

CARRIER-MEDIATED TRANSPORT OF LEAD AND CADMIUM IONS THROUGