Influence of the kind and concentration of ethoxylated alcohols on the transport of citric acid through polymer inclusion membranes

Marcin Dudek^{*}, Marta Przewoźna, Piotr Gajewski, Mariusz B. Bogacki

Poznan University of Technology, Institute of Chemical and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland ^{*}Corresponding author: e-mail: dudekmarcin@yahoo.com

Research into the influence of ethoxylated alcohols on the citric acid transport through polymer inclusion membranes (PIMs) has been carried out. This process may be used in the future as one of the methods of citric acid isolation. Ethoxylated alcohols, which were GENAPOL® X020, X060 and X150, served as both: plasticizer and carrier. The results showed that the maximum values of citric acid flux $[mol/(m^2 \cdot s)]$ were equal to: $1.02 \cdot 10^{-4}$ (X020), $1.57 \cdot 10^{-4}$ (X060) and $1.77 \cdot 10^{-4}$ (X150). The obtained results allow proceeding further study on using the polymer inclusion membranes, as an alternative to traditional methods of citric acid separation, which are precipitation and extraction.

Keywords: citric acid, polymer inclusion membranes, ethoxylated alcohols.

INTRODUCTION

Separation process is one of the most energy-consuming and expensive stage of production in chemical industry. Developing an eco-friendly, cheap and waste-free technology of isolation citric acid from fermentation solutions would mean not only getting rid of large quantity of dangerous to the environment and man substances used during production, or apparatus simplification, but also could save a lot of money. Membrane techniques can be such a technological solution.

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is one of the most widely used organic acid in the world. We can find its application in many branches of industry, mainly in pharmaceutical, cosmetic and food industry¹. Because of its wide application, citric acid became valuable product of great industrial meaning. The main method of citric acid production is fermentation using microorganisms, such as *Aspergillus niger, Aspergillus wentii*^{1, 2} and *Yarrowia lipolytica*³. The source of carbon in the production process can be sucrose, juices or sugar starch, all used as nutrient medium, but also glycerol fraction, created during biodiesel production⁴.

Fermentation processes are safe and eco-friendly. Because of these facts, in recent years, biological methods of citric acid production were developed significantly, which resulted in lowering the production costs and the quantity of generated harmful waste^{5, 6}.

A problem occurs after the process of fermentation – the problem of isolation desirable product from fermentation broth. So far, one of the most common methods of separation has been isolating citric acid as precipitated calcium citrate, using calcium hydroxide. Citric acid is obtained by using sulfuric acid on precipitate. Then, the solution is filtrated, removing gypsum (byproduct). Afterwards, citric acid is crystallized. The main disadvantage of this method is generating great amounts of polluted calcium sulfate. Citric acid can be also extracted from the fermentation broth. This method requires the usage of dangerous for the environment organic solvents and expensive active compounds^{7, 8}.

In relation to chemical industry modernization, taking care of the environment and also the economical aspect of the production process, new technological solutions are being developed. These solutions should reduce the cost of production and the number of flaws, regarding the process of isolation citric acid from fermentation broth. Therefore, a recently intensive research in the field of application membrane techniques as a separation method during citric acid production is conducted.

Polymer inclusion membranes (PIMs) are relatively a new type of liquid membranes, which probably can be used to extract citric acid from fermentation broth. For the preparation of PIMs, most common polymer matrixes are either cellulose triacete (dissolved in methylene chloride) or polyvinyl chloride (dissolved in tetrahydrofuran). Quantities of active compounds used in preparation process are very low, as well as they are slowly eluted from membranes, so their potential malignance can be omitted^{10, 11, 12}.

Until recently, polymer inclusion membranes were mainly used in metal ions transport^{13, 14, 15, 16, 17}, however recent studies show that PIMs can be used in the separation process of organic compounds¹⁸, including citric acid¹⁹. Application of polymer inclusion membranes can become an alternative to traditional methods of citric acid isolation (extraction and precipitation methods), because PIMs do not require large amounts of solvents, often expensive and harmful to the environment, which makes them eco-friendly and safe. Membranes, used in this study, are cheap, their usage does not generate byproducts, and furthermore, appropriate selection of compounds in the membrane maximizes parameters of separation process.

