

LEAD-CADMIUM IONS RECUPERATIVE SEPARATION BY CHITOSAN–sEPDM–POLYPROPYLENE HOLLOW FIBER COMPOSITE MEMBRANES

Alexandru GORAN^a, Hussam Nadum Abdalraheem AL-ANI^{a,b},
Alexandra-Raluca GROSU^a, Geani Teodor MAN^{a,c},
Vlad-Alexandru GROSU^{d,*}, Aurelia Cristina NECHIFOR^a

ABSTRACT. Although batteries containing heavy metals and toxic chemicals, including lead and cadmium, are supposed to be selectively collected, they still end up on municipal waste processing platforms. The separation of cadmium and lead ions is a problem that is circumscribed to the development of urban mining. This paper presents the recuperative separation of lead and cadmium ions by a composite membrane based on chitosan (Chi), sulfonated ethylene–propylene–diene terpolymer (sEPDM), and polypropylene hollow fiber (PPyHF). The performances of selected membranes are presented comparatively, both from the point of view of the morpho-structural characteristics, as well as of the performances in the target ion separation process, with recently reported results obtained with composite membranes based on chitosan.

Keywords: membranes, composite membranes, chitosan, sEPDM, hollow fiber, cadmium separation, lead separation.

^a Analytical Chemistry and Environmental Engineering Department, Politehnica University of Bucharest, Polizu 1-7, 011061-Bucharest, Romania

E-mails: alexandru@santego.ro; man_geani@yahoo.com; hussamalani32@gmail.com; andra.grosu@upb.ro; aurelia.nechifor@upb.ro

^b Chemical Industries Department, Institute of Technology, Middle Technical University, Al Zafaraniyah, Baghdad 10074, Iraq

^c National Research and Development Institute for Cryogenics and Isotopic Technologies-ICSI Râmnicu Vâlcea, 4th Uzinei Street, Râmnicu Vâlcea 240050, Romania

^d Department of Electronic Technology and Reliability, Faculty of Electronics, Telecommunications and Information Technology, University Politehnica of Bucharest, Bucharest 061071, Romania; vlad.grosu@upb.ro

* Corresponding author: vlad.grosu@upb.ro



INTRODUCTION

The urban mining develops along with the diversification of products that reach urban waste processing platforms [1,2]. If we focus only on the batteries containing heavy metals and toxic chemicals such as lead, cadmium, zinc, lithium, mercury or acids, then we have a complex perspective of the problems that can arise from the separation, concentration and recovery of these substances [3,4]. Of course, the objectives of the urban mining are broader, but the problem of separating waste containing heavy metal ions on waste processing platforms is an important priority [5,6].

Even if the level of training of the population reaches a high standard of education regarding environmental protection and the need for selective collection (avoid throwing batteries, for example, in household waste), the objective regarding the recovery of metals from used batteries remains [7,8].

The separation of lead and cadmium ions can be performed by precipitation [9], extraction [10], ion exchange [11], electrolysis [12], electrodialysis [13], nanofiltration [14], emulsion membranes [15], ionic flotation [16], but the multitude of technical possibilities should not deceive those who want the recuperative separation of these ions, especially in the case of dilute solutions (under 10^{-5} mol/L) [17,18].

Membranes and membrane processes have recently been reported [19–21] as a viable alternative for the separation, concentration or purification of various ion systems (inorganic or organic), but research is in continuous progress to realize long-lasting membranes, increased contact surfaces of the source phase with the membrane, increased ion fluxes and elevated concentration factors [22].

This paper presents the recuperative separation of lead and cadmium ions by a composite membrane based on chitosan (Chi), sulfonated ethylene–propylene–diene terpolymer (sEPDM), and polypropylene hollow fiber (PPyHF), compared to Chi–PPyHF membranes and Chi–sulfonated polyetheretherketone (sPEEK)–PPyHF membranes, respectively.

RESULTS AND DISCUSSION

The recuperative separation of lead and cadmium from waste that occurs during processing on integrated platforms for greening and recycling of materials in large cities, involves processing from dilute solutions, in which the metal ions are in concentrations of no more than 10^{-5} mol/L in relatively concentrated hydrochloric environments, from 2 to 4 mol/L. This leads to the formation of chloride ion complexes, according to equations (1) and (2) below (of complexes with the number of chloride ions less than or equal to 4):



with $i=1,2,3$ or 4 (for lead); and $i=1,2,3,4,5$ or 6 (for cadmium).

In these equilibria both pH and pCl must be taken into account, since the speciation of the two ions is particularly sensitive to the variation of each parameter, both individually and simultaneously [23–25].

The separation process addressed in this work is pertraction [26,27]. The hydrochloric feed solution (the source phase, SP) and the stripping solution (receiving phase, RP) circulate through the two-compartmented pertraction module (Figure 1). The two compartments are separated by the selected composite membrane (M) placed in the pertraction module (MM).

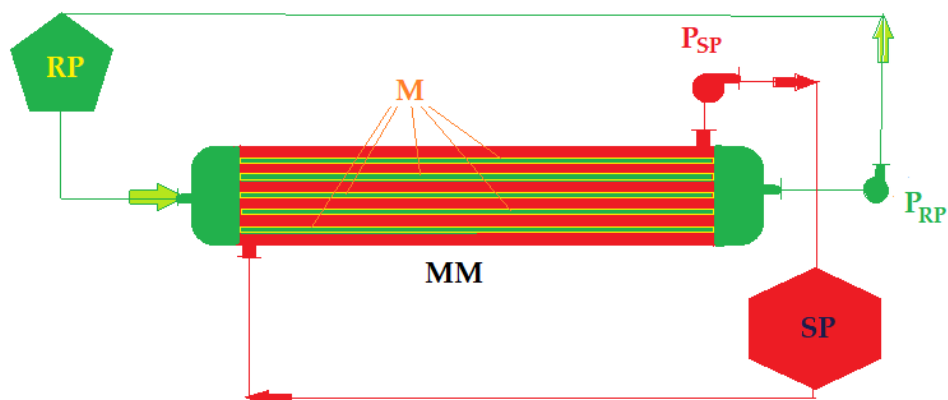


Figure 1. Schematic presentation of pertraction installation: SP–source phase; RP–receiving phase; MM–hollow fiber pertraction module; P_{SP}–pump of source phase; P_{RP}–pump of the receiving phase.

In all the studied cases the source phase is acidic, so that the basic polymer of the composite membrane, chitosan, is found in cationic form ($-\text{NH}_3^+$). From a theoretical point of view, the source solution containing the two ions of interest is obtained at a strongly acidic pH (Figure 2a and 2b) which causes both ions (Cd^{2+} and Pb^{2+}) to exist as polyatomic anions with a negative charge (MCl_3^- and MCl_4^{2-} , for the cadmium ion, the complex with six chloride ions can also be reached). The receiving solution is either ammonia 1 mol/L (Figure 2a) which leads to the recovery of cadmium ion, or deionized water at a temperature of 10–12 °C, that leads to the recovery of lead (Figure 2b).

For the case in Figure 2b, where the feed phase is less concentrated in hydrochloric acid (0.5 mol/L), the formation of predominantly cadmium chloride CdCl_2 (non-ionic) occurs. This is not transported by the cationic membrane, therefore mainly lead ions will be transported.

