SOLVENT RESISTANT NANOFILTRATION MEMBRANES BASED ON FUNCTIONALIZED CELLULOSE WITH CROWN ETHERS FOR LEAD RETENTION FROM ALCOHOLS

Ştefan Ioan VOICU[1], Ludmila IARCA[2], Antoneta Doina RADU[3], Corneliu TRIŞCĂ RUSU[4]

Prezența plumbului în soluții de solvenți organici reprezintă un impediment în utilizarea acestora în anumite tipuri de aplicații unde se cer condiții de puritate avansată (industrie alimentară, medicină, electronică, chimie analitică, optică). În vederea îndepărtării, prin nanofiltrare, a plumbului sau a urmelor de ioni de plumb, din soluții apoase etanolice, s-au sintezat membrane de celuloză cu eteri coroana imobilizați, pe suprafață. Imobilizarea s-a realizat dupa activarea alcalină a membranei de celuloza şi legarea covalentă a derivaților amino eter coroană (utilizând clorura de cianuril drept moleculă de spațiere între membrană şi eterul coroana). Materialele sintetizate au fost caracterizate prin spectroscopie FT-IR şi microscopie SEM. Membranele au fost testate la indepartarea ionilor de plumb prin nanofiltrare din soluții etanolice apoase, simulând astfel produse spirtoase obținute prin distilare în vase artizanale din materiale ce conțin plumb (cazane de țuică).

The presence of lead in organic solvents is an impediment to their use in certain types of applications where conditions require advanced purity (food, medicine, electronics, analytical chemistry, optics). In order to remove lead or traces of lead ions, by nanofiltration, from aqueous ethanol solutions, cellulose membranes are synthesized with crown ethers immobilized on the membrane surface. Immobilization was achieved after alkaline activation of cellulose membrane and immobilization of amino derivatives of crown ethers (using cyanuric chloride as spacing molecule between the membrane and crown ether). Synthesized materials were characterized by FT-IR spectroscopy and SEM microscopy. The membranes were tested to remove the lead ions from aqueous ethanol solutions by nanofiltration, simulating on this was alcoholic products obtained by distillation in vessels made from materials with lead (schnaps caldron).

Keywords: cellulose, crown ethers, nanofiltration, lead removal

[1] Lecturer, Department of Analytical Chemisty and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: svoicu@gmail.com
[2] Ph.D. Student, Department of Analytical Chemisty and Environmental Engineering University POLITEHNICA of Bucharest, e-mail: ludmila_iarca@yahoo.com
[3] Ph.D. Student, Department of Analytical Chemisty and Environmental Engineering University POLITEHNICA of Bucharest, e-mail: doina_radu@gmail.com
[4] Ph.D. Student, Department of Analytical Chemisty and Environmental Engineering University POLITEHNICA of Bucharest, e-mail: ctrisca2002@yahoo.com

1. Introduction

The development of new membrane materials and processes currently knows a major interest for membrane preparation, and optimization of process engineering and application development in various fields [1-2]. The nanofiltration, defined as the membrane process intermediate between reverse osmosis and ultrafiltration knows a continuous development due to nano-scale particles that must be separated from different systems and due to complexity of involved transfer processes [3].

Since the beginning of this type of membrane process (years '80), one of the most used material was cellulose [4]. Cellulose and their derivatives present in generally linear structures and the presence of acetyl groups and hydroxyl chain induces high performance for the membranes used in processes like ultrafiltration, osmosis and reverse osmosis [5-7]. The main source of cellulose for membranes is cotton linters. Most recently microcrystalline cellulose was obtained by changing the legs of cotton. Cellulose derived from such materials has a narrow molecular weight distribution and very advanced purity [8].

Even the membranes can be prepared from all acetylated derivatives of cellulose, the best performances has been achieved by using a derivative with substitution degree between 2.4 and 2.5, which combines good solubility in organic solvents with a wide range of possible interactions between separation system and the membrane, due to free hydroxyl groups. Molecular weight average of cellulose for membranes is 25000-80000 D which corresponds to a degree of polymerization of 100-300 [9].

The advantages of acetylated derivatives of cellulose membranes consist in obtaining of high flux and selectivity, accessible manufacturing technology, abundant and renewable raw materials [10-12].

The disadvantages of these polymers are represented by the low thermal resistance, restricted optimum pH range (2 ÷ 8), low resistance to oxidation by chlorine, membranes must be kept wet and are biodegradable, which requires the use in sterile environments [13-14]. These disadvantages restrict the applications to aqueous systems with low salt containing and also require the use of these membranes in sterile environments. These disadvantages have been required the study and the development of some new polymeric materials for making membranes [15].

However, acetylated derivatives, nitrate, hydroxyethyl or carboxymethyl cellulose are still an important basis for synthesis of membranes for reverse osmosis and ultrafiltration [16, 17].

The use of cellulose membranes in nanofiltration processes is well known due to advantages offered by this polymer (high chemical resistance to organic solvents, mechanical strength) [18]. But the topical problem remains the selectivity of cellulose membranes that can be improved by derivatization of membrane, or by synthesis of composite membranes [19].

Drioli et al [20] have synthesized a cellulose based composite membrane with dispersed different types of crown ethers in the membrane structure (diaza-18-crown-6, hexaza-18-crown-6-18, hexathia-crown-6 and dibenzo-18-crown-6) for retention of gold, silver and copper.

In this paper is presented the synthesis of new cellulose membranes superficially grafted with crown ethers. This material combines the advantages of cellulose as resistant polymer to organic solvents with the complexant capacity of crown ethers.

The obtained membranes were used for the separation of lead ions from aqueous ethanolic solutions simulating in this way the purification of alcoholic products obtained by distillation in vessels from materials with lead (caldrons for the preparation of alcoholic drinks) [16].

2. Experimental

2.1. Activation of cellulose membranes. Commercial cellulose membranes (from Visking), designed for membrane processes with pressure gradient, were activated in alcoholic potassium hydroxide solution in order to obtain alkali cellulose (Cell-A-K^+) by using iso-propanol (Fluka) and potassium hydroxide (Merk).

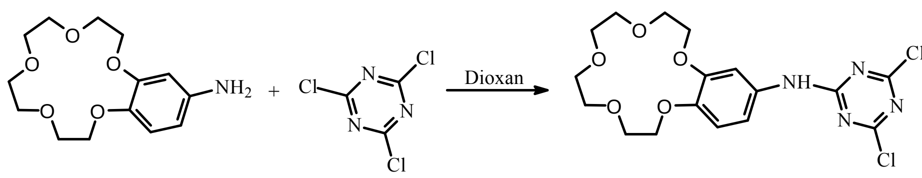
2.2. Functionalization of 4'-amino benzo 15 crown ether with cyanuric chloride (15C5). The intermediary based on 15 crown 5 ether (Fluka) was obtained by reaction between cyanuric chloride (Fluka) and crown ether in dioxane at 40°C for 4 hours (Scheme 1a). Reaction product was isolated by evaporation.

2.3. Functionalization of alkali cellulose membranes. Alkali cellulose membranes were functionalized in dioxane with the obtained crown ether derivative by heating at 60°C for 4 hours (Fig. 1b) in alkaline medium (generated by membrane) at pH=11.5-12.5. After reaction, membranes were washed with deionized water in order to remove traces of unreacted reagents and salts.

2.4. Lead retention on synthesized membranes. The membranes were used in a nanofiltration process in order to remove lead from aqueous alcoholic solutions of lead acetate. The analysis of lead quantity in feed solution respectively permeate was performed by atomic absorption.

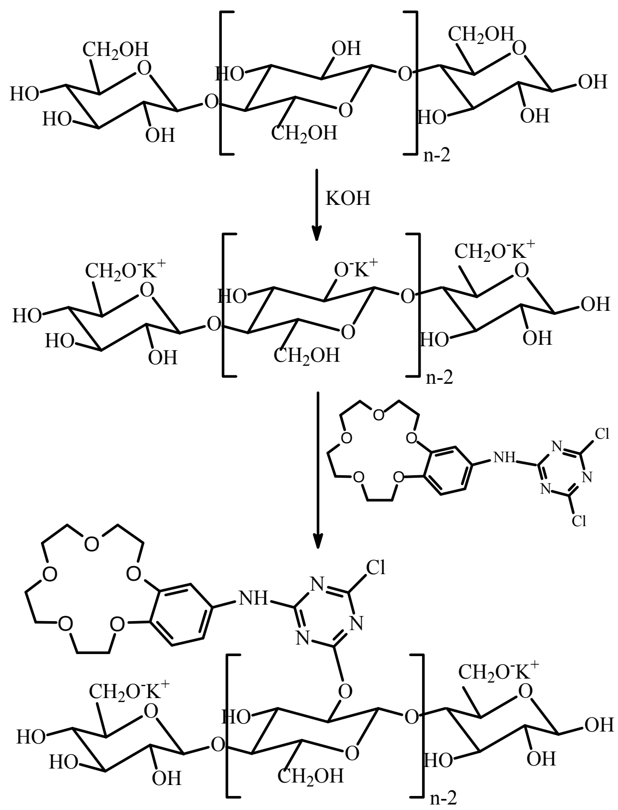
2.5. Analysis methods and instruments

The scanning electron microscopy was performed using the Hitachi S4500 FESEM. The infrared spectroscopy analysis was performed using a Brucker Tensor 27 instrument with diamond ATR annex. The atomic absorption was performed with a Perkin Elmer instrument at 260 nm. The nanofiltration process was performed into a CELFA installation by re-circulating the feed solution using plane membranes with a 90 mm diameter at 12 atm (pressure realized with inert gas) [17].



15C5 CC I

a



b

Fig 1. Functionalization reaction of crown ether with cyanuric chloride (a) and reactions for functionalized cellulose membrane synthesis (b)

3. Results and discussion

In order to avoid the disadvantage of nanofiltration which requires high pressures (and consequently a part of the crown ethers is eluted during the filtration process), the present study suggests the chemical binding of crown ethers on cellulose membrane thus not affecting the process efficiency (Fig. 1).

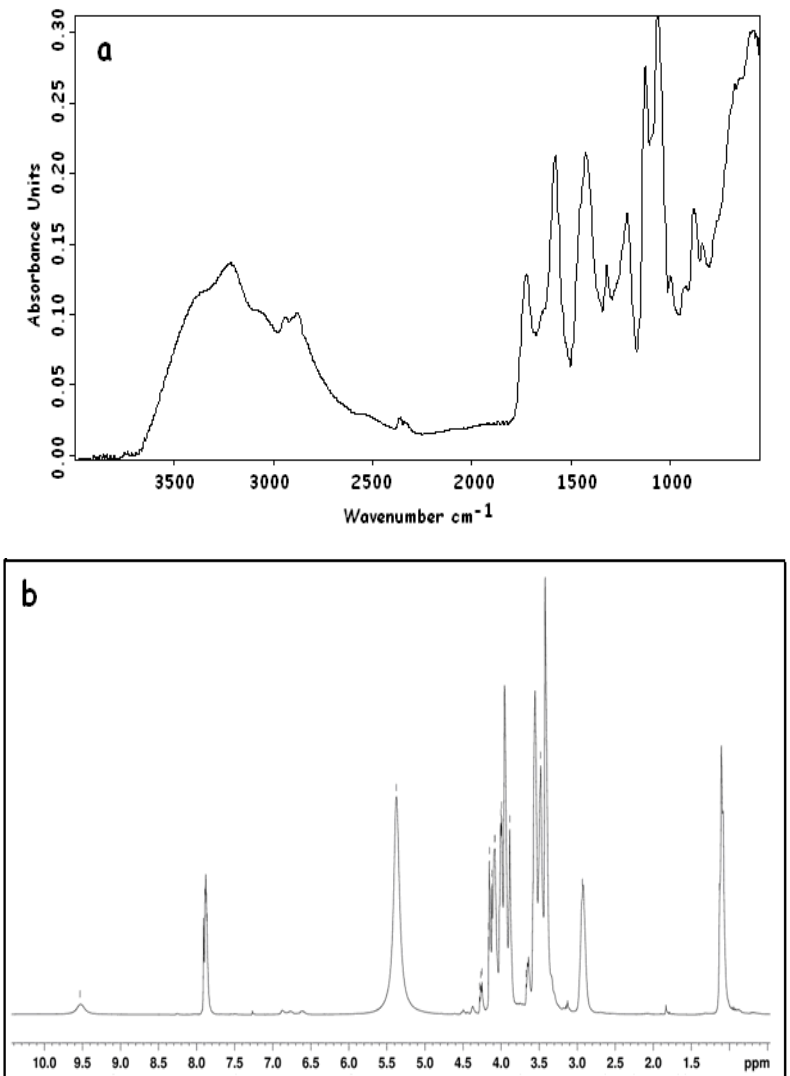
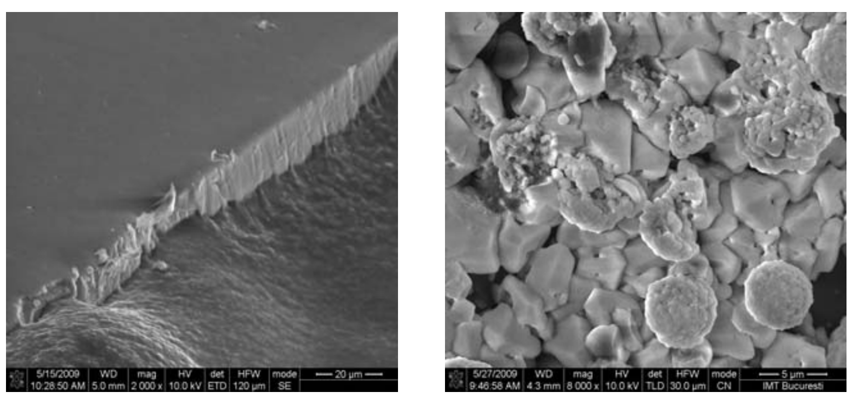


Fig. 2. FT-IR spectrum (a) and NMR spectrum (b) of amino benzo crown-15-ether functionalized with cyanuric chloride

The first characterized compound was the intermediate (I) resulted in reaction between crown ether derivative and cyanuric chloride. The main advantage of using cyanuric chloride as spacer is given by the aromatic characteristic of the ring. After the reaction of a first chloride atom at 40°C, the aromatic ring is deactivated and the formation of dimmers is less probable. The reaction at a second chloride atom must be performed at more then 60°C and the pH value is adjust at 11.5-12.5 by alkali cellulose membrane.

The synthesized compound was characterized by FT-IR spectroscopy (Bruker Tensor 27 with diamond ATR annex) and ^{1}H-NMR spectrometry (Bruker NMR AM 300, 300 MHz, in $CDCl_3$), the spectra are presented in Fig. 2. In FT-IR spectrum the absorption peaks from 880 cm^{-1} and 1650 cm^{-1} are attributed to =C- respectively =N- bonds in the aromatic ring plane. The 1580 cm^{-1} absorption band is attributed to –NH– formation bond after the intermediate synthesis. The absorption band at 1270 cm^{-1} is specific for –O– bond from crown ether molecule. The NMR spectrometry was performed in $CDCl_3$ and the data are: H NMR ($CDCl_3$ – d_6) δ_H: 1.13 (1H, s), 2.93 (1H, s), 7,89 (1H, q, J=4.35) with chemical shift for –NH– bond formation at $\delta_H \approx 2.93$ ppm [21-22].

The Scanning Electron Microscopy (Fig. 3) reveals a uniform and compact structure for un-functionalized cellulose membranes (Fig. 3a) on surface and cross-section. After functionalization and retention of lead on membrane surface (Fig. 3b) the formation of lead salt crystals was observed. This aspect is due to polarization concentration effect of the membrane combined with complexing effect given by the crown ethers.



a b

Fig. 3. Scanning Electron Microscopy on celllulosic membranes: a - non functionalized membrane and b - functionalized membrane after lead nanofiltration.

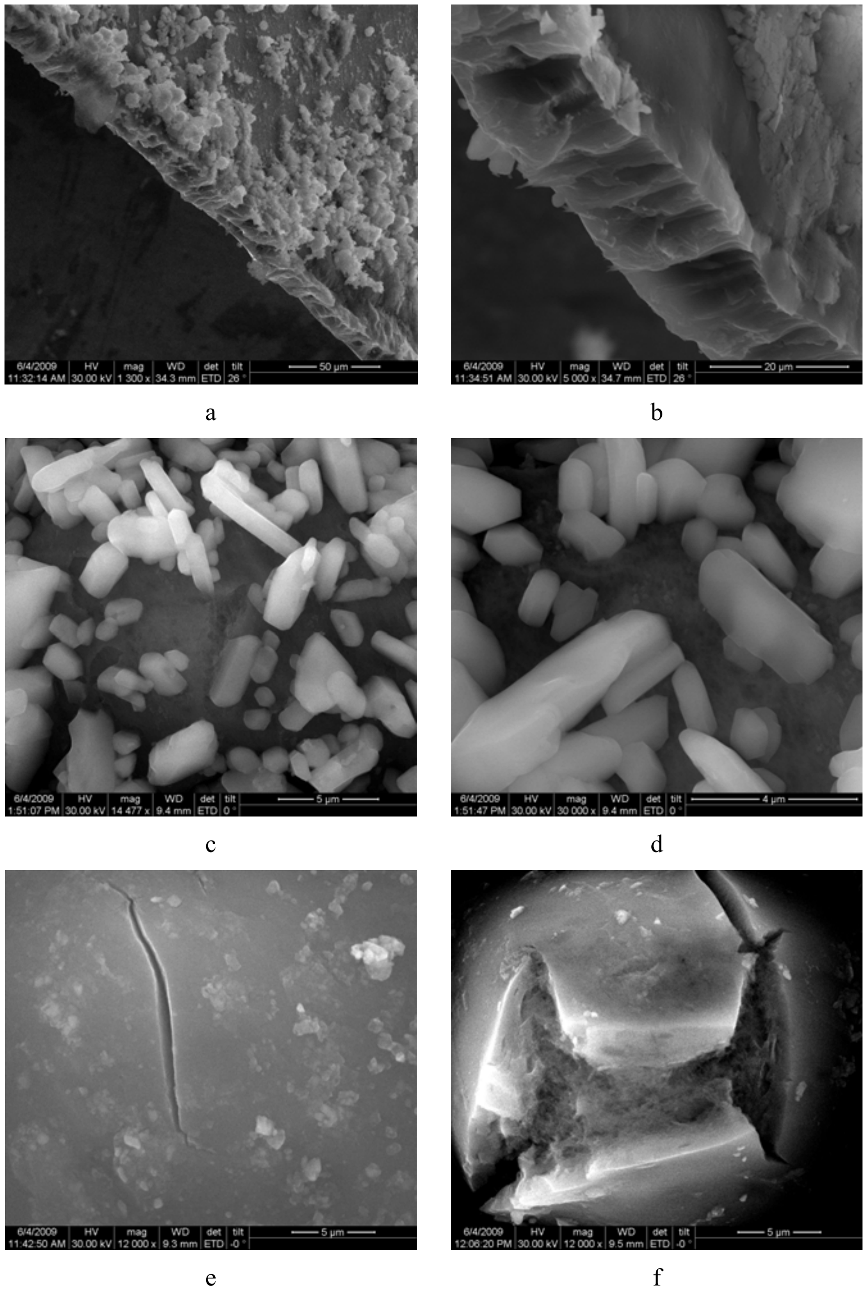


Fig. 4. SEM images of alkali cellulose membranes after nanofiltration process: a and b - initial surface; c and d - crystals formed on membrane surface; e, f-micro-cracks details on surface after lead nanofiltration

A careful study of the surface of these membranes was performed. Studying the shades and color of the forms we can observe the presence of two different crystals. Darker spherical crystals with high density and higher molecular weight, were assigned to lead salts and the cubic lighter crystalline forms (lower molecular weight) were attributed to traces of potassium salts remained in membrane after the activation.

After nanofiltration it was observed that some membranes become friable. The examination by Scanning Electron Microscopy of the membrane microstructure (Fig. 4) revealed micro rifts which became more and more obvious at the alkali cellulose membranes (Fig. 4e and f) and also it can be observed the formation of potassium crystals the surface of functionalized membranes with crown ethers after nanofiltration (Fig. 4c and d). After the analysis of activation procedure and the immobilization of crown ethers and supplement synthesis experiments for replacing the dioxan with di-ethylene-glycol it were observed that the dioxan traces present a negative influence for the quality of the membranes. The cellulose membranes processed in dioxan became friable, breakable and difficult to manipulate.

The comparative data for lead retention (from synthetic aqueous ethanol solutions with 10^{-5} M initial concentration) onto regenerated cellulose membranes (MI) and respectively onto regenerated cellulose grafted with crown ether 15C5 with superficial concentration 10^{-6} (MII), 10^{-5} (MIII) and 10^{-4} (MIV) are presented in Table 1. The results indicate an increase of retention with the increase of grafting degree of membrane with crown ether in the following order MI<(MII) < (MIII) <(MIV). The best performances are presented by the membrane MIII.

Table 1

Comparative data for lead retention on cellulose membrane and cellulose membrane with 15C5 crown ether

Nr. Crt.	Lead initial quantity (g)	Retained Pb quantity (mg)			
		MI	MII	MIII	MIV
1	0.0400	13.06	23.10	25.45	33.00
2	0.0600	19.51	28.40	32.33	40.27
3	0.0700	17.45	24.75	30.20	35.80
4	0.1000	19.18	30.25	41.30	43.10

The obtained results show that the functionalization degree and lead quantity retained on the membrane is correlated with the total lead quantity from the system.

If the solution quantity which contains lead is big, the efficiency of membrane decreases, fact which suggests that the procedure is favorable for the removal of metal traces from alcoholic solutions.

4. Conclusions

The synthesis of cellulose membranes with immobilized crown ethers on surface for lead or traces of lead removal from alcoholic aqueous solutions by nanofiltration was performed. After the alkaline activation of cellulose membrane, the amino derivatives of crown ethers were covalently immobilized using the cyanuric chloride as spacer linker. The synthesized materials were characterized by FT-IR and Scanning Electron Microscopy.

The nanofiltration results with obtained synthesized membranes indicate an increase of lead retention with the increase of functionalization degree of the membrane. It can be also observed that with the increase of initial total lead quantity from ethanol aqueous solution the retention capacity of membrane decrease.

Acknowledgement

Authors recognise financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials".

R E F E R E N C E S

[1] *C. Corobea, D. Donescu, S. Raditoiu, S.I. Voicu, G. Nechifor*, „Materiale membranare. IV. Nanoparticule functionalizate pentru ultrafiltarea coloidala o ionilor cuprici", Revista de Chimie 57 (9), 2006, pp. 981-987.

[2] *B. Serban, M. Bercu, S.I. Voicu, A.C. Nechifor, C. Cobianu*, „Sinteza si caracterziarea unei noi polianiline dopata cu sulfat acid de ciclodextrina", Revista de Chimie 57 (9), 2006, pp.978-980.

[3] *M. Bumbac, B. Serban, C. Luca, G. Nechifor, S.I. Voicu*, „Studii privind extractia sinergetica a cationilor alcalini Na^+ si K^+ in prezanta unor amestecuri p-tertbuilcalix[4]arena – eteri coroana" Revista de Chimie 57 (9), 2006, pp. 927-930.

[4] *D. Garganciuc, G. Batranescu, G. Nechifor, M. Olteanu*, „Funcționalizarea polimerilor de tipul polisulfonei şi polifenilenoxidului pentru realizarea unor membrane cu afinitate", Materiale Plastice 45 (1), 2008, pp. 29-33.

[5] *S.I. Voicu, A.C. Nechifor, B. Serban, G. Nechifor, M. Miculescu*, „Formylated Polysulfone Membranes for Cell Immobilization" Journal of Optoelectronics and Advanced Materials 9(11), 2007, p.3423-3426.

[6] *G. Nechifor, S.I. Voicu, A.C. Nechifor, S. Garea*, „Nanostructure hybrid membrane polysulfone-carbon nanotubes for hemodyalisis" Desalination 241, 2009, pp. 342-348.

[7] *G. Nechifor, B. Albu, D. Rata, G. Popescu*, „Membrane în procesele de separate: VII. Îndepărtarea compuşilor organici din soluții apoase" Revista de Chimie 47(3), 1996, pp.260-264.

[8] *B.G. Albu, D. Rață, G. Nechifor, G. Popescu*, „Membrane în procesele de separare: VI. Caracterizarea membranelor microporoase" Revista de Chimie 47(1), 1996, pp. 36-45.

[9] *A.C. Nechifor, E. Ruse, B. Serban, G. Nechifor*, „Materiale membranare II. Electrodializa cu membrane din polietercetone modificate chimic" Revista de Chimie 53(5), 2002, pp.472 – 482

[10] *B. Van der Bruggen, M. Manttari, M. Nystrom*, „Drawbacks of applying nanofiltration and how to avoid them: A review", Separation and Purification Technology 63, 2008, pp.251-263.

[11] *A. Nechifor, G. Popescu, C. Neacşu, B. Albu, N. Luca, G. Nechifor*, „Membrane în procesele de separare. IV. Purificarea colorantilor prin ultrafiltrare", Revista de Chimie 41 (9), 1990, pp.703-711.

[12] *A.C. Nechifor, E. Ruse, G. Nechifor*, „Materiale membranare - I. Polietercetone", Revista de Chimie 52(10), 2001, pp. 531-541.

[13] *T. Visser, N. Masetto, M. Wessling*, „Materials dependence of mixed gas plasticization behavior in asymmetric membranes", Journal of Membrane Science 306 (1-2), 2007, pp. 16-28.

[14] *S. Darvishmanesh, J. Degreve, B. Van der Bruggen*, „Physicochemical characterization of transport in nanosized membrane structures" Physical Chemistry Chemical Physics 11(2), 2010, pp. 404-411.

[15] *S.I. Voicu, N.D. Stanciu, A.C. Nechifor, D.I. Vaireanu, G. Nechifor*, „Synthesis and Characterization of Ionic Conductive Polysulfone Composite Membranes", Romanian Journal of Information Science and Technology 12 (3), 2009, pp. 410-422.

[16] *B. Van der Bruggen, L. Braeken, C. Vandecasteele*, „Flux decline in nanofiltration due to adsorption of organic compounds", Separation and Purification Technology 29(1), 2002, pp. 23-31.

[17] *B. Van der Bruggen, L. Braeken, C. Vandecasteele*, „Evaluation of parameters describing flux decline in nanofiltration of aqueous solutions containing organic compounds" Desalination 147(1-3), 2002, pp. 281-288.

[18] *J. Wang, R. Faber, M. Ulbricht, M.*, „Influence of pore structure and architecture of photo-grafted functional layers on separation performance of cellulose-based macroporous membrane adsorbers", Journal of Cromatography A 1216(37), 2009, pp. 6490-6501.

[19] *H. Susanto, S. Franzka, M. Ulbricht*, "Dextran fouling of polyethersulfone ultrafiltration membranes-Causes, extent and consequences", Journal of Membrane Science 296(1-2), 2007, pp. 147-155.

[20] *A. Gherrou, H. Kerdjoudj, R. Molinari, P. Seta, E. Drioli*, „Fixed sites plasticized cellulose triacetate membranes containing crown ethers for silver(I), copper(II) and gold(III) ions transport", Journal of Membrane Science 228, 2003, pp. 149-157.

[21] *F.D. Balacianu, A.C. Nechifor, R. Bartos, S.I. Voicu, G. Nechifor*, „Synthesis and characterization of Fe_3O_4 magnetic particles-multiwalled carbon nanotubes by covalent functionalization", Optoelectronics and Advanced Materials – Rapid Communications 3(3), 2009, pp. 219-222.

[22] *A.C. Nechifor, M.G. Stoian, S.I. Voicu, G. Nechifor*, „Modified Fe_3O_4 coloidal dispersed magnetic particles as carrier in liquid membranes", Optoelectronics and Advanced Materials – Rapid Communications 4(8), 2010, pp. 1118-1123.