CHITOSAN-POLYPROPYLENE HOLLOW FIBERS COMPOSITE MEMBRANE FOR COPPER-ZINC IONS PERTRACTION

Florentina Mihaela PĂNCESCU[1], Andreea FERENCZ (DINU)[2], Vlad-Alexandru GROSU[3], Alexandru GORAN[4], Gheorghe NECHIFOR[5]

Composite membranes based on cellulosic derivatives or related natural compounds with ionizing groups represent one of the viable alternatives for separation, concentration and purification of acidic aqueous solutions containing copper and zinc ions. This work presents the preparation and characterization of a chitosan–polypropylene hollow fiber composite membrane. The prepared membrane was tested in the pertraction process of copper and zinc ions from strongly acidic solutions. The obtained results show that this type of membrane achieves both the separation and the concentration of the tested solutions. The contribution of each component of the composite membrane was comparatively evaluated under the same working conditions.

Keywords: composite membranes; chitosan; polypropylene hollow fiber; pertraction; cupper-zinc separation.

1. Introduction

Membranes play an important role in the development of separation, purification and/or concentration processes and technologies, which can also be applied to the recovery of recyclable electrical and electronic waste [1-3].

[1] PhD student, Faculty of Chemical Engineering and Biotechnologies, Dep. of Analytical Chemistry and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: florynicorici@yahoo.com

[2] PhD student, Faculty of Chemical Engineering and Biotechnologies, Dep. of Analytical Chemistry and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: andra_d24@yahoo.com

[3] Lecturer, Department of Electronic Technology and Reliability, Faculty of Electronics, Telecommunications and Information Technology, University Politehnica of Bucharest 061071, Romania, e-mail: vlad.grosu@upb.ro

[4] PhD student, Faculty of Chemical Engineering and Biotechnologies, Dep. of Analytical Chemistry and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: alexandru@santego.ro

[5] Prof., Faculty of Chemical Engineering and Biotechnologies, Dep. of Analytical Chemistry and Environmental Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: gheorghe.nechifor@upb.ro

Because they are applicable in small economic units, but especially in integrated industrial platforms, membrane processes have increasingly attracted the attention of researchers [4-6].

Membranes and membrane processes are highly selective [7], have increasingly better productivity [8] and, above all, are technically and economically viable because they require low investments and low material consumption [9.10].

For the recycling of electrical or electronic waste, liquid membranes [11], polymer membranes [12], but especially composite ones [13–15] have been studied.

From the point of view of the design of the pertraction modules, those based on the hollow fiber membrane type are the most suitable [16,17], and the materials used are polymers or combinations of artificial synthetic polymers, but especially those of natural origin (cellulose and its derivatives) [18–20].

A real interest in separation and/or concentration arises from the ionic combinations resulting from acid attack on wastes in galvanic cells [21]. Two of these systems have been studied in detail: the Cu–Zn combination from acid fuels and the Pb–Cd combination from acid batteries [22,23]. The separation of copper and zinc elements is of particular interest, as they can later be used as biocidal or bactericidal materials with wide applications in biomedicine [24–26].

This paper presents the preparation and characterization of a chitosan-polypropylene hollow fiber composite membrane (Chi-PPHFM), and its testing in the pertraction system of copper and zinc ions from strongly acidic solutions (HCl).

2. Experimental part

The reagents and materials used in the present work were of analytical purity. $CuSO_4 \cdot 5H_2O$, $ZnSO_4$, NaCl, chitosan, and glacial acetic acid (analytical grade, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used in the studies. Sodium hydroxide pellets (NaOH), hydrochloric acid solution HCl 35% (ultrapure) and NH_4OH 25% (analytical grade) were purchased from Merck KGaA Darmstadt, Germany.

The purified water, characterized by a conductivity of 18.2 µS/cm, was obtained with a RO Millipore system (MilliQR Direct 8 RO Water Purification System, Merck, Darmstadt, Germany) [27].

The hollow fibers polypropylene membranes (PPHFM) were provided by GOST Ltd., Perugia, Italy. Their characteristics and performances are synthetically presented in Fig. 1 [28,29].