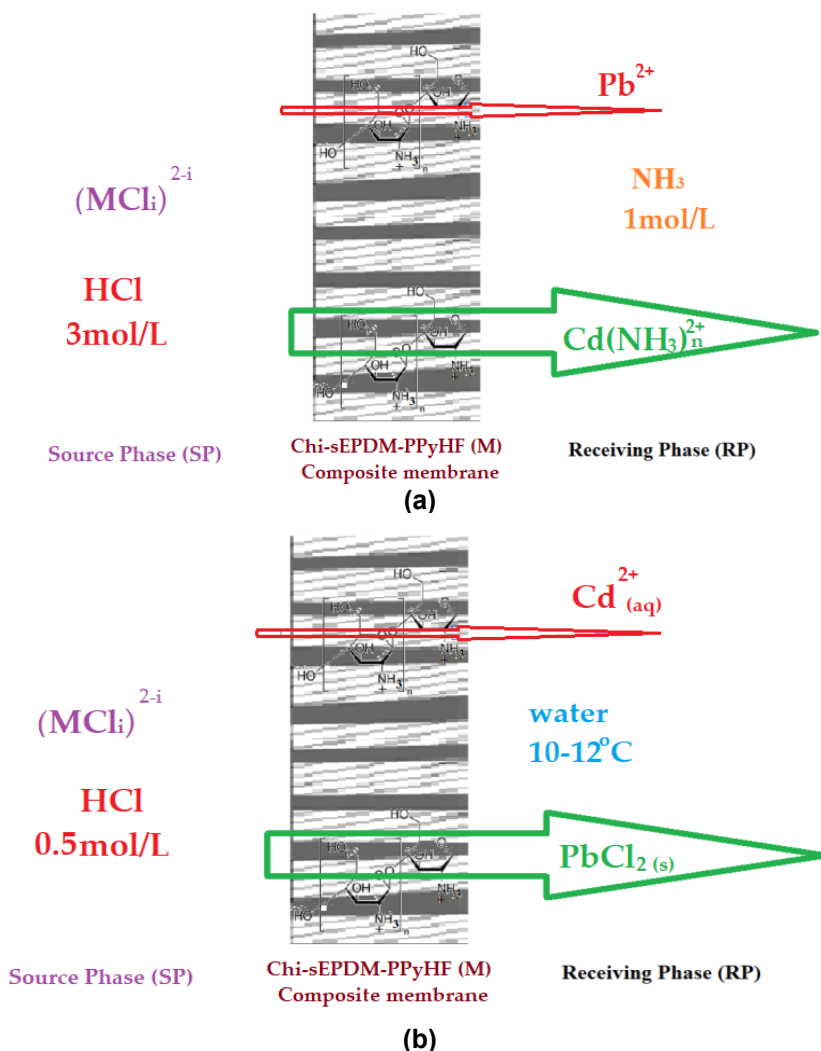


Figure 2. The hypothetical presentation of the separation schemes based on the data of the stability constants and the chosen working conditions:
(a) 3 mol/L hydrochloric acid solution containing an equimolar mixture of Cd and Pb ions (10^{-5} mol/L) and the ammonia as receiving phase 1 mol/L; and
(b) hydrochloric acid 0.5 mol/L containing an equimolar mixture of Cd and Pb ions (10^{-5} mol/L) with the receiving phase deionized water of 10–12 °C.

The membranes considered in this study are chitosan composites (Chi), deposited on polypropylene hollow fiber membrane (PPyHF) directly or by means of a linking polymer (sulfonated polyetheretherketone (sPEEK) or sulfonated ethylene-propylene-diene terpolymer (sEPDM)), obtained by impregnation method, presented extensively in previous works [28,29].

The practical objectives of the study were to determine the evolution over time of the performances of the prepared membranes, both from a physical point of view (primarily preserving the integrity of the composite membrane) and of the process performances: the ionic flux (J) and the recovery (R) of the considered ions.

The first objective considered that the components of the prepared composite membranes can ensure the separation [30] but also the lifetime of the obtained membranes, which can be an important limiting parameter [31].

To support the importance of the second parameter, the composition of the membranes, Figure 3 shows the images of the sections made with the scanning electron microscope (SEM) for the three membranes considered for the separation tests, after an operating time of 35 days, under the same working conditions:

- a) Chi-PPyHF
- b) Chi-sPEEK-PPyHF
- c) Chi-sEPDM-PPyHF

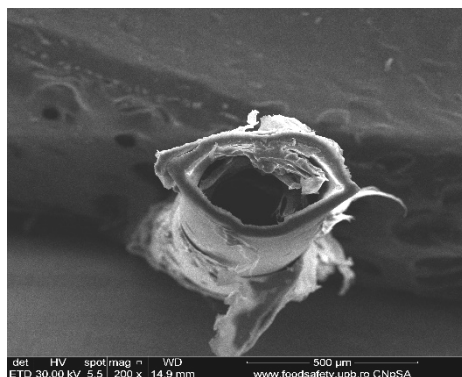
The images show that Chi-PPyHF membranes are progressively degraded in the following order:

Chi-PPyHF > Chi-sPEEK-PPyHF > Chi-sEPDM-PpyHF

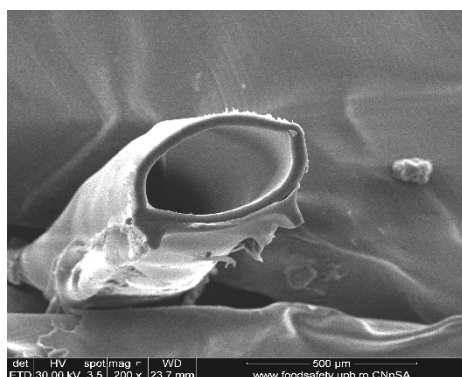
Thus, the exfoliation of the superficial layer of chitosan can be highlighted (Figure 3a), lateral swelling of the sPEEK-Chi layer (Figure 3b) or just the appearance of small sEPDM-Chi growths (Figure 3c).

This behavior can be argued through the interaction of polypropylene (PPyHF) hollow fiber membrane support with chitosan and sPEEK or sEPDM. On the other hand, it can be interpreted by capillary absorption. The walls (Figure 4a) of the support membrane have pores of about 0.3 μm (Figure 4b), which favours the penetration of chitosan (Figure 4c).

