

Evaluation of Kinetic Parameters at the Transport of Indole-3-acetic Acid Through Bulk Liquid Membranes

ECATERINA ANCA SERBAN¹, IOANA DIACONU^{1*}, ELENA RUSE¹, GEORGIANA ILEANA BADEA², ADRIANA CUCIUREANU³, GHEORGHE NECHIFOR¹

¹ University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-3 Gh. Polizu Str., 011061, Bucharest, Roumania

² Centre of Bioanalysis, National Institute for Biological Sciences, 296 Splaiul Independentei, 060031, Bucharest, Romania.

³ National Institute for Research and Development for Industrial Ecology-ECOIND, 90-92 Sos. Panduri, 050663, Bucharest, Romania

Indole-3-acetic acid is a growth phytohormone considered the most important representative of auxin class. This paper presents the assessment of some kinetic parameters in the process of transport of indole-3-acetic acid taking into consideration the kinetic model of consecutive irreversible first order reactions. It was pursued the influence upon the process of parameters such as: feed phase concentration, stripping phase concentration in the presence of two type carriers: tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO). Depending on these transport parameters were calculated kinetics parameters such as: pseudo-first-order apparent membrane entrance and exit rate constants, the maximum flux at the entrance and exit out of the membrane. The highest values of the transport flux is obtained in the presence of carrier trioctylphosphine oxide (TOPO) at the concentration in the feed phase of 10⁻⁴ mol/L indole-3-acetic acid and a concentration of 10⁻² mol/L NaOH in the stripping phase.

Keywords: *indole-3-acetic acid, bulk liquid membrane, tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), kinetic model*

The use of the bulk liquid membranes has been applied in many fields of research, due to their ability to transport certain compounds of interest, such as: analytical chemistry, organic chemistry and inorganic chemistry; biomedical engineering, pharmaceutical industry, chemical industry, biotechnology, environmental protection, as well as in wastewater treatment. Separation, removal or recovery of organic compounds, toxic metals and products of fermentation were realized using the system of de transport through liquid membranes [1-10].

Currently, liquid membranes are used for the transport and separation of cations [2, 5, 28], anions [2,19], isomers [2, 35], amines [20], organic acids [4-19, 21-24], drugs [3, 12,17,19], amino acids [10], vitamins [13,22-23], antibiotics [21, 24] (products of biosynthesis in group), etc.

The use of liquid membranes offers a viable alternative to extraction solvent processes due to the selectivity and application on diluted solutions. The main advantage of using liquid membranes is related to obtaining a high flux of transport compared with other types of membranes (e.g. polymer membranes, inorganic membranes or hybrid organic-inorganic membranes) due to large diffusion coefficients [1-4].

Bulk liquid membranes technology is increasingly due to its advantages in fundamental (basic) research as it can be showed in the large number of articles published about the selective separation of organic acids such as: indole-3-acetic acid [16], benzoic acid [7,9], para-aminobenzoic acid [21-22], acetylsalicylic acid [17], 5-amino-acetylsalicylic acid [17], salicylic acid [17], butyric acid [6], propionic acid [22, 27], pantothenic acid [21-24], cinnamic acid [21], succinic acid [21, 24, 26], folic acid [21-24], lauric acid [25], phenol [15], para-nitrophenol [4], para-aminophenol [14], gentamicin and codeine etc. [3-24]

The transport and separation of organic acids through liquid membranes occurs following a chemical potential gradient. The dissociation constant (pKa), the initial pH of the aqueous solutions, the solubility of the solute in the aqueous phases and in the membrane solvent [5] are important parameters in membrane transport processes of organic acids. Operational parameters that usually influence significantly the efficiency of the transport are: the transport time, the feed phase concentration, nature and stripping phase concentration [17].

The efficiency and selectivity of liquid membrane transport processes is greatly enhanced through the use of appropriate carriers. For transport and separation of organic acids most used carriers are: tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), trioctylamine (TOA), Amberlite LA-2 and di-(2-ethylhexyl)phosphoric acid (D, EHPA), trioctyl methyl ammonium chloride (Aliquate 336) and Alamine 336 [4-35].

Transport and separation studies through liquid membrane of organic acids pursued not only optimization of these processes by studying the process parameters as well as the elaboration of mathematical models of transport.

Considering the studies in the field of organic acids transport in this paper an assessment of some kinetic parameters that characterize the transport of indole-3-acetic acid through bulk liquid membranes is realized.