Polymer inclusion membranes can be prepared with various kinds of plasticizers and carriers. The plasticizer is responsible for making the membrane flexible and for neutralizing effects of polar polymer matrix groups. Plasticizer should also be compatible with the polymer matrix of the membrane. The commonly used substances are NPOE or TEHP²⁰. Carriers, often referred to as active compounds, are responsible for mass transport (metal or organic) through membranes. Selective separation of compounds can be done, depending on the type of carrier. The most often used active compounds are: CYANEX® 921 or 923 (derivative of phosphinic acid), TBP (derivative of orthophosphoric acid) and TOA or Aliquat 321 (tertiary and quaternary amines)¹². There can also be found substances, which can be both,

a plasticizer and a carrier – for example ethoxylated alcohols, used in this study.

This paper reports the influence of the kind and amount of the used oxyethylate (being both carrier and plasticizer) in the preparation of membranes, on the transport of citric acid through polymer inclusion membranes. Cellulose triacete (CTA) was used as polymer matrix, whereas the active substances were: GENAPOL® X020, X060 and X150 (Fig. 1, produced by Clariant Corporation, analytically pure).

$$C_{13}H_{27} - \underbrace{-OC_2H_4}_{x} - \underbrace{-OH}_{x} OH$$
$$x = 2, 6, 15$$

Figure 1. GENAPOL® structure: for X020, x = 2; for X060, x = 6; for X150, x = 15

EXPERIMENTAL

To prepare polymer inclusion membranes, used in the study, the following reagents were used: solution of 1.25 g cellulose triacete (CTA, Sigma-Aldrich, >98%) dissolved in 100 cm³ of methylene chloride (POCH Gliwice, >99%) and 10% (v/v) solution of oxyethylates (responsible for being plasticizer, as well as carrier) - GENAPOL® X020, X060 and X150, dissolved in methylene chloride. 1.5 cm³ of CTA solution was used to make each membrane, although the volume of oxyethylate solutions varied from 0.025 to 1 cm³ (in the case of using GENAPOL® X150, maximum volume of the oxyethylate solution was 0.5 cm³ - using more resulted in preventing membrane removal from Petri dish, due to the too low mechanical endurance of the membrane). The mass fraction of oxyethylate varied from about 0.1 to about 0.9 (Table 1-3). The solutions of CTA and oxyethylates were mixed in appropriate proportions, poured to Petri dishes and then put away for the time necessary for the solvent to evaporate. After 24 hours, membranes were removed from Petri dishes and then they were weighed. Also the thickness was measured on eight points (five repetitions in every point) on the membrane surface with using thickness gauge PosiTector (accuracy 0.1 µm). Before the process of organic acid transport, membranes were soaked in deionized water for 24 hours.

The transport rate of citric acid through polymer inclusion membranes was measured, using the apparatus shown in Figure 2. It consists of two glass chambers, separated from each other with a membrane. The chamber with the supplying phase contained 60 cm³ of 0.1 mol/dm³ water solution of citric acid (monohydrate, analytically pure, POCH Gliwice), whereas the chamber with the receiving phase was filled with 60 cm³ of deio-



Figure 2. Experimental apparatus 1 – receiving phase, 2 – supplying phase, 3 – membrane, 4 – stirrers, 5 – electrode

nized water (R $\approx 1.5M\Omega$). The working surface of the membrane was equal to 4.15 cm². Two stirrers, one in each chamber, provided constant mixing of two phases. The apparatus was placed in water bath, which held the temperature of the process at approximately 25°C. The conductivity was measured every 7 minutes, using an electrode (pH/Conductivity Meter CPC-501 ELME-TRON) placed in the receiving phase chamber. The process lasted 24 hours. Based on the calibration curve, conductivity was converted to the molar concentration of citric acid in the receiving phase.

RESULTS

Starting from Fick's second law, some simplifications were assumed¹³:

a) both the supplying and receiving phase reactions very fast lead to the chemical equilibria,

b) the citric acid concentration in the membrane is negligibly small, compared to the concentration of the oxyethylate, which results in allowing to assume constant carrier concentration within the membrane,

c) diffusion of the compound in the liquid film on the surface of the membrane is much faster than the diffusion of the complex through the membrane,

d) mass transport through the membrane is a result of Fickian diffusion and the concentration gradient of citric acid – oxyethylate complex is linear,

e) both the supplying and the receiving phase are ideally mixed.

