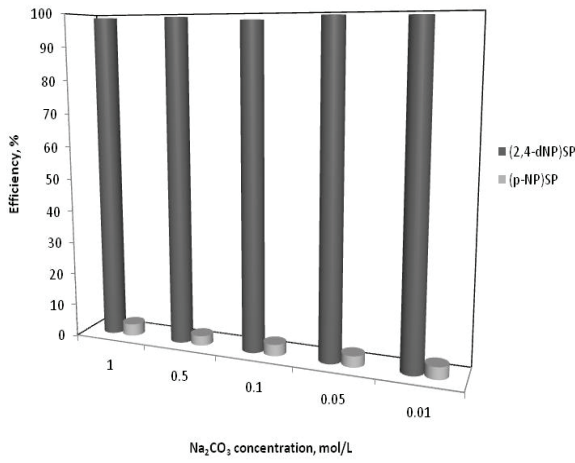


Fig. 1. Sodium carbonate concentration influence upon the transport of 2,4-dNP and pNP through bulk liquid membranes. Experimental conditions: feed phase(FP) $[2,4\text{-dNP}] = 10^{-3}$ mol/L and $[p\text{NP}] = 10^{-4}$ at $\text{pH} = 2$, membrane-chloroform, strip phase(SP) = 1; 0,5; 0,1; 0,05; 0,01 mol/L Na_2CO_3 , transport time = 3h

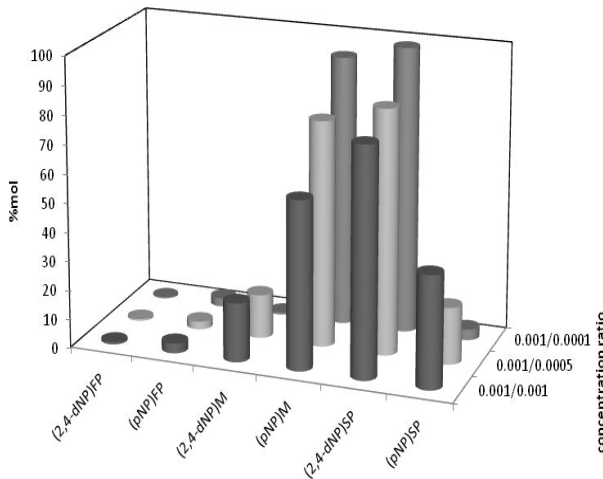
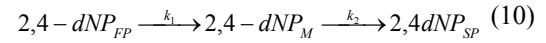


Fig. 2. The transport of 2,4-dNP and pNP at different concentration ratio for the feed phase: $[2,4\text{-dNP}]/[p\text{NP}] = 10^{-3}/10^{-3}$; $10^{-3}/5 \cdot 10^{-4}$; $10^{-3}/10^{-4}$; experimental conditions: feed phase (FP) $[2,4\text{-dNP}]/[p\text{NP}] = 10^{-3}/10^{-3}$; $10^{-3}/5 \cdot 10^{-4}$; $10^{-3}/10^{-4}$ at $\text{pH} = 2$, membrane (M): chloroform, stripping phase (SP): Na_2CO_3 10^{-2} mol/L, transport time = 3h

3.3. Kinetic aspects of the 2,4-dNP transport through bulk liquid membranes

The analysis of the membrane system in time allowed the assessment of some kinetic parameters of the 2,4-dNP pertraction in the presence of pNP. The experimental data confirmed a kinetic characteristic to consecutive irreversible first order chemical reaction, frequently used to describe pertraction in bulk liquid membranes (Alpaydin et al., 2011; Alpoguz et al., 2010; Gubbuk et al., 2010; León and Guzman, 2008; Minhas et al., 2010; Religa et al., 2009; Zhang et al., 2009).