Experimental part

Materials and method

Reagents and equipment

For the transport experiments performed all the reagents used were analytically grade and were used without further purification. The indole-3-acetic acid was purchased from Merck. Hydrochloric acid necessary for preparation of the

* email: diaconuioana12@yahoo.com

feed phase and sodium hydroxide necessary for preparation of the stripping phase were purchased from Merck.

In the transport studies were used as carriers: tri-*n*-butylphosphate (TBP) and trioctylphosphine oxide (TOPO) both purchased from Merck. The chloroform used as a solvent for the membrane was purchased from Sigma-Aldrich.

The membrane system consists from:

- Feed phase: solution of indole-3-acetic acid in the concentration range of 10^{-4} - 10^{-3} mol/L in the presence of hydrochloric acid concentration of 10^{-2} mol/L, at $pH=2$. Feed phase volume was 20 cm^3 ;

- Membrane: chloroform in which the one of the carriers was dissolved, tributyl phosphate solution at the concentration of 10^{-2} mol/L or trioctylphosphine oxide solution at the concentration of 10^{-2} mol/L. The membrane volume was 50 cm^3 ;

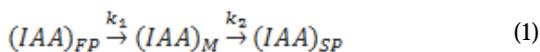
- Stripping phase: sodium hydroxide solution in the concentration range of 10^{-2} - 10^{-1} mol/L. The stripping phase volume was 7 cm^3 .

For the preparation of the feed phase and of the stripping phase was used saturated distilled water with chloroform and for membrane preparation was used chloroform saturated with water. The experiments of transport were realized in a wall in wall type transport cell presented in previous papers [12, 14-19]. The working temperature was room temperature ($22 \pm 2^\circ\text{C}$) at a stirring speed of the phases of 180 rot/ min. At the end of transport experiments the content of the indole-3-acetic acid was analyzed through molecular absorption spectrometry in the UV range. Thus a spectrophotometer LAMDA UV-Vis-NIR (Perkin Elmer Life and Analytical Sciences) was used. Indole-3-acetic acid presents a characteristic absorption band at a wavelength $\lambda = 280 \text{ nm}$ both for acid and alkaline medium corresponding to content in the feed phase and the stripping phase.

The content of the indole-3-acetic acid from membrane phase was assessed from the mass balance of the three phases of the membrane system.

Results and discussions

Assessing in time of the reduced concentrations of indole-3-acetic acid demonstrated that its pertraction through bulk liquid membrane transport system is realized after a kinetic model of consecutive irreversible first order reactions according to the equation (1):



where k_1 and k_2 represent pseudo-first-order apparent membrane entrance and exit rate constants, s^{-1} ;

According to this model kinetic the variation in time of reduced concentrations respects relationships:

$$\frac{dR_{FP}}{dt} = -k_1 R_{FP} = J_{FP} \quad (2)$$

$$\frac{dR_M}{dt} = -k_1 R_{FP} - k_2 R_M \quad (3)$$

$$\frac{dR_{SP}}{dt} = -k_1 R_M = J_{SP} \quad (4)$$

where:

J_{FP} , J_{SP} represent the flux at the entrance and exit out of membrane, $\text{mol}/\text{cm}^2 \text{ s}$,

R_{FS} , R_M si R_{FR} represent reduced concentrations in the three phases of membrane system calculated with relations:

$$R_{FS} = \frac{C_{FS}}{C_0} \quad (5)$$

$$R_M = \frac{C_M}{C_0} \quad (6)$$

$$R_{FR} = \frac{C_{FR}}{C_0} \quad (7)$$

C_{FS} , C_M , C_{FR} represent concentrations of the indole-3-acetic acid in feed phase, the membrane and the stripping phase at the time t , in mol/L

C_0 represent initial concentration in the feed phase, in mol/L

By integrating the equations 2-4 are obtained the variation functions of reduced concentrations in time described by equations 8-10.

$$R_{FS} = e^{-k_1 t} \quad (8)$$

$$R_M = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (9)$$

$$R_{FR} = 1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \quad (10)$$

Through the fitting of equations 8-10 with the experimental data pseudo-first-order apparent membrane entrance and exit rate constants k_1 and k_2 are obtained. From the dependence $R_m = f(t)$ one can determine the maximum concentration of indole-3-acetic acid from the membrane. This maximum amount at the concentration of indole-3-acetic acid concentration in the membrane, R_m^{\max} , is obtained when then $dR_m/dt=0$.

Thus it results:

$$R_M^{\max} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}} \quad (11)$$

The time at which is obtained the maximum of concentration from solute in membrane can be assessed with equation (12):

$$t_{\max} = \frac{\ln(k_1 / k_2)}{k_1 - k_2} \quad (12)$$

At $t=t_{\max}$, a maximum value of the flux at the entrance and exit out of membrane is obtained and can be described by the equations (13) and (14):

$$\left. \frac{dR_{FS}}{dt} \right|_{\max} = -k_1 \left(\frac{k_1}{k_2} \right)^{-k_1 / (k_1 - k_2)} \equiv J_{FS}^{\max} \quad (13)$$

$$\left. \frac{dR_{FR}}{dt} \right|_{\max} = -k_2 \left(\frac{k_1}{k_2} \right)^{-k_2 / (k_1 - k_2)} \equiv J_{FR}^{\max} \quad (14)$$

It is observed that the flux at the entrance and exit out of membrane are equal but the by contrary sign to. At the same time in the membrane at $t = t_{\max}$ is obtain a stationary status because:

$$\left. \frac{dR_m}{dt} \right|_{\max} = 0 \quad (15)$$

The experimental data obtained, presented in the figures 1 and 2 demonstrate a good correlation of the transport process of indole-3-acetic acid with the kinetic model of consecutive first order reactions.

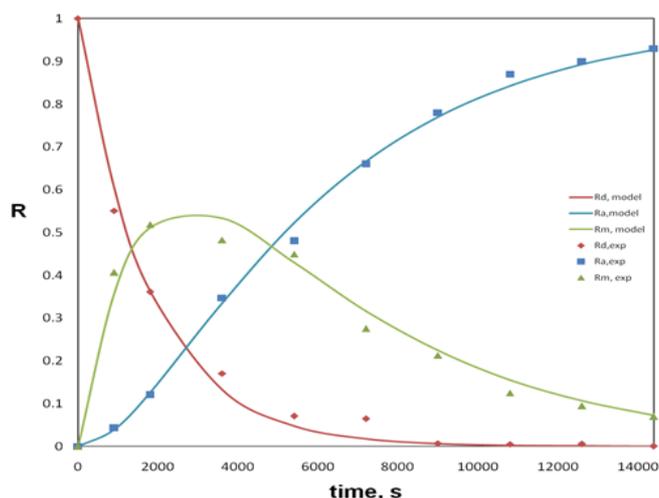


Fig. 1. The experimental results obtained at the pertraction of indole-3-acetic acid

Working conditions

Feed phase(d): indole-3-acetic acid solution at concentration 3×10^{-4} mol/L in the presence of hydrochloric acid concentration of 10^{-2} mol/L; Membrane(m): tributyl phosphate solution concentration of 10^{-2} mol/L in chloroform; Stripping phase(a): sodium hydroxide solution at concentration of 10^{-2} mol/L; R: represent the reduced concentrations.

Influence of the feed phase concentration

The influence of the concentration of indole-3-acetic acid from the feed phase was studied in the range 10^{-4} - 10^{-3}

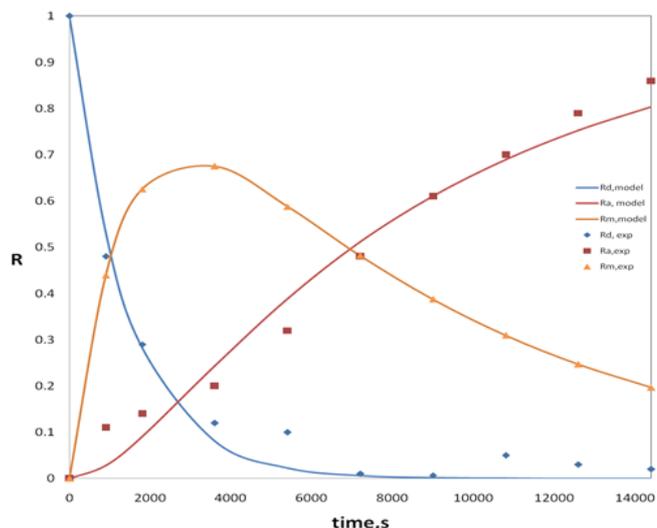


Fig. 2. The experimental results obtained to pertraction of indole-3-acetic acid

3 mol/L indole-3-acetic acid. The experiments were realized at $pH=2$ considered as optimum based on speciation diagrams presented in a previous paper [12; 14-19].

The concentration of sodium hydroxide in the stripping phase was of 10^{-2} mol/L. The kinetic parameters were calculated: k_1 , k_2 , R_m^{max} , t_{max} , J_d^{max} , J_a^{max} and the values obtained are presented in tables number 1 and 2.

It finds that in the field of studied of variation of the concentrations indole-3-acetic acid does not show a significant influence upon the studied kinetic parameters.

Table 1

THE KINETIC PARAMETERS AT THE PERTRACTION OF THE INDOLE-3-ACETIC ACID AT VARIOUS CONCENTRATIONS IN THE FEED PHASE IN THE PRESENCE OF CARRIER TRIBUTYLPHOSPHATE

Concentration of indole-3-acetic acid, mol/L	$k_1 \cdot 10^4, s^{-1}$	$k_2 \cdot 10^4, s^{-1}$	R_m^{max}	t_{max}, s	$J_d^{max} \cdot 10^4$ mol/cm ² s	$J_a^{max} \cdot 10^4$ mol/cm ² s
10^{-4}	7.2882	1.8917	0.6232	2499	-1.1790	1.1790
$3 \cdot 10^{-4}$	5.6183	2.1485	0.5514	2770	-1.1846	1.1846
$6 \cdot 10^{-4}$	5.1213	1.4355	0.6093	3450	-0.8747	0.8747
10^{-3}	5.2270	1.8252	0.5686	3092	-1.0379	1.0379

Table 2

THE KINETIC PARAMETERS AT THE PERTRACTION OF THE INDOLE-3-ACETIC ACID AT VARIOUS CONCENTRATIONS OF THE FEED PHASE IN THE PRESENCE OF CARRIER TRIOCTYLPHOSPHINE OXIDE

Concentration of indole-3-acetic acid, mol/L	$k_1 \cdot 10^4, s^{-1}$	$k_2 \cdot 10^4, s^{-1}$	R_m^{max}	t_{max}, s	$J_d^{max} \cdot 10^4$ mol/cm ² s	$J_a^{max} \cdot 10^4$ mol/cm ² s
10^{-4}	10.6356	2.4114	0.6496	1803	-1.5620	1.5620
$3 \cdot 10^{-4}$	7.0080	1.2686	0.6853	2977	-0.8694	0.8694
$6 \cdot 10^{-4}$	11.3508	1.2680	0.7590	2173	0.9626	0.9626
10^{-3}	9.0386	1.1575	0.7394	2607	-0.8559	0.8559

Table 4

THE KINETIC PARAMETERS AT THE PERTRACTION OF THE INDOLE-3-ACETIC ACID AT VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE IN THE STRIPPING PHASE IN THE PRESENCE OF CARRIER TRIBUTYLPHOSPHATE (TBP)

Concentration of indole-3-acetic acid, mol/L	$k_1 \cdot 10^4, s^{-1}$	$k_2 \cdot 10^4, s^{-1}$	R_m^{max}	t_{max}, s	$J_d^{max} \cdot 10^4, mol/cm^2s$	$J_a^{max} \cdot 10^4, mol/cm^2s$
10^{-2}	9.0386	1.1575	0.7394	2607	-0.8559	0.8559
10^{-1}	5.1572	2.0151	0.5473	2990	-1.103	1.103

Table 3

THE KINETIC PARAMETERS AT THE PERTRACTION OF THE INDOLE-3-ACETIC ACID AT VARIOUS CONCENTRATIONS OF SODIUM HYDROXIDE IN THE STRIPPING PHASE IN THE PRESENCE OF CARRIER TRIOCTYLPHOSPHINE OXIDE (TOPO)

Concentration of indole-3-acetic acid, mol/L	$k_1 \cdot 10^4, s^{-1}$	$k_2 \cdot 10^4, s^{-1}$	R_m^{max}	t_{max}, s	$J_d^{max} \cdot 10^4, mol/cm^2s$	$J_a^{max} \cdot 10^4, mol/cm^2s$
10^{-2}	9.0386	1.1575	0.7394	2607	-0.8559	0.8559
10^{-1}	10.8158	1.7274	0.7056	2018	-1.2189	1.2189

Experimental data obtained highlight higher values of the rate constants at the interface feed phase – membrane than those at interface membrane - stripping phase. The maximum fluxes at the entrance and exit out of membrane are of the same order of size all on range of concentration of indole-3-acetic acid variation.