These assumptions allow describing a relation between the temporary to initial concentration of citric acid, time-dependent with the following formula:

$$-\frac{1}{2} \cdot \ln \left(1 - \left(\frac{2 \cdot C}{C_0} \right) \right) = k \cdot t \tag{1}$$

where: C – temporary concentration of citric acid in time t, in the receiving phase $[mol/dm^3]$, C₀ – initial concentration of citric acid in the supplying phase $[mol/dm^3]$, t – time [s], k – rate constant.

Using Formula 1, rate constant k was calculated, which was later used to determine parameters of citric acid transport, such as ion flux (J_0 [mol/m²·s]), permeability coefficient (P [m/s]) and diffusion coefficient (D [m²/s]):

$$J_0 = \frac{V}{A} \cdot k \cdot C_0 \tag{2}$$

$$P = \frac{V}{A} \cdot k \tag{3}$$

$$D = \frac{P \cdot d}{\kappa} \tag{4}$$

where: A – membrane surface $[m^2]$, V – volume of receiving/supplying phase $[m^3]$, d – thickness of membrane [m].

The change of temporary to initial citric acid concentration ratio in time, for GENAPOL® X020 as a carrier, is shown in Figure 3 (for more clarity, only few carrier concentrations were shown). As it can be seen, the change of carrier concentration in the membrane causes the change of citric acid transport rate through membranes. In the beginning, along with the growth of carrier concentration in the membrane, also the



Figure 3. Temporary to the initial citric acid concentration ratio vs. time of the process; regarding X020. Supplying phase: 60 cm³ 0.1 mol/dm³ citric acid; receiving phase: 60 cm³ of the deionized water

transport rate grows, up to the volume of the carrier in membrane equal to 0.02–0.03 cm³ (mass fraction of the carrier equal about 0.5). Afterwards, the growth of carrier concentration causes a decrease of the citric acid transport rate. Similar results are observed with other oxyethylates: X060 (Fig. 4) and X150 (Fig. 5). As it can be seen, also in these cases the change of carrier concentration in the membrane results in the change of transport rate. In both, GENAPOL® X060 and X150, maximum values were achieved with 0.03 cm³ oxyethylate



Figure 4. Temporary to the initial citric acid concentration ratio vs. time of the process; regarding X060. The supplying phase: 60 cm³ 0.1 mol/dm³ citric acid; receiving phase: 60 cm³ of the deionized water



Figure 5. Temporary to the initial citric acid concentration ratio vs. time of the process; regarding X150. The supplying phase: 60 cm³ 0.1 mol/dm³ citric acid; receiving phase: 60 cm³ of the deionized water

in the membrane (mass fraction of carrier equal about 0.5 for X060 and 0.8 for X150).

Figure 6 presents the relation between membranes thickness and volume of oxyethylate applied during membrane preparation (volume varied from 0.0025 to 0.05 cm³). As it could be observed, for volume range





from 0.0025 to about 0.025-0.003 cm³ the membranes thickness increases with increasing the amount of the carrier. For oxyethylate volume above 0.003 cm³, the thickness stabilizes on the constant level (small growth of thickness with the increasing volume of carrier). Stabilizing of the thickness is connected with the precipitation of the carrier on the membrane surface. For higher amounts of the applied oxyethylates, only part of the carrier volume is built into the membrane structure. The rest of the carrier is precipitated on the membranes surface, which can be clearly observed during membrane preparation.

Based on formulas (2, 3, 4) shown earlier, the parameters of citric acid transport through the membranes were calculated (rate constant of the process – k, citric acid flux – J_o , permeability coefficient – P and diffusion coefficient – D), for all three oxyethylates: X020 – Table 1; X060 – Table 2; X150 – Table 3.

When analyzing the results shown in Tables 1, 2 and 3, it can be seen, that with the growth of oxyethylate amount in the membrane also grows the transport rate of citric acid through the membrane. The designated transport parameters reach their maximum value with the mass of the oxyethylate within the membrane equal to 0.023–0.025 g for X020 (Table 1) and X060 (Table 2), and 0.039 g for X150 (Table 3) - the volume of carriers equal to about 0.025-0.03 cm³. Then, with further increase of oxyethylate amount in the membrane, parameters of transport decrease, for X020 and X150 quite rapidly, however X060 has gentler decline of these parameters. The decrease of citric acid transport, for membranes with volume of oxyethylate more than 0.03 cm^3 , is connected with the carrier precipitation on membranes surface. Above the volume of 0.03 cm³ of carrier in the membrane, membranes thickness stabilizes (Fig. 6), which is caused by precipitation of additional amount of oxyethylate and results in covering the membranes surface with carrier. The extra layer of the precipitated carrier creates additional resistance, which leads to decrease of transport parameters.

When assessing the results for the lowest amounts of oxyethylates in membranes, it can be seen, that for the membranes with the mass of oxyethylate lower than 0.005 g (in all cases), the process of transport did not occur. The first signs of citric acid transport were spotted for the oxyethylate mass in the membrane equal about 0.007 g (oxyethylate and membrane mass ratio circa

Table 1.	Parameters describing citric acid transport through PIM for different oxyethylate GENAPOL® X020 concentrations. Jo	_
	citric acid flux, P - permeability coefficient, d - membrane thickness, k - transport rate constant, D - diffusion coefficier	ıt.
	Supplying phase: 60 cm ³ 0.1 mol/dm ³ citric acid; receiving phase: 60 cm ³ of the deionized water	

Oxyethylate volume [cm ³]	Oxyethylate mass [g]	Membrane mass [g]	Oxyethylate and membrane mass ratio	J₀·10 ⁴ [mol/m²·s]	P·10 ⁵ [m/s]	d∙10 ⁶ [m]	k·10 ⁵ [1/s]	D·10 ⁹ [m²/s]
0.0025	0.0023	0.0232	0.101	0.0004	0.0007	11.50	0.005	0.0001
0.005	0.0047	0.0268	0.175	0.0004	0.0007	12.16	0.005	0.0001
0.0075	0.0070	0.0251	0.280	0.0337	0.0646	13.95	0.447	0.0077
0.01	0.0094	0.0267	0.351	0.3544	0.6790	14.13	4.70	0.1231
0.015	0.0141	0.0333	0.422	0.4750	0.9097	17.54	6.30	0.1414
0.02	0.0187	0.0393	0.477	0.9278	1.7800	21.13	12.3	0.3761
0.025	0.0234	0.0478	0.490	1.0210	1.9552	22.16	13.5	0.4333
0.03	0.0281	0.0488	0.576	0.7990	1.5300	22.76	10.6	0.2870
0.05	0.0469	0.0685	0.684	0.3040	0.5820	23.04	4.03	0.1341
0.07	0.0656	0.0877	0.748	0.0395	0.0757	25.62	0.524	0.0250
0.1	0.0937	0.1158	0.809	0.0957	0.1830	29.37	1.27	0.0720

Table 2. Parameters describing citric acid transport through PIM for different oxyethylate GENAPOL® X060 concentrations. Jo – citric acid flux, P – permeability coefficient, d – membrane thickness, k – transport rate constant, D – diffusion coefficient. Supplying phase: 60 cm³ 0.1 mol/dm³ citric acid; receiving phase: 60 cm³ of the deionized water

Oxyethylate volume [cm ³]	Oxyethylate mass [g]	Membrane mass [g]	Oxyethylate and membrane mass ratio	J₀·10 ⁴ [mol/m²*s]	P [.] 10 ⁵ [m/s]	d·10 ⁶ [m]	k·10 ⁵ [1/s]	D·10 ⁹ [m²/s]
0.005	0.0050	0.0266	0.186	0.0009	0.0017	10.90	0.012	0.0003
0.0075	0.0074	0.0279	0.266	0.0385	0.0737	11.32	0.510	0.0083
0.01	0.0099	0.0355	0.279	0.4724	0.9047	13.82	6.27	0.1703
0.015	0.0149	0.0389	0.382	0.9557	1.8301	15.13	12.7	0.2769
0.02	0.0198	0.0444	0.446	1.3800	2.6400	21.97	18.3	0.5272
0.025	0.0248	0.5260	0.471	1.5710	3.0031	23.64	21.1	0.6640
0.03	0.0297	0.0566	0.525	1.5112	2.8940	25.08	21.0	0.6679
0.05	0.04956	0.0740	0.670	1.3797	2.6422	26.87	18.3	0.4986
0.07	0.0694	0.1039	0.668	1.4600	2.8000	29.33	19.4	0.7652
0.1	0.0991	0.1374	0.721	1.1700	2 2300	34.75	15.5	0.7780

Table 3. Parameters describing citric acid transport through PIM for different oxyethylate GENAPOL® X150 concentrations. Jo – citric acid flux, P – permeability coefficient, d – membrane thickness, k – transport rate constant, D – diffusion coefficient. Supplying phase: 60 cm³ 0.1 mol/dm³ citric acid; receiving phase: 60 cm³ of the deionized water

Oxyethylate volume [cm ³]	Oxyethylate mass [g]	Membrane mass [g]	Oxyethylate and membrane mass ratio	J₀·10 ⁴ [mol/m²·s]	P [.] 10 ⁵ [m/s]	d · 10 ⁶ [m]	k·10 ⁵ [1/s]	D·10 ⁹ [m²/s]
0.005	0.0065	0.0230	0.283	0.0083	0.0159	10.47	0.110	0.002
0.01	0.0130	0.0340	0.382	0.0766	0.1467	14.20	1.02	0.021
0.015	0.0195	0.0400	0.485	0.2388	0.4574	14.56	3.17	0.066
0.02	0.0260	0.0405	0.642	0.5196	0.9950	16.28	6.89	0.162
0.025	0.0325	0.0489	0.665	1.2900	2.4700	17.27	17.1	0.427
0.03	0.0390	0.0501	0.778	1.7728	3.3950	17.33	23.5	0.588
0.04	0.0520	0.0634	0.820	1.0848	2.0774	17.63	14.4	0.366
0.05	0.0650	0.0724	0.898	1.4337	2.7456	17.70	19.0	0.486

0.28). These results can be explained with percolation theory, therefore the lowest concentrations of oxyethylates in the membranes can be considered as percolation threshold^{21, 22, 23}.

Figure 7 shows the relation between ion flux and volumes of different oxyethylates in membranes. As it can be seen, for very small amounts of the carrier, the transport of citric acid does not occur. Then, with the growth of the amount of oxyethylate in the membrane, an increase of transport parameters can be observed, reaching the maximum at oxyethylate and membrane mass ratio equal to: 0.48 for X020; 0.52 for X060 and 0.78 for X150. Further growth of oxyethylate concentration results in the decrease of citric acid transport parameters, however depending on the used kind of carrier, it is either mild (X060) or sharp (X020 and X150). As it can be observed, maximum values of transport were



Figure 7. Values of ion flux vs. volume of the used oxyethylate

obtained for pretty much the same volumes of oxyethylate solutions, used for the preparation of membranes, however its values grew with the amount of oxyethylated groups in the compounds.

On the basis of the obtained results and publication of other authors^{21, 22, 23}, it is possible to propose fixed-site



Figure 8. Suggested citric acid fixed-site jumping transport mechanism

jumping as the transport mechanism (Fig. 8). Probably, the transport of the citric acid trough PIM occurs due to interactions between carboxylic groups of the acid and oxyethylated groups of the carrier. It could be assumed that only citric acid can displace in the membranes structure and the carrier is motionless. The results obtained in this study, confirm this assumption. Firstly, it could be observed that the transport increases with increasing the number of the oxyethylated groups in the carrier chain (for the same carrier volume). In the case, where the citric acid creates a stable complex with the carrier, which diffuses across the membrane, this dependence should be opposite. Also, the decrease of transport rate with increasing the number of oxyethylated groups in the compound should be observed, because it is expected, that with the increasing number of oxyethylated groups, the compound is less mobile. Additionally, these results confirm that the citric acid interacts with oxyethylated groups of carrier. Secondly, the occurrence of percolation threshold is being observed. For the transport mechanism, where the complex diffuses across the membrane, the percolation threshold should not be seen. In the fixed-site jumping mechanism, some minimal volume of the carrier in the membranes structure is necessary to create the pathway for "jumping" through the membrane. Because the carrier is motionless, the transport occurs only if the connection between the two sides of membrane exists. For that purpose, the minimal concentration of carrier in the membrane is necessary, which is manifested by the presence of the percolation threshold. In addition, the transport parameters of membranes with more than minimal concentration of carrier (above the percolation threshold), are growing very fast with the increase of carriers volume (rapid increasing number of transport pathways) (Fig. 7).