The kinetic scheme which describes the pertraction of 2,4-dNP through bulk liquid membrane is given by Eqs. (10-13), where: k_1 , k_2 represent pseudo-first-order apparent membrane entrance and exit rate constants, s^{-1} ; R_{FP} , R_M and R_{FR} represent the undimensional reduced concentrations from the feed, membrane and stripping phase and are calculated with the Eqs. (14-16).



$$R_{FP} = e^{-k_1 t} \quad (11)$$

$$R_M = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (12)$$

$$R_{SP} = 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \quad (13)$$

$$R_{FP} = \frac{C_{FP} \cdot V_{FP}}{C_{FP0} \cdot V_{FP}} \quad (14)$$

$$R_M = \frac{C_M \cdot V_M}{C_{FP0} \cdot V_{FP}} \quad (15)$$

$$R_{SP} = \frac{C_{SP} \cdot V_{SP}}{C_{FP0} \cdot V_{FP}} \quad (16)$$

where: C_{FP} , C_M , C_{SP} represents the feed, membrane and stripping phase concentration, mol/L; C_{FS0} , represents the initial concentration from the feed phase, mol/L; V_M , V_{SP} represents the feed, membrane and stripping phase volume, cm^3 .

The maximum solute concentration in the membrane is calculated from the dependence $R_m = f(t)$ when $dR_m/dt = 0$ by Eqs. (17, 18):

$$R_M^{max} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}} \quad (17)$$

$$t_{max} = \frac{\ln \left(\frac{k_1}{k_2} \right)}{k_1 - k_2} \quad (18)$$

The pseudo-first-order apparent membrane entrance and exit rate constants can be used at the determination of the maximum flux (Eq. 19) according to the Eq. (17), where: J_{FPmax} = membrane entrance flux ; J_{SPmax} = membrane exit flux.

$$J_{max} = -k_1 \left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_1-k_2}} = k_2 \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1-k_2}} = -J_{FPmax} = J_{SPmax} \quad (19)$$

The experimental data confirmed a good accordance with the model. The correlation coefficient is higher than 0.99. This is illustrated in Fig. 3. Analyzing the compared results from Table 1 we have found that the pseudo-first-order apparent membrane entrance rate constant, pseudo-first-order apparent membrane exit rate constant, the time at

which the R_{max} is observed and maximum flux in the stripping phase depend on the concentration ratio $[2,4\text{-dNP}]/[pNP]$. The maximum values are obtained at the concentration ration $[2,4\text{-dNP}]/[pNP] = 10^{-3}/10^{-4}$ allowing the separation of 2,4-dNP from pNP.

4. Conclusions

In the present paper the possibility of separation of two phenolic derivatives 2,4-dNP and pNP. In order to realize this was used a membrane system formed from an acid feed phase formed from the two nitrophenols at different molar ratio, a chloroform membrane and a stripping phase formed from sodium carbonate.

The experimental data showed that the separation of the two is influenced in an essential way by the concentration ratio $[2,4\text{-dNP}]/[pNP]$.

Table 1. Kinetic aspects at the transport of 2,4-dNP in the presence of pNP. Experimental conditions: feed phase: $[2,4\text{-dNP}]/[pNP] = 10^{-3}/10^{-3}$; $10^{-3}/5 \cdot 10^{-4}$; $10^{-3}/10^{-4}$ at pH=2, membrane: chloroform, stripping phase Na_2CO_3 10^{-2} mol/L, time=3h

Concentration ration for the substrate $[2,4\text{-dNP}]/[pNP]$	k_1 $\times 10^3$ [s^{-1}]	k_2 $\times 10^4$ [s^{-1}]	R_{max}	t_{max} , [s]	J_{FSmax} $\times 10^4$ [s^{-1}]	J_{SPmax} $\times 10^4$ [s^{-1}]
$10^{-3}/10^{-3}$	1.65	1.56	0.78	1575	-1.22	1.22
$10^{-3}/5 \cdot 10^{-4}$	1.94	2.24	0.75	1253	-1.69	1.69
$10^{-3}/10^{-4}$	2.02	3.68	0.68	1028	-2.52	2.52