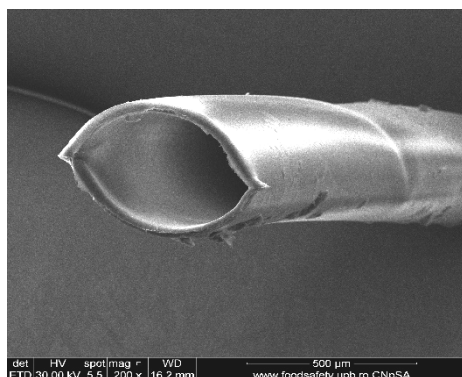
Of course, inside the PPyHF capillaries, hydrophobic interactions can also take place with the hydrocarbon chains of the polymers put in contact, which explains the particular stability of Chi-sEPDM-PPyHF membrane.



(a)



(b)



(c)

Figure 3. The images of the membranes sections obtained by scanning electron microscopy (SEM): **(a)** Chi-PPyHF composite membrane; **(b)** Chi-sPEEK-PPyHF composite membrane; **(c)** Chi-sEPDM-PPyHF composite membrane.

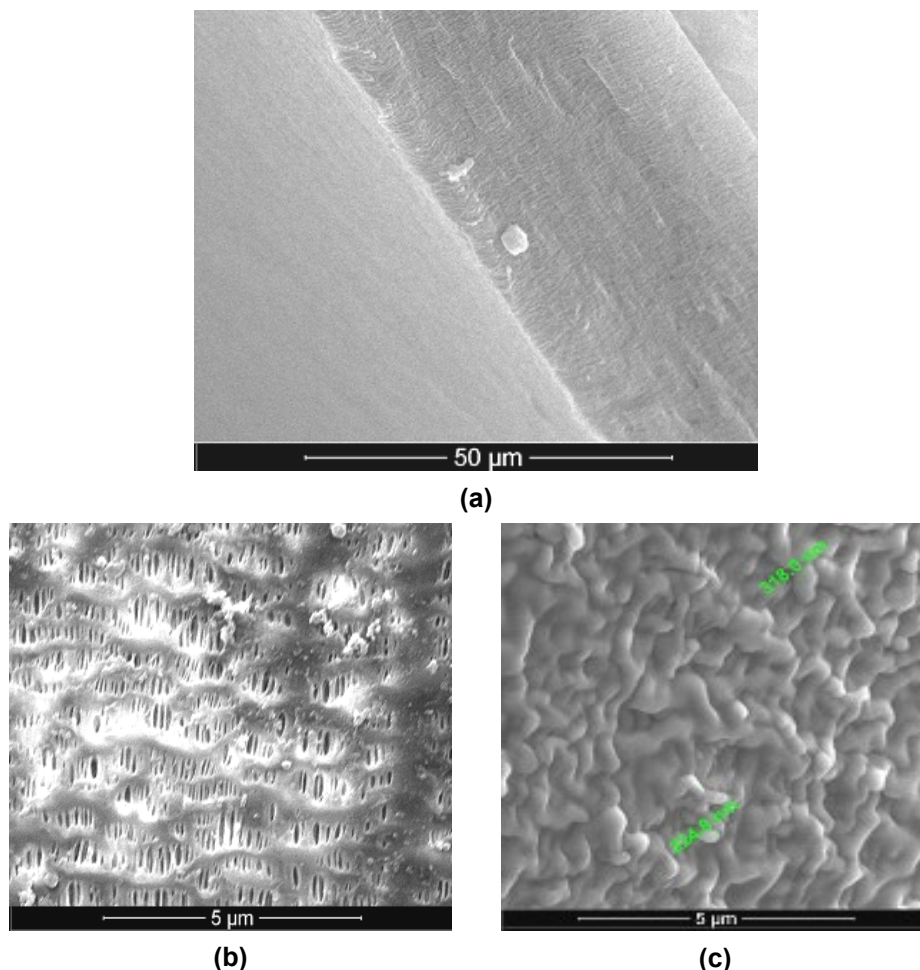


Figure 4. Images of the PPyHF membrane section by scanning electron microscopy (SEM): **(a)** cross-section; **(b)** detail of the pores; **(c)** membrane covered with chitosan.

The images obtained by scanning electron microscopy are correlated with both global ion fluxes from the pertraction process (Figure 5), and with the degree of ion recovery with the help of the three types of membranes. They are tested in the regime of separation of cadmium and lead from equimolar feed solutions (in the source phase, SP) 10^{-5} mol/L: 10^{-5} mol/L, at a concentration of hydrochloric acid 3 mol/L, by pertraction with a hydrochloric acid solution of 1 mol/L ($pH = 0$, $pCl = 0$) (Figure 6).

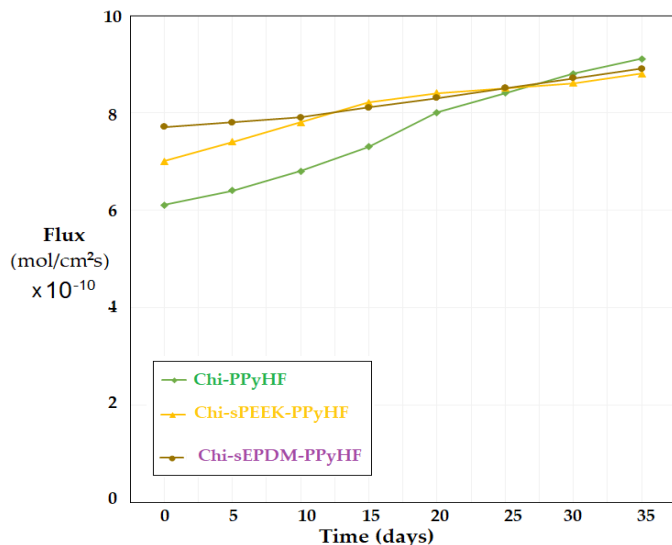


Figure 5. Global ionic fluxes of chitosan-based composite membranes vs. time.

The chitosan deposited on polypropylene hollow fiber membrane has the lowest performances (increasing the ionic flux being a measure of membrane degradation or exfoliation), but by introducing an intermediate layer of sPEEK or sEPDM adhesion of chitosan to polypropylene hollow fibers membrane, the performance of flow and recovery improve both in size and durability (Figures 5 and 6). The illustrated results indicate that in the first 15 days of operation the membranes keep relatively constant both the values of total ion flux and degree of recovery, but after this limit the Chi-PPyHF and Chi-sPEEK-PPyHF membranes lose their performance.

The best performing membrane (Chi-sEPDM-PPyHF), in terms of durability over time and constancy of the ion flux, was tested in order to evaluate the concentration factor (f) and the selectivity (S).

The concentration factor is given by equation (3):

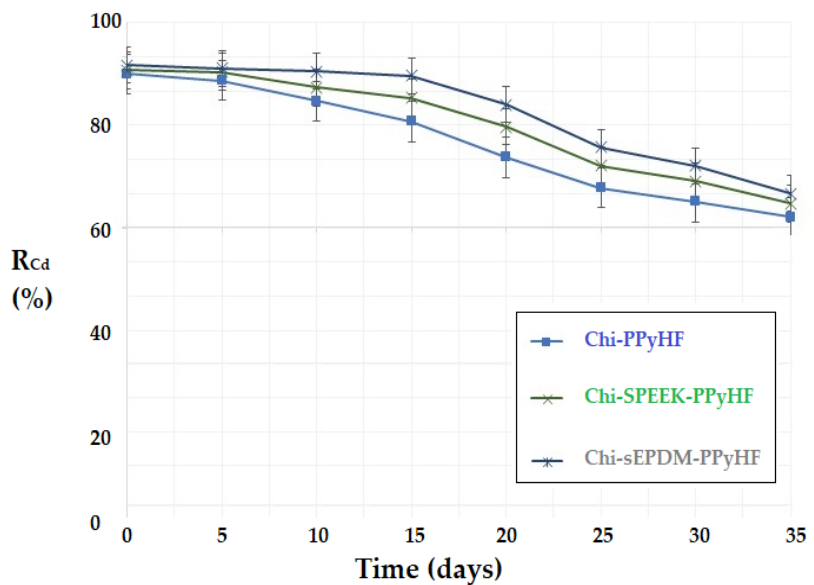
$$f = C_f/C_0 \quad (3)$$

in which f is the concentration factor, C_f the final concentration of the target ion in the receiving phase, and C_0 the concentration of the target ion in the source phase.

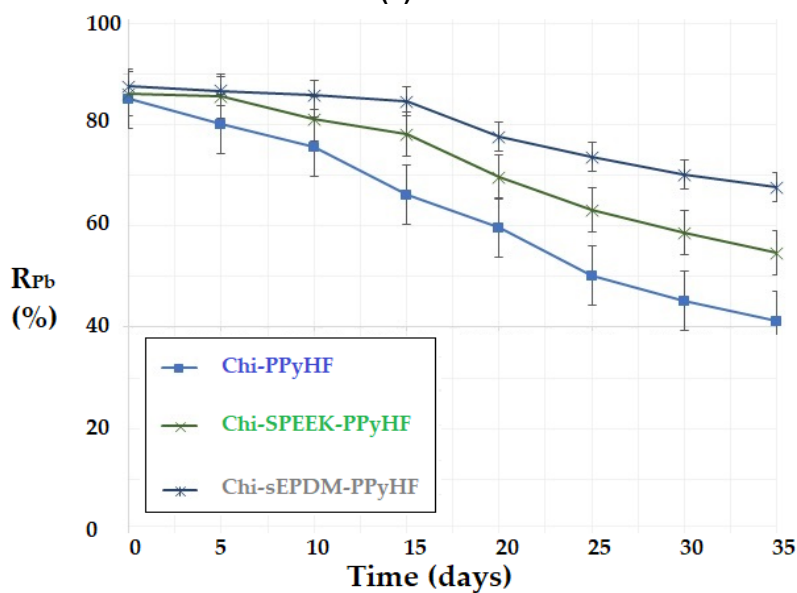
The global selectivity factor (S) in equation (4) is the ratio between the concentration ratios of the two ions, in the receiver phase (RP) and in source phase (SP).

$$S = [C_{Cd}/C_{Pb}]_{RP} / [C_{Cd}/C_{Pb}]_{SP} \quad (4)$$

LEAD-CADMIUM IONS RECUPERATIVE SEPARATION BY CHITOSAN-sEPDM-POLYPROPYLENE HOLLOW FIBER COMPOSITE MEMBRANES



(a)



(b)

Figure 6. Performance of composite membranes based on chitosan: (a) cadmium recovery depending on time; and (b) lead recovery depending on operating time.

To ensure a concentration factor f (which represents the final concentration of the considered ion in the receiving phase to the initial concentration of this ion in source phase) as high as possible, the volumetric ratio between the source and receiver phases must be as high as possible. Thus, a constant volume of the source phase (10 L), consisting of 3 mol/L or 0.5 mol/L hydrochloric acid solutions, containing cadmium and lead ions in equimolar quantities 10^{-5} : 10^{-5} mol/L, is contacted with receiving solutions consisting of 1 mol/L ammonia solution (receiving phase) or demineralized water 10–12 °C, with volumes of 5L, 3L, 1L or 0.5L.

Table 1 shows the evolution of the concentration factor and the selectivity of the test membrane.

Table 1. Concentration factor (f) and individual ion selectivity (S_M) obtained with Chi-sEPDM-PPyHF membrane

Volumetric ratio V_{SP}/V_{RP}	10L/5L	10L/3L	10L/1L	10L/0.5L
f_{Pb}	1.86	2.97	8.78	17.65
f_{Cd}	1.89	3.12	9.21	18.43
S_{Pb}	0.91	0.85	0.77	0.69
S_{Cd}	0.85	0.81	0.72	0.64

The concentration factor obtained for the two cations increases non-linearly with the increase in the volumetric ratio between the source phase and the receiver phase for both cations, being higher for the cadmium ion throughout the study interval.

The selectivity of the extraction process decreases with the increase of the volumetric ratio, the values being lower for cadmium throughout the study interval. In practice, a maximum concentration factor of almost 19 times can be obtained and at a selectivity of at least 60%.

CONCLUSIONS

The recovery of metals from waste processed on urban greening platforms (urban mining) is developing rapidly because heavy metals, in addition to the negative impact on the environment, are also an important raw material that requires recycling.

In the case of the present study, the recuperative separation of lead and cadmium ions from concentrated acid solutions with a content of metal ions below 10^{-5} mol/L is pursued.

To achieve the objectives, the pertraction process is used with composite membranes based on chitosan (Chi), sulfonated ethylene-propylene-diene

terpolymer (sEPDM), and polypropylene hollow fiber (PPyHF) in comparison with Chi-PPyHF and Chi-sulfonated polyetheretherketone (sPEEK-PPyHF).

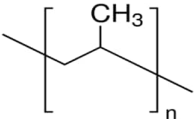
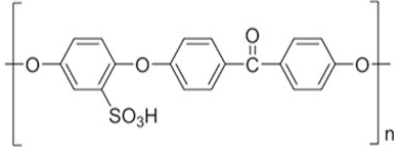
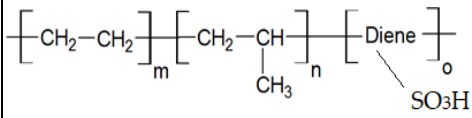
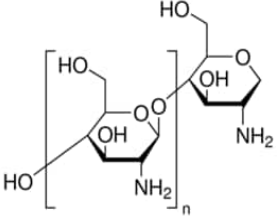
Chi-sulfonated polyetheretherketone (sPEEK-PPyHF) composite membranes show superior results compared to other membranes, both in terms of lifetime (preserving physical characteristics for at least 15 days of operation) and separation properties (concentration factor of almost 19 times and at a selectivity of at least 60%).

EXPERIMENTAL SECTION

Materials

The characteristics of the polymeric compounds and derivatives used in the study are presented in Table E1.

Table E1. The characteristics of the used polymeric and derivative compounds.

Polymer Compounds	Symbol	Molar mass (Da)	Solubility	pKa
	PPyHF	>10 ⁶	soluble in toluene	-
	sPEEK	28000	organic polar solvents	1.9
	sulfonated ethylene-propylene-diene terpolymer (sEPDM)	3500-6000	soluble in toluene	1.9 to 2.2
	Chi	5600	acidulated water	6.5

The hollow polypropylene fibers used as support of the membranes were provided by GOST Ltd., Perugia, Italy (Figure E1).

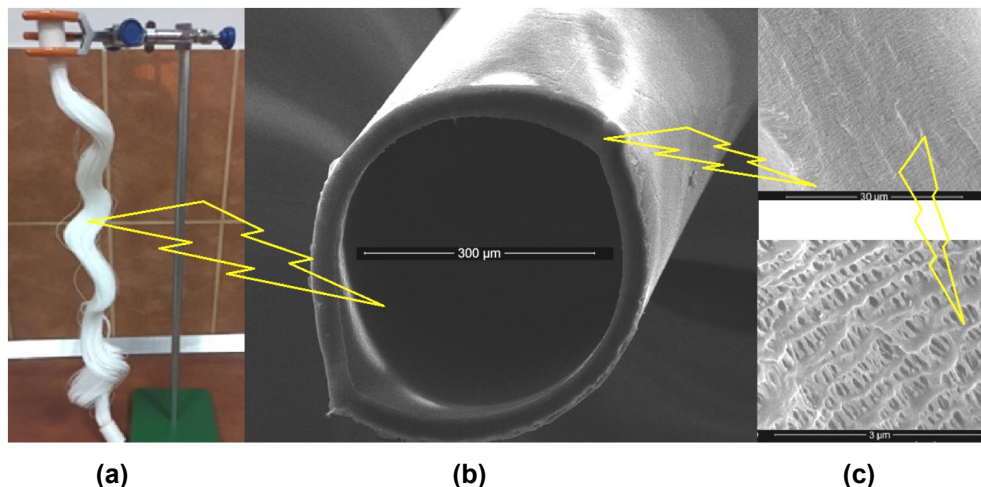


Figure E1. The characteristics of the used polypropylene hollow fiber membranes (PPyHF): **(a)** general view; **(b)** SEM section; and **(c)** cross-section details of the pores.

The determination of the concentration of metal ions is carried out by the dedicated extractive-spectro-photometric or electrochemical method.

Validation of ion concentration results is determined by atomic absorption spectrometry (AAS), using characteristic wavelengths.

Equipment

The scanning microscopy studies, SEM and HR-SEM were performed on a Hitachi S4500 system (Hitachi High–Technologies Europe GmbH, Mannheim, Germany).

The UV–Vis analyses of the solutions were done on a Spectrophotometer CamSpec M550 (Spectronic CamSpec Ltd., Leeds, UK).

The electrochemical processes were followed up with a PARSTAT 2273 Potentiostat (Princeton Applied Research, AMETEK Inc., Berwyn, Pennsylvania, US). It has been used a glass cell with three electrodes setup.

The *pH* and *pCl* of the medium were followed up with a combined selective electrode (HI 4107, Hanna Instruments Ltd, Leighton Buzzard, UK) and a multi-parameter system (HI 5522, Hanna Instruments Ltd., Leighton Buzzard, UK).

To assess and validate the content in metal ions, the atomic absorption spectrometer AAnalyst 400 AA Spectrometer (Perkin Elmer Inc., Shelton, Connecticut, US) with a single-element hollow-cathode lamp was used, driven by WinLab32–AA software (Perkin Elmer Inc., Shelton, Connecticut, US).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the valuable help and friendly assistance of Eng. Roxana Truşcă for performing the scanning microscopy analysis.

REFERENCES

1. V. Rai; D. Liu; D. Xia; Y. Jayaraman; J.-C.P. Gabriel; *Recycling*, **2021**, *6*, 53.
2. A. Khaliq; M.A. Rhamdhani; G. Brooks; S. Masood; *Resources*, **2014**, *3*, 152-179.
3. Y. Zhao; O. Pohl; A.I. Bhatt; G.E. Collis; P.J. Mahon; T. R  ther; A.F. Hollenkamp; *Sustain. Chem.*, **2021**, *2*, 167-205.
4. F.M. P  ncescu; A. Ferencz (Dinu); V.A. Grosu; A. Goran; G. Nechifor; *U.P.B. Sci. Bull., Series B*, **2023**, *85* (1), 77-88.
5. A.E. Kostanyan; V.V. Belova; Y.A. Zakhodyaeva; A.A. Voshkin; *Membranes*, **2023**, *13*, 418.
6. J.M. Carretas; L.M. Ferreira; P.M.P. Santos; S.S. Gomes; M.F. Ara  jo; L. Maria; J.P. Leal; *Membranes*, **2023**, *13*, 467.
7. S. Koter; P. Szczepa  ski; M. Mateescu; G. Nechifor; L. Badalau; I. Koter; *Sep. Purif. Technol.*, **2013**, *107*, 135-143.
8. K. Filipowiak; P. Dudzi  ska; K. Wieszczycka; T. Buchwald; M. Nowicki; A. Lewandowska; A. Marcinkowska; *Materials*, **2021**, *14*, 5008.
9. K. Witt; W. Urbaniak; M.A. Kaczorowska; D. Bo  jewicz; *Polymers*, **2021**, *13*, 1454.
10. I.M. Nafliu; H.N.A. Al-Ani; A.R. Grosu (Miron); P.C. Albu; G. Nechifor; *Mat. Plast.*, **2019**, *1*, 32–36.
11. S. Yuan; J. Wang; X. Wang; S. Long; G. Zhang; J. Yang; *Polym. Eng. Sci.*, **2015**, *55*, 2829–2837.
12. A.R. Grosu; I.M. Nafliu; I.S. Din; A.M. Cimbru; G. Nechifor; *UPB Sci. Bull. Ser. B Chem. Mater. Sci.*, **2020**, *82*, 25–34.
13. E. Radzimska-Lenarcik; I. Pyszka; A. Kosciuszko; *Materials*, **2021**, *14*, 4436.
14. A.C. Nechifor; S. Cotorcea; C. Bung  u; P.C. Albu; D. Pa  cu; O. Oprea; A.R. Grosu; A. P  r  ac; G. Nechifor; *Membranes*, **2021**, *11*, 256.
15. M.-W. Wan; C.-C. Kan; B.D. Rogel; M.L.P. Dalida; *Carbohydr. Polym.*, **2010**, *80*, 891–899.
16. Z. Yang; Y. Chai; L. Zeng; Z. Gao; J. Zhang; H. Ji; *Molecules*, **2019**, *24*, 4205.

- 17.M.F. Hamza; Y. Wei; H.I. Mira; A.A.H. Abdel-Rahman; E. Guibal; *Chem. Eng. J.*, **2019**, 362, 310–324.
- 18.F. Wang; L.J. Wang; J.S. Li; X.Y. Sun; W.Q. Han; *Trans. NonFerr. Met. Soc. China*, **2009**, 19, 740–744.
- 19.A. Demirbas; E. Pehlivan; F. Gode; T. Altun; G. Arslan; *J. Colloid Interface Sci.*, **2005**, 282, 20–25.
- 20.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; *Membranes*, **2021**, 11, 429.
- 21.I.A. Dimulescu; A.C. Nechifor; C. Bărdacă; O. Oprea; D. Pașcu; E.E. Totu; P.C. Albu; G. Nechifor; S.G. Bungău; *Nanomaterials*, **2021**, 11, 1204.
- 22.A.C. Nechifor, A. Goran; V.-A. Grosu; C. Bungău; P.C. Albu; A.R. Grosu; O. Oprea; F.M.Păncescu; G. Nechifor; *Membranes*, **2021**, 11, 445.
- 23.Naida S. Gill; F. B. Taylor; W. E. Hatfield; W. E. Parker; Carol S. Fountain; Fred L. Bunger; Tetrahalo Complexes of Dipositive Metals in the First Transition Series, in *Inorganic Syntheses.*, **1967**, 9, 136–142.
- 24.K.C. Liddell; R.G. Bautista; *Hydrometallurgy*, **1988**, 21(1), 113-124.
- 25.P. Szczepański; H. Guo; K. Dzieszkowski; Z. Rafiński; A. Wolan; K. Fatyeyeva; J. Kujawa; W. Kujawski; *J.Membr. Sci.*, **2021**, 638, 119674.
- 26.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; *Membranes*, **2022**, 12, 833.
- 27.I.S. Din; A.M. Cimbru; A.A.K.K. Rikabi; S.K. Tanczos; S. Ticu (Cotorcea); G. Nechifor; *Rev. Chim. (Bucharest)*, **2018**, 69(7), 1603-1607.
- 28.M. Ghimpusan; G. Nechifor; A.C. Nechifor; S.O. Dima; P. Passeri; *J. Environ. Manag.* **2017**, 203, 811–816.
- 29.P. Szczepański; *Membranes* **2023**, 13, 236.
- 30.V.A. Fedorov; M.A. Kuznechikhina; I.V. Kanarsh; G.M. Kirnyuk; G.E. Chernikova; *Sov. J. Coord. Chem.*, **1978**, 4, 33–38.
- 31.K.S. Rao, G.R. Chaudhury, B.K. Mishra, *Resin. Int. J. Miner. Process.*, **2010**, 97, 68–73.