CONCLUSIONS

This study enables to determine the influence of the used oxyethylates (GENAPOL® X020, X060 and X150) and their concentration, on the citric acid transport parameters through polymer inclusion membranes. The result analysis allows a conclusion, that along with the growth of oxyethylate concentration in the membrane, there is an increase of transport parameters, such as ion flux and permeability. The increase of parameters is observed, until the oxyethylate and membrane mass ratios reach around 0.5 for X020 and X060, and 0.78 for X150. The results show that membranes with higher, than the mentioned above, oxyethylate mass ratio, have lower values of citric acid transport parameters, in comparison to the maximum values. This may be caused by oxyethylate precipitation on the surface of the membrane.

The obtained results indicate that the maximum values of ion fluxes, permeability and diffusion coefficients were received with similar volumes of the oxyethylate in the membrane $(0.025-0.03 \text{ cm}^3)$, however these values increase with the growth of oxyethylated groups in used oxyethylates.

Processes of citric acid transport through PIMs, carried out with membranes with the lowest amounts of oxyethylates (less than 0.005 cm³, mass fraction less than 0.2) showed that citric acid was not being transported through the membranes. The first signs of transport were observed for oxyethylate mass in the membrane equal to 0.007 g (X020 and X060) and 0.0065 g (X150). These facts can be explained by percolation theory²³, whereas the lowest oxyethylates concentration, which allows the citric acid transport through the membrane to occur, can be considered as percolation threshold. According to the latest studies, the presence of percolation threshold, along with the rapid increase of citric acid transport above it, can prove that citric acid is transported through the membrane in accordance with the theory of facilitated transport^{21, 22, 23}, where the carrier is motionless and the transport takes place on account of transition of citric acid particles between carrier particles (fixed-site jumping). In addition, it is observed, that the increase of transport parameters values is followed by the growth of number of oxyethylated groups in the carrier, which can lead to a conclusion that they are responsible for the transport of citric acid. Furthermore, with the increase of oxyethylated groups, also the viscosity of the carrier grows, which also confirms the thesis of motionless carrier.

This study also confirms the role of oxyethylates as plasticizers, responsible for making the membrane flexible, and carriers of organic acids, allowing the transport to take place. The right composition of substances, used in the preparation of membranes, and also parameters of the process (time, temperature, stirring), can lead to maximization of the transport process, all of which require further studies.

ACKNOWLEDGEMENT

This work was carried out in part of the framework of Statutory Research 32-376/2013/DS, conducted at the Poznan University of Technology.

LITERATURE CITED

1. Kristiansen, B., Mattey, M. & Linden, J. (2002). *Citric acid biotechnology* (1st ed.). Taylor and Francis.

2. Dhillon, G.S., Brar, S.K., Verma, M. & Tyagi, R.D. (2011). Recent advances in citric acid bio-production and recovery. *Food Bioprocess Technol.* 4(4), 505–509. DOI: 10.1007/s11947-010-0399-0. 3. Papanikolaou, S., Muniglia, L., Chevalot, I., Aggelis, G. & Marc, I. (2002). *Yarrowia lipolytica* as a potential producer of citric acid from raw glycerol. *J. Appl. Microbiol.* 92 (4), 737–744. DOI: 10.1046/j.1365-2672.2002.01577.x.

4. Rywińska, A., Rymowicz, W., Żarowska, B. & Wojtatowicz, M. (2009). Biosynthesis of citric acid from glicerol by acetale mutants of Yarrowia lipolytica in fed-batch fermentation. *Food Technol. Biotechnol.* 47, 1–6.

5. Soccol, C., Vandenberghe, L. & Rodrigues, C. (2008). *Current Developments in solid-state fermentation. Production of Organic Acids by Solid-state Fermentation*, (pp. 205–229). Springer New York, Retrieved October, 2011, from Springer-Link, http://link.springer.com/book/10.1007/978-0-387-75213-6/ page/1. DOI: 10.1007/978-0-387-75213-6 10.

6. da Silva, G.P., Mack, M. & Contiego, J. (2009). Glicerol: A promising and abundant carbon source for industrial microbiology. *Biotechnol. Adv.* 27, 30–39. DOI: 10.1016/j.biotechadv.2008.07.006.

7. Kirsch, T., Ziegenfuss, H. & Maurer, G. (1997). Distribution of citric, acetic and oxalic acids between water and organic solutions of tri-n-octylamine. *Fluid Phase Equilib*. 129, 235–266.

8. Juang, R.S., Huang, R.H. & Wu, R.T. (1997). Separation of citric and lactic acids in aqueous solutions by solvent extraction and liquid membrane processes. *J. Membr. Sci.* 136, 89–99.

9. Walkowiak, W., Kozłowski, C.A., Pellowski, W. (2003). Zastosowanie polimerowych membran inkluzyjnych do wydzielania i separacji jonów metali. *Membrany teoria i praktyka* (pp. 47–78). Toruń, Poland, Wydawnictwo UMK.

10. Kim, J.S., Kim, S.K. & Ko, J.W. (2000). Selective transport of cesium ion in polymeric VTA membrane containing calixcrown ethers. *Talanta* 52, 1143–1148.

11. Sakai, Y., Kadota, K. & Hayashita, T. (2010). The effect of the counter anion on the transport of thiourea in a PVC-based polymer inclusion membrane using Capriquat as carrier. *J. Membr. Sci.* 346(2), 250–255. DOI: 10.1016/j.memsci.2009.09.038.

12. Pereira, N., St. John, A. & Cattrall, R. (2009). Influence of composition of polymer inclusion membranes on their homogeneity and flexibility. *Desalination* 236(1–3), 327–333. DOI: 10.1016/j.desal.2007.10.083.

13. Nghiem, L.D., Mornane, P., Potter, I.D., Perera, J.M., Cattrall, R.W. & Kolev, S.D. (2006). Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs). *J. Membr. Sci.* 281(1–2), 7–41. DOI: 10.1016/j.memsci.2006.03.035.

14. Lamb, J.D. & Nazarenko, A.Y. (1997). Lead(II) ion sorption and transport using polymer inclusion membranes containing tri-octylphosphine oxide. *J. Membr. Sci.* 134(2), 327–333. DOI: 10.1016/S0376-7388(97)00115-4.

15. Gajda, B., Skrzypczak, A. & Bogacki, M.B. (2010). Separation of cobalt (II), nickel (II), zinck (II) and cadium (II) ions from chloride solutions. *Physicochem. Probl. Miner. Process.* 46, 289–294.

16. Pospiech, B. & Walkowiak, W. (2007). Separation of copper(II), cobalt(II) and nickel(II) from chloride solutions by polymer inclusion membranes. *Sep. Purif. Technol.* 57(3), 461–465. DOI: 10.1016/j.seppur.2006.07.005.

17. Almeida, M. (2012). Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs). *J. Membr. Sci.* 416, 9–23. DOI: 10.1016/j.memsci.2012.06.006

18. Matsumoto, M., Takagi, T. & Kondo, K. (1998). Separation of lactic acid using polymeric membrane containing a mobile carrier. *J. Ferment. Bioeng.* 85(5), 483–487. DOI: 10.1016/S0922-338X(98)80066-4.

19. Gajewski, P. & Bogacki, M.B. (2012). Influence of Alkyl Chain Length in 1-Alkylimidazol on the Citric Acid Transport Rate across Polymer Inclusion Membrane, *Separ. Sci. Technol.* 47, 1374–1382. DOI: 10.1080/01496395.2012.672517.

20. Arous, O., Saad Saoud, F. & Kerdjoudj, H. (2010). Cellulose triacetate properties and their effect on the thin

films morphology and performance. Innovations in Thin Film Processing and Characterisation. 17–20 November 2009, (pp. 1–5), Nancy, France.

21. Munro, T.A. & Smithe, B.D. (1997). Facilitated transport of amino acids by fixed-site jumping. *Chem. Commun.* 2167–2168.

22. Riggs, J.A. & Smith, B.D. (1997). Facilitated Transport of Small Carbohydrates through Plasticized Cellulose Triacetate. *J. Am. Chem. Soc.* 119(11), 2765–2766.

23. White, K.M., Smith, B.D., Duggan, P.J., Sheahan, S.L. & Tyndall, E.M. (2001). Mechanism of facilitated saccharide transport through plasticized cellulose triacetate membranes. *J. Membr. Sci.* 194, 165–175.