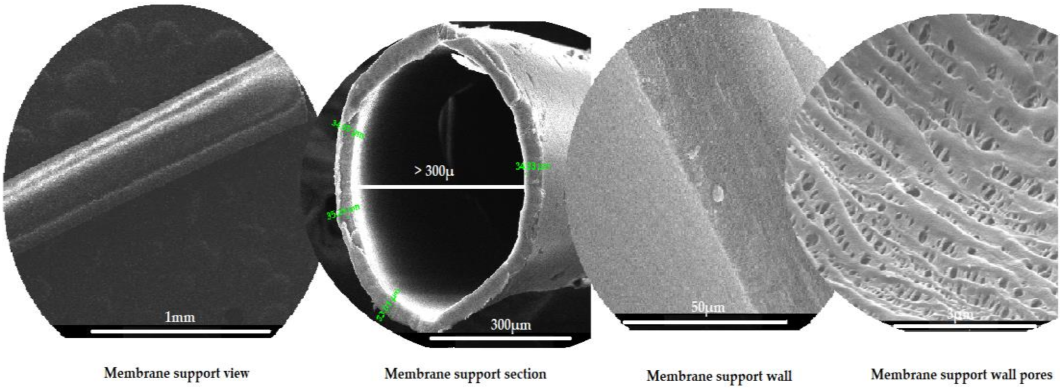
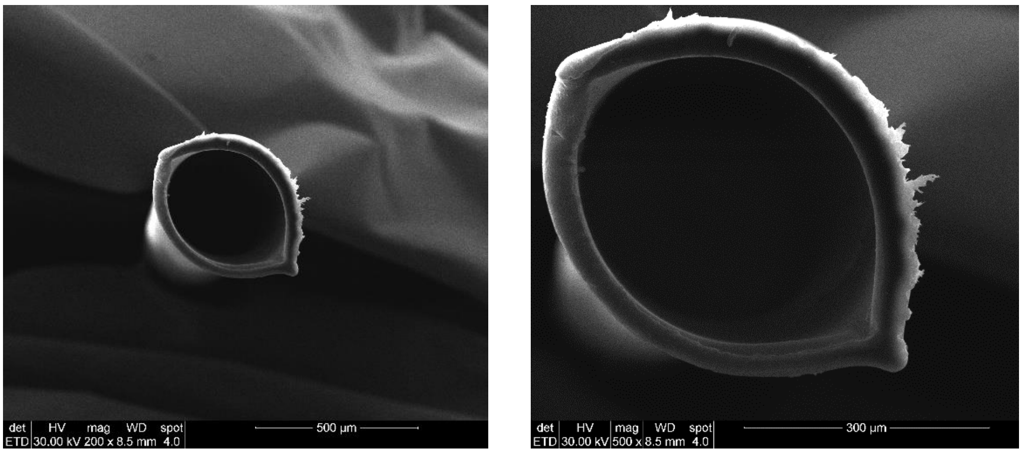


Fig. 1. The dimensional characteristics of the polypropylene hollow fibers membranes (PPHFM)

To obtain the chitosan impregnated hollow fibers polypropylene membranes (Chi-PPHFM), a solution of 3% chitosan in 3% acetic acid is subjected to ultrafiltration [30,31].

The obtained membranes were characterized by Fourier Transform InfraRed spectroscopy (FTIR) using a FTIR Tensor 27 from Bruker (Bruker Co., Ettlingen, Germany), determination of ion exchange capacity (i.e.c) and scanning electron microscopy (SEM) with a S Hitachi S4500 system (Hitachi High–Technologies Europe GmbH, Mannheim, Germany) (Fig. 2).



a) b)

Fig. 2. The scanning electron microscopy (SEM) image of the chitosan- polypropylene hollow fibers membranes (Chi-PPHFM) obtained by ultrafiltration of chitosan solution in acid acetic: a) cross-section; b) cross-section (detail)

The pertraction of 10^{-4}-10^{-6} mol/L copper and zinc solutions in 3 mol/L hydrochloric acid solution is carried out in an installation previously presented in detail (Fig. 3) [32,33].

In the present case, the source phase (SP) (feed solution) has a volume of 1000mL, and the receiving phase solution (RF) has a volume of 100mL. The flow rate of the source phase is 100 mL/min, and the flow rate of the receiving phase is 10 mL/min.