Influence of the stripping phase concentration

In the stripping phase was used a sodium hydroxide solution at the concentrations in the range of 10^{-2} mol/L – 10^{-1} mol/L. In the feed phase was used indole-3-acetic acid solution at the concentration 10^{-3} mol/L at pH=2 obtained with hydrochloric acid. The kinetic parameters obtained in case of using of two carriers are presented in table 3 and 4.

It finds that a tendency of growth of the maximum fluxes at the entrance and exit out of membrane with increasing concentration of sodium hydroxide by stripping phase. Variation of the concentrations of sodium hydroxide does not reflect a significant variation on rate constants.

Influence of the carrier

It was studied the transport of indole-3-acetic acid in the presence of two carriers generally used in the membrane transport of organic acids: tributylphosphate (TBP) and trioctylphosphine oxide (TOPO). Optimal concentration of carrier was of 10^{-2} mol / L [36]. Analyzing the data presented in table 1- 4 it is found that in the presence carrier trioctylphosphine oxide (TOPO) the rate constants at interface feed phase| membrane have the highest values. The two carriers tributylphosphate and trioctylphosphine oxide do not have important influence upon the other studied kinetic parameters.

Conclusions

In the present paper was studied the transport of indole-3-acetic acid in the presence of two carriers, namely tributylphosphate and trioctylphosphine oxide. It was concluded that the pertraction process of indole-3-acetic acid is performed after a model of consecutive irreversible first order reactions. It was studied the influence of operational parameters such as: the concentration of indole-3-acetic acid from feed phase and concentration of

sodium hydroxide from strinning phase on some kinetic parameters, namely: $k_1, k_2, R_m^{max}, t_{max}, J_{FS}^{max}, J_{FR}^{max}$

The concentration of indole-3-acetic acid in feed phase does not significantly influence the values of kinetic parameters studied.

Increased concentration of sodium hydroxide from stripping phase is reflecting into a slight tendency of increase of maximum fluxes. The influence of the carrier was observed in the value of pseudo-first-order apparent membrane entrance rate constants rate. These have the highest values in case of trioctylphosphine oxide carrier.

References

1. DIACONU, I., RUSE, E., ABOUL-ENEIN, H.Y., BUNACIU, A.A., Crit Rev. Anal. Chem., **46**, no. 4, 2016, p. 332.
2. KISLIK, V.S., Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment, Elsevier, B.V., The Netherlands, 2010
3. PABBY, J.A., RIZVI, S. S. H., SASTRE, A. M., Handbook of Membrane Separations. Chemical, Pharmaceutical, Food and Biotechnological Applications, Membrane Extraction in Preconcentration, Sampling, and Trace Analysis, CRC Press, Boca Raton, 2009, p. 345-369.
4. SZCZEPANSKI, P., DIACONU, I., Separ. Sci. Technol., **47**, 2012, p. 1725-1732
5. DATTA, D., KUMAR, S., USLU, H., Hindawi Publishing Corporation J. of Chem., 2015, p. 1.
6. SCHLOSSER, S., SABOLOVA, E., Chem. Pap., **53**, 2000, p. 403.
7. SZCZEPANSKI, P., STANISLAW, K., Separ. Sci. Technol., **46**, no. 16, 2011, p. 2465.
8. SZCZEPANSKI, P., Sep. Purif Technol., **71**, no. 1, 2010, p. 121.
9. STANISLAW, K., SZCZEPANSKI, P., Chem. Pap., **65**, 2011, p. 584.
10. ERSOZ, M., VURAL, U.S., OKDAN, A., PEHLIVAN, E., YILDIZ, S., J. Membr. Sci., **140**, 1995, p. 263.
11. ZAHARIA, I., ABOUL-ENEIN, H.Y., DIACONU, I., RUSE, E., BUNACIU, A.A., NECHIFOR, GH., J. Iran. Chem. Soc., **10**, no. 6, 2013, p. 1129.
12. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, GH., Dig. J. of Nanomater. Bios., **7**, no. 3, 2012, p. 1303.
13. KUMAR, S., KAMSONLIAN, S., CHOMAL, N., Int. J. Chem. Eng. and Appl., **5**, no. 6, 2014, p. 506.
14. DIACONU, I., ABOUL-ENEIN, H.Y., BUNACIU, A.A., RUSE, E., MIREA, C. M., NECHIFOR, GH., Rev. Roum. Chim., **60**, no. 5-6, 2015, p. 501.

15. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, GH., *Ovidius University Annals of Chemistry*, **23**, no. 1, 2012, p. 53.
16. SERBAN, E.A., DIACONU, I., RUSE, E., MIREA, M. C., NECHIFOR, GH., *Rev. Chim. (Bucharest)*, **67**, no. 4, 2016, p. 634.
17. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, GH., *Rev. Chim. (Bucharest)*, **66**, no. 2, 2015, p. 169.
18. DIACONU, I., ABOUL-ENEIN, H.Y., AL-OMAR, M.A., NECHIFOR, GH., RUSE, E., BUNACIU, A.A., EFTIME TOTU, E., *Arab. J.Chem.*, **4**, 2011, p. 99.
19. DIACONU, I., MIREA, C. M., SERBAN, E.A., RUSE, E., NECHIFOR, GH., *Rev. Chim. (Bucharest)*, **66**, no. 7, 2015, p. 926.
20. RUSE, E., JOSCEANU, A.M., LUCA, C., CERBU, E., OPREA, M., *Rev. Chim. (Bucharest)*, **49**, no. 8, 1998, p. 556.
21. CASCAVAL, D., GALACTION, A.I., *St. Cerc. St. CICBIA*, **11**, no. 1, 2010, p. 129.
22. CASCAVAL, D., GALACTION, A.I., KLOETZER, L., *Rom. Biotechnol. Lett.*, **15**, no. 2, 2006, p. 5146.
23. GALACTION, A.I., BOMPA, A.S., KLOETZER, L., TURNEA, M.A., CASCAVAL, D., *Solvent Extr. Ion Ex.*, no. 33, 2015, p. 313.
24. GALACTION, A.I. CASCAVAL, D., NICUTA, N., *Biochem. Eng. J.*, **42**, 2008, p. 28.
25. OUKEBDANE, K., DIDI, M.A., AZZOUZ, A., VILLEMIN, D., *Scientific Study&Research*, **5**, no. 1-2, 2004, p. 59.
26. DRAGOI, E.N., CURTEANU, S., CASCAVAL, D., GALACTION, A.I., *Environ. Eng. Manag. J.*, **14**, no. 3, 2015, p. 533.
27. KUMAR, S., WASEWAR, K.L., BABU, B.V., *Chem. Eng. Technol.*, **31**, no. 11, 2008, p. 1584.
28. CHANG, S.H., SOM, A.M., KRISHNAN, J., *Int. J. of Chem. Eng. and Appl.*, **5**, no. 4, 2014, p. 315.
29. TAKEO, A., TSUKUBE, H., *Liquid membranes: chemical applications*. 1990, CRC Press., 1990, p. 2.
30. SAN ROMAN, M.F., BRINGAS, E. IBANEZ, R., ORTIZ, I., *J. Chem. Technol. Biotechnol.*, **85**, 2010, p. 2.
31. REDDY, T.R., RAMKUMAR, J., CHANDRAMOULEESWARAN, S., REDDY, A.V.R., *J. Membr.Sci.*, **351**, 2010, p. 11.
32. MOSKVIN, L.N., NIKITINA, T.G., *J.Anal.Chem.*, **59**, 2004, p. 2.
33. MA, M., CHEN, B., LUO, X., TAN, H., HE, D., XIE, Q., YAO, S., *J. Membr.Sci.*, **234**, 2004, p.101.
34. KAMINSKI, W., KWAPINSKI, W., *Pol. J. Environ. Stud.*, **9**, 2000, p. 37.
35. FERREIRA, Q., COELHO, I. M., RAMALHETE, N., MARQUES, H.M.C., *Separ. Sci. Technol.*, **41**, no. 16, 2006, p. 3553.
36. SERBAN, E. A., DIACONU, I., RUSE, E., NECHIFOR GH., *Conference: 16th International Multidisciplinary Scientific Geoconference (SGEM 2016) Location: Albena, BULGARIA Date: JUN 30-JUL 06, 2016, ECOLOGY, ECONOMICS, EDUCATION AND LEGISLATION CONFERENCE PROCEEDINGS, SGEM 2016, VOL II Book Series: International Multidisciplinary Scientific GeoConference-SGEM, 2016, p. 133*

Manuscript received: 28.12.2016