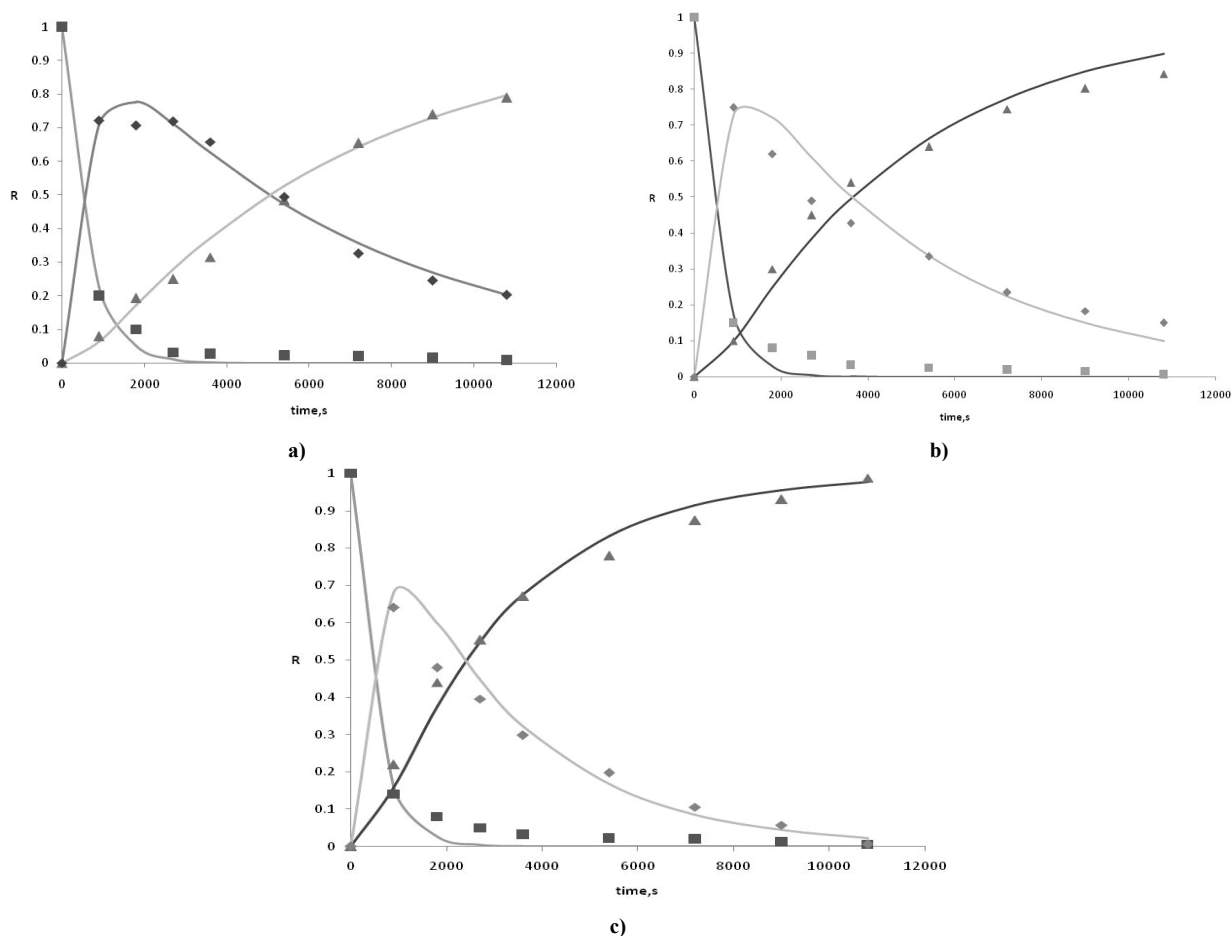


Fig. 3. Experimental results at the pertraction of 2,4-dNP through bulk liquid membranes in the presence of pNP. Feed phase (■): $[2,4\text{-dNP}]/[pNP] =$ a) $10^{-3}/10^{-3}$; b) $10^{-3}/5 \cdot 10^{-4}$; c) $10^{-3}/10^{-4}$ at pH = 2; Membrane (◆) chloroform; Stripping phase (▲): Na_2CO_3 10^{-2} mol/L, transport time = 3h; continuous line represents the values calculated using the kinetic model

Thus at the molar ratio $[2,4\text{-dNP}]/[pNP] = 10^{-3}/10^{-4}$ a separation of the two compounds can be realized. A time dependence analysis of the pertraction of 2,4-dNP in the presence of pNP allowed a kinetic assessment of the pertraction of the 2,4-dNP.

The model that describes the process is a kinetic model of two consecutive irreversible first order reactions in the system with interfaces. The results demonstrated an influence of the concentration ratio $[2,4\text{-dNP}]/[pNP]$ upon the kinetic parameters. Maximum values were obtained for the concentration ratio $[2,4\text{-dNP}]/[pNP] = 10^{-3}/10^{-4}$.

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