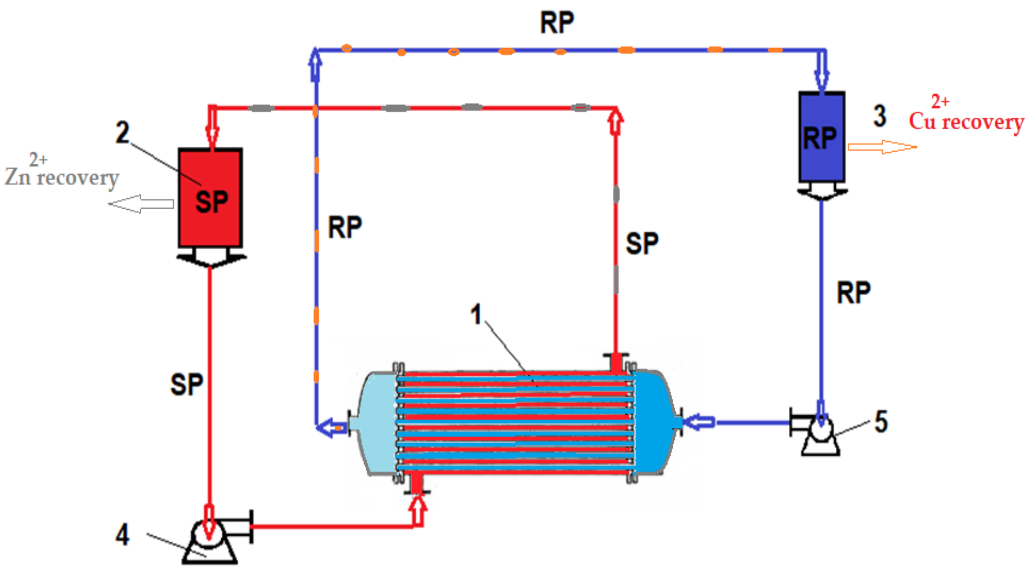


Fig. 3. Schematic of the installation for pertraction [32,33]: SP – source phase, RS – receiving phase. 1. Hollow fiber pertraction module; 2. SP reservoirs; 3. RP reservoirs; 4. SP pump; 5. RP pump.

The pertraction efficiency (*PE* %) for the task ion was calculated as follows [33,34], based on ionic solution concentration:

$$PE(\%) = \frac{(c_0 - c_f)}{c_0} \cdot 100 \quad (1)$$

Where: *cf* and c_0 being, respectively, the final and initial concentration of the solute.

The concentration factor (*CF*) was calculated by *cf* and c_0 rapport:

$$CF = \frac{(c_f)}{c_0} \quad (2)$$

3. Results and discussions

Solutions containing copper and zinc ions are obtained in large quantities in the case of the hydrometallurgical recovery of waste electronics and electrotechnical industry, but significant quantities are also found in the chemical and chemical-pharmaceutical or car manufacturing industries [35,36].

The valorization of copper and zinc elements take place after the separation from dilute solutions of the two ions (10^{-4}-10^{-6} mol/L) from a strongly acidic solution (hydrochloric acid 3mol/L).

The separation carried out in this study is based on the stability of complexes with excess chloride ion and strongly acidic medium:

$$Cu^{2+}_{(aq)} + 4\ Cl^{-}_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} \quad (3)$$

$$Zn^{2+}_{(aq)} + 4\ Cl^{-}_{(aq)} \rightleftharpoons [ZnCl_4]^{2-}_{(aq)} \quad (4)$$

The difference between the stability of the two complexes is so great [37] that it is possible to use pertraction with the help of polypropylene hollow fiber membrane (PPHFM), when the membranes act as contactors, or with chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM), when the membranes act as ion exchangers.

The scanning electron microscopy characteristics of the two types of used membranes are presented in Table 1.

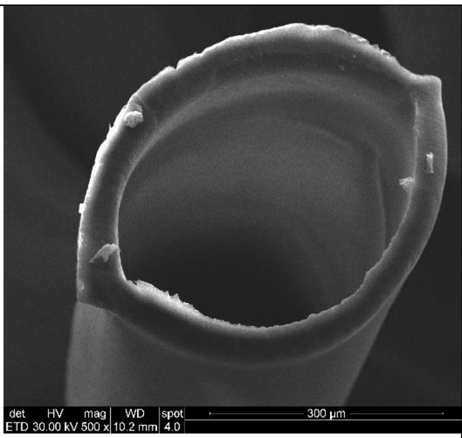
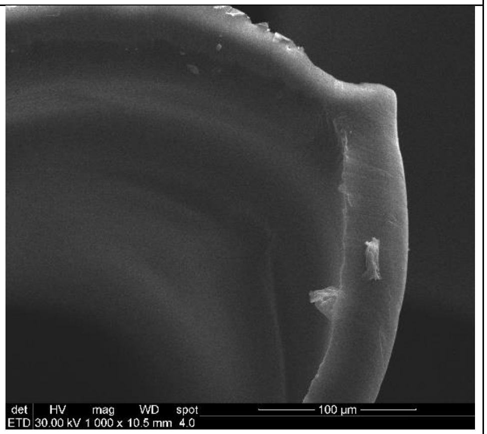
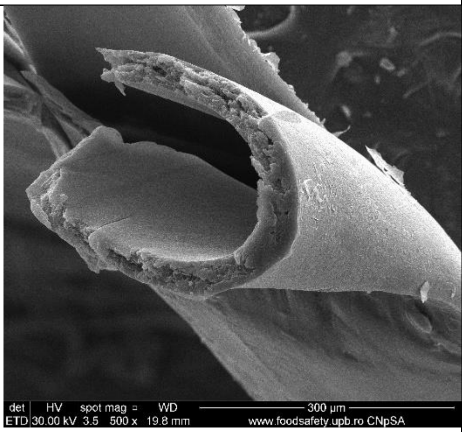
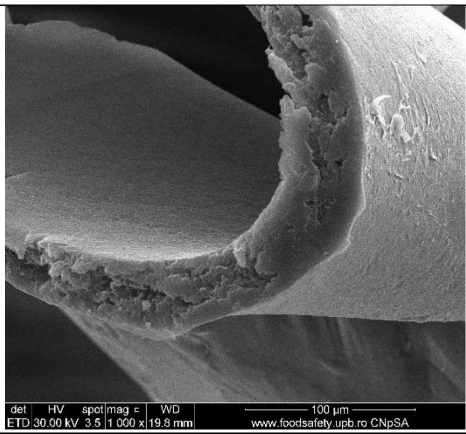
The appearance of the polypropylene hollow fiber membrane (PPHFM) support fibers is uniform and smooth, while the surface and section of the chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM) is rough, indicating the coverage of the support membrane, but also the appearance of chitosan inside it.

Fig. 4 shows the Fourier Transform InfraRed spectrum (FTIR) in which the specific absorption bands for both polypropylene (Fig. 4a) and chitosan (Fig. 4b) can be observed. In the case of polypropylene, the hydrophobicity of the membrane material can be an advantage in the exploitation of the membrane contactor, while the hydrophilicity of chitosan (considering the amino groups) allows the exploitation of the module (Fig. 3) as an ion exchange pertractor (i.e.c. = 1.73).

The results of the separation of copper and zinc ions from the source phase with a concentration of 10^{-4}–10^{-6} mol/L in hydrochloric acid 3 mol/L, in the receiving phase 0.1 mol/L ammonia solution, using the support membrane module (PPHF), show that the permeability of zinc ions is higher than that of copper ions (Fig. 5).

Table 1

Comparative scanning electron microscopy (SEM) characteristics of the tested membranes

Membrane Symbol	SEM images	
PPHFM		
Chi-PPHFM		

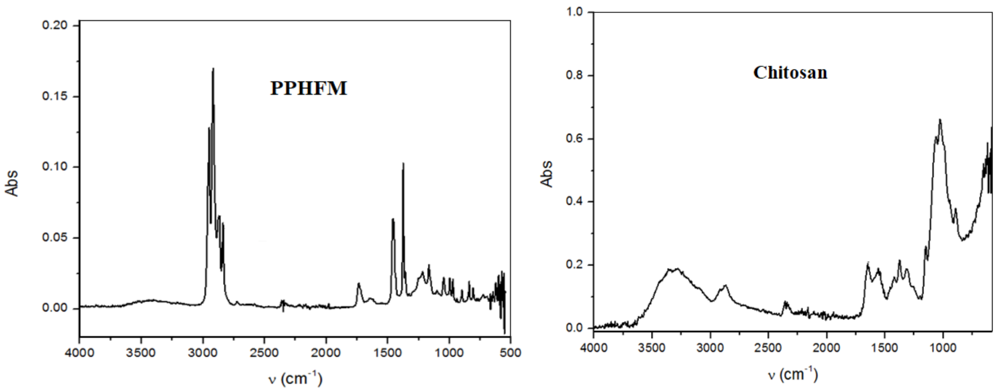


Fig. 4. Fourier Transform InfraRed Spectrum of a) PPHFM and b) Chitosan

This fact is most likely explained by the much higher stability of the $[ZnCl_4]^{2-}$ anion than that of the $[CuCl_4]^{2-}$ anion. Thus, the hydrophobic polypropylene membrane allows the passage of the $[ZnCl_4]^{2-}$ anion through hydrophobic interactions with the pore walls but prevents the permeation of the $[CuCl_4]^{2-}$ anion, which, being unstable, mostly releases Cu^{2+} cations which, being hydrated, do not penetrate to the same extent into the pores of the polypropylene membrane (Fig. 6).

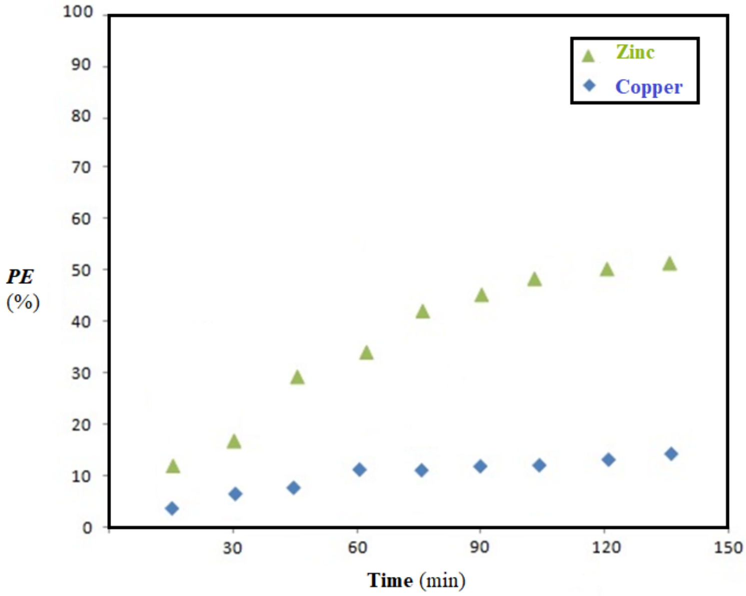


Fig. 5. Pertraction efficiency (*PE*) separation through polypropylene hollow fiber membrane (PPHF) from 10^{-6} mol/L the source phase solution

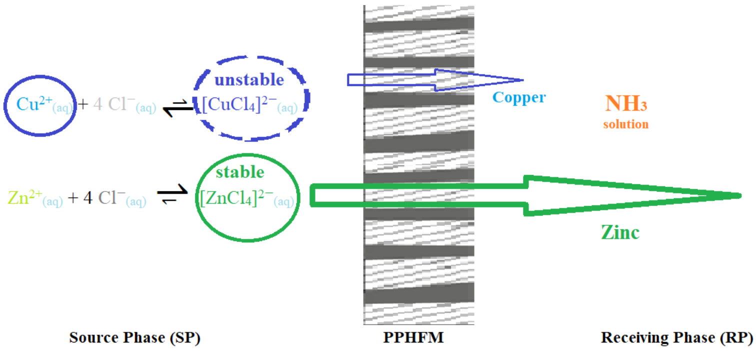


Fig. 6. Schematic presentation of the copper-zinc separation trough polypropylene hollow fiber membrane (PPHF) for source phase 10^{-6} mol/L

In the case of chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM), under the same working conditions, the results obtained (Fig. 7) show a clearly higher zinc extraction efficiency. The improvement of zinc anion $[ZnCl_4]^{2-}$ permeability is explained by the interaction with the ammonium cations coming from chitosan, which thus ensures a faster passage through the walls of the composite membrane. At the same time, the copper cations are expelled, remaining completely in the source phase (Fig. 8).

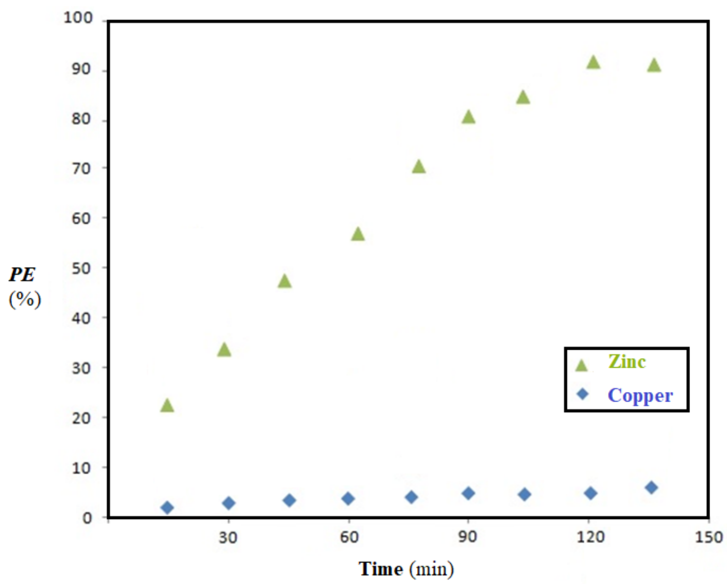


Fig. 7. Pertraction efficiency (PE) separation trough chitosan-polypropylene hollow fiber membrane (Chi-PPHF) from 10^{-6} mol/L the source phase solution

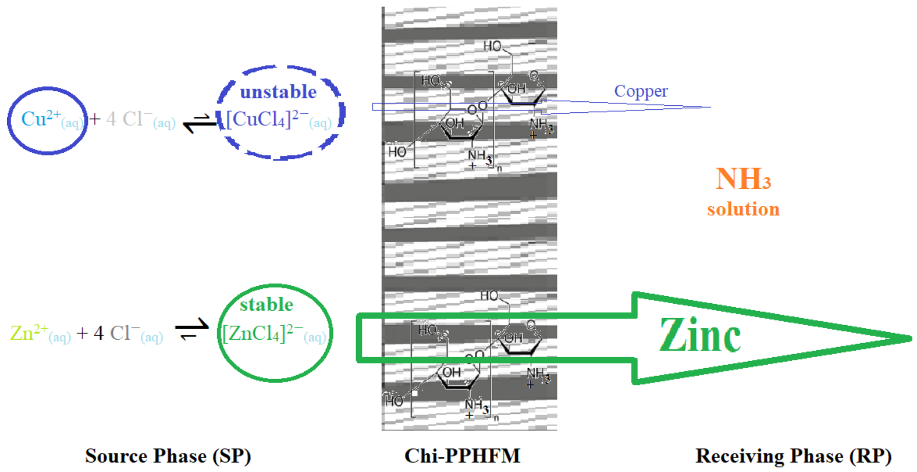


Fig. 8. Schematic presentation of the copper-zinc separation through chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM

The pertraction efficiency of hydrochloric solution (3 mol/L) of zinc and copper, determined after two hours of operation, depends on the initial concentration of the source phase (Table 2), indicating that for concentrated solutions containing both ions, either increasing the adsorption surface of the membranes or operating in multiple extraction steps is required.

Table 2

Pertraction efficiency (*PE*%) for several source phase concentrations of zinc and copper ions in 3mol/L hydrochloric acid

Source phase concentration (mol/L)	Pertraction efficiency (%)			
	PPHFM		Chi-PPHFM	
	Zinc	Copper	Zinc	Copper
10^{-6}	50.4	12.1	93.2	5.6
10^{-5}	42.9	10.2	82.7	4.9
10^{-4}	35.6	8.4	64.5	4.0

From a practical point of view, both the support membrane and the composite membrane can be used to separate zinc, through the pertraction process, from concentrated hydrochloric acid solutions (3 mol/L) containing both zinc and copper.

6. Conclusions

Separation and/or recovery of copper and zinc from waste electronics and electrotechnical industries can be achieved by pertraction using both membranes and composite membranes.

In the present study, the separation of copper and zinc from 3 mol/L hydrochloric acid solutions was addressed using both polypropylene hollow fiber membrane (PPHFM) and chitosan–polypropylene hollow fiber composite membrane (Chi–PPHFM). The chitosan–polypropylene hollow fiber (Chi–PPHFM) composite membrane was made by ultrafiltration of a chitosan solution through the polypropylene hollow fiber support membrane (PPHFM) and was characterized by electron microscopy, FTIR spectroscopy and process performance.

The results for the composite membrane are better both in terms of extraction efficiency and achieving a higher separation factor. Thus, for dilute solutions (10^{-6} mol/L) it is possible to achieve a pertraction efficiency almost 15 times higher for zinc and a concentration factor of approximately 10.

It can be appreciated that the contribution of chitosan to the improvement of the performance of the composite membrane compared to the support membrane is about 90%.

R E F E R E N C E S

[1]. *V. Rai, D. Liu, D. Xia, Y. Jayaraman, J.-C.P. Gabriel*, Electrochemical Approaches for the Recovery of Metals from Electronic Waste: A Critical Review. Recycling vol. **6**, 2021, p. 53. https://doi.org/10.3390/recycling6030053

[2]. *A. Khaliq, M.A. Rhamdhani, G. Brooks, S. Masood*, Metal Extraction Processes for Electronic Waste and Existing Industrial Routes: A Review and Australian Perspective. *Resources* vol. **3**, **2**014, 152-179. https://doi.org/10.3390/resources3010152

[3]. *Y. Zhao, O. Pohl, A.I. Bhatt, G.E. Collis, P.J. Mahon, T. Rüther, A.F. Hollenkamp,* A Review on Battery Market Trends, Second-Life Reuse, and Recycling. Sustain. Chem. **2**, **2021**, 167-205. https://doi.org/10.3390/suschem2010011

[4]. *K. Khider, D. E. Akretche, A. Larbot,* Purification of water effluent from a milk factory by ultrafiltration using Algerian clay support, Desalination, **vol. 167**, 2004, pp. 147-151.

[5]. *T. Mohammadi, A. Esmaeelifar,* Wastewater treatment using ultrafiltration at a vegetable oil factory, Desalination, **vol. 166**, 2004, pp. 329-337.

[6]. *E. Ellouze, R. B. Amar, A. H. B. Salah,* Crossflow microfiltration using ceramic membranes applied to the cuttlefish effluents treatment: effect of operating parameters and the addition of pre or post-treatment, Desalination, **vol. 177**, no. 1-3, 2005, pp. 229-240.

[7]. *D. Abdessemed, G. Nezzal, R. Ben Aïm,* Treatment of wastewater by ultrafiltration, Desalination, **vol. 126**, no. 1-3, 1999, pp. 1-5.

[8]. *C. Fersi, M. Dhahbi,* Treatment of textile plant effluent by ultrafiltration and/or nanofiltration for water reuse, Desalination, **vol. 222**, no. 1-3, pp. 263-271.

[9]. *Y. M. Lo, D. Cao, S. Argin-Soysal, J. Wang, T.-S. Hahm,* Recovery of protein from poultry processing wastewater using membrane ultrafiltration, Bioresource Techology, **vol. 96**, no. 6, 2005, pp. 687-698.

[10]. *D. Falsanisi, L. Liberti, M. Notarnicola,* Ultrafiltration (UF) Pilot Plant for Municipal Wastewater Reuse in Agriculture: Impact of the Operation Mode on Process Performance, Water, **vol. 1**, 2009, pp. 872-885.

[11]. *S. Koter, P. Szczepański, M. Mateescu, G. Nechifor, L. Badalau, I. Koter,* Modeling of the cadmium transport through a bulk liquid membrane. Sep. Purif. Technol. **Vol.107**, 2013, pp.135-143. https://doi.org/10.1016/j.seppur.2013.01.032

[12]. *Filipowiak, K.; Dudzińska, P.; Wieszczycka, K.; Buchwald, T.; Nowicki, M.; Lewandowska, A.; Marcinkowska, A.* Novel Polymer Sorbents with Imprinted Task-Specific Ionic Liquids for Metal Removal. Materials, vol. **14**, 2021, 5008. https://doi.org/10.3390/ma14175008

[13]. *K. Witt, W. Urbaniak, M.A. Kaczorowska, D. Bożejewicz,* Simultaneous Recovery of Precious and Heavy Metal Ions from Waste Electrical and Electronic Equipment (WEEE) Using Polymer Films Containing Cyphos IL 101. Polymers, vol. **13,** 2021, 1454. https://doi.org/10.3390/polym13091454

[15]. *I.M. Nafliu, H.N.A. Al-Ani, A.R. Grosu (Miron), P.C. Albu, G. Nechifor,* Iono-molecular separation with composite membranes. VIII. recuperative aluminium ions separation on capilary polypropylene S-EPDM composite membranes. Mat. Plast. **vol. 56**, no. 1, 2019, pp. 32-36 https://doi.org/10.37358/mp.18.4.5064

[16] *S. Yuan, J. Wang, X. Wang, S. Long, G. Zhang, J. Yang,* Poly(arylene sulfide sulfone)hybrid ultrafiltration membrane with TiO_2-g-PAA nanoparticles: preparation and antifouling performance, Polymer Engineering and Science, **vol. 55**, 2015, pp. 2829-2837.

[17]. *A.R. Grosu, I.M. Nafliu, I.S. Din, A.M. Cimbru, G. Nechifor,* Neutralization with simultaneous separation of aluminum and copper ions from condensed water through capillary polypropylene and cellulose. UPB Sci. Bull. Ser. B Chem. Mater. Sci. **vol. 82**, 2020, pp. 25–34.

[18]. *E. Radzyminska-Lenarcik, I. Pyszka, A. Kosciuszko,* Separation and Recovery of Gold(III), Palladium(II) and Platinum(IV) by Solvent Extraction Using a New β-Diketone Derivative from Acidic Solutions. Materials**,** vol. **14,** 2021, 4436. https://doi.org/10.3390/ma14164436

[19]. *A.C. Nechifor, S. Cotorcea, C. Bungău, P.C. Albu, D. Pașcu, O. Oprea, A.R. Grosu, A. Pîrțac, G. Nechifor*, Removing of the Sulfur Compounds by Impregnated Polypropylene Fibers with Silver Nanoparticles-Cellulose Derivatives for Air Odor Correction. Membranes **vol. 11**, 2021, 256. https://doi.org/10.3390/membranes11040256

[20]. *A. Colburn, R.J. Vogler, A. Patel, M. Bezold, J. Craven, C. Liu, D. Bhattacharyya, Composite* Membranes Derived from Cellulose and Lignin Sulfonate for Selective Separations and Antifouling Aspects. Nanomaterials, vol. **9**, 2019, 867. https://doi.org/10.3390/nano9060867

[21]. *A. Djelad, A. Morsli, M. Robitzer, A. Bengueddach, F. Di Renzo, F. Quignard*, Sorption of Cu(II) ions on chitosan-zeolite X composites: Impact of gelling and drying conditions. Molecules vol. **21**, 2016, 109.

[22]. *M.-W. Wan, C.-C. Kan, B.D. Rogel, M.L.P. Dalida,* Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. Carbohydr. Polym. Vol. **80**, 2010, pp. 891–899.

[23]. *Z. Yang, Y. Chai, L. Zeng, Z. Gao, J. Zhang, H. Ji*, Efficient removal of copper ion from wastewater using a stable chitosan gel material. Molecules, vol. **24**, 2019, 4205.

[24]. *M.F. Hamza, Y. Wei, H.I. Mira, A.A.H. Abdel-Rahman, E.* Guibal, Synthesis and adsorption characteristics of grafted hydrazinyl amine magnetite-chitosan for Ni(II) and Pb(II) recovery. Chem. Eng. J. vol. **362**, 2019, pp. 310–324.

[25]. *F. Wang, L.J. Wang, J.S. Li, X.Y. Sun, W.Q. Han*, Adsorption behavior and mechanism of cadmium on strong-acid cation exchange resin. Trans. NonFerr. Met. Soc. China, vol. **19**, 2009, pp. 740–744.

[26]. *A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan*, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on amberlite IR-120 synthetic resin. J. Colloid Interface Sci. vol. **282**, 2005, pp. 20–25.

[27]. *A.C. Nechifor, A. Pîrțac, P.C. Albu, A.R. Grosu, F. Dumitru, I.A; Dimulescu (Nica), O. Oprea, D. Pașcu, G. Nechifor, S.G. Bungău,* Recuperative Amino Acids Separation through Cellulose Derivative Membranes with Microporous Polypropylene Fiber Matrix. Membranes, vol. **11**, 2021, 429. doi: 10.3390/membranes11060429

[28]. *I.A. Dimulescu, A.C. Nechifor, C. Bărdacă, O. Oprea, D. Paşcu, E.E. Totu, P.C. Albu, G. Nechifor, S.G. Bungău*, Accessible Silver-Iron Oxide Nanoparticles as a Nanomaterial for Supported Liquid Membranes. Nanomaterials vol. **11**, 2021, 1204. https://doi.org/10.3390/nano11051204

[29]. *A.C. Nechifor, A. Goran, V.-A. Grosu, C. Bungău, P.C. Albu, A.R. Grosu, O. Oprea, F.M. Păncescu, G. Nechifor*, Improving the Performance of Composite Hollow Fiber Membranes with Magnetic Field Generated Convection Application on pH Correction. Membranes, vol. **11**, 2021, 445. https://doi.org/10.3390/membranes11060445

[30]. *Xue, Y.; Fu, R.; Xu, T.* (-03). Preparation of speek and speek/chitosan composite proton-exchange membranes for application in direct methanol fuel cells. Acta Polymerica Sinica, vol. **03**, 2010, pp. 285-291.

[31]. *A.M. Cimbru, A.A.K.K. Rikabi, O. Oprea, A.R. Grosu, S.-K. Tanczos, M.C. Simonescu, D. Pașcu, V.-A. Grosu, F. Dumitru, G. Nechifor, pH* and *pCl* Operational Parameters in Some Metallic Ions Separation with Composite Chitosan/Sulfonated Polyether Ether Ketone/Polypropylene Hollow Fibers Membranes. Membranes, vol. **12**, 2022, 833. https://doi.org/10.3390/membranes12090833

[32] *I.S. Din, A.M. Cimbru, A.A.K.K. Rikabi, S.K. Tanczos, S. Ticu (Cotorcea), G. Nechifor,* Iono-molecular Separation with Composite Membranes VI. Nitro-phenol separation through

sulfonated polyether ether ketone on capillary polypropylene membranes. Rev. Chim. (Bucharest) vol. **69**, no.7, 2018, pp. 1603-1607, https://doi.org/10.37358/rc.18.7.6379

[33] *M. Ghimpusan, G. Nechifor, A.C. Nechifor, S.O. Dima, P. Passeri,* Case studies on the physical-chemical parameters' variation during three different purification approaches destined to treat wastewaters from food industry. J. Environ. Manag. vol. **203**, 2017, pp. 811–816, doi:10.1016/j.jenvman.2016.07.030.

[34]. *V.A. Fedorov, M.A. Kuznechikhina, I.V. Kanarsh, G.M. Kirnyuk, G.E. Chernikova,* Formation of mixed zinc halide complexes in aqueous solutions. Sov. J. Coord. Chem. Vol. **4**, **1978**, pp. 33–38.

[35]. *K.S. Rao, G.R. Chaudhury, B.K. Mishra,* Kinetics and equilibrium studies for the removal of cadmium ions from aqueous solutions using Duolite ES Resin. Int. J. Miner. Process. vol. **97**, 2010, pp. 68–73.

[36]. *P. Szczepański, H. Guo, K. Dzieszkowski, Z. Rafiński, A. Wolan, K. Fatyeyeva, J. Kujawa, W. Kujawski,* New reactive ionic liquids as carriers in polymer inclusion membranes for transport and separation of Cd (II), Cu (II), Pb (II), and Zn (II) ions from chloride aqueous solutions. J. Membr. Sci., vol. **638**, 2021, 119674.

[37]. *A.E. Martell, R.M. Smith,* Critical Stability Constants; First Supplement; Plenum Press: New York, NY, USA, 1982; Volume 5, p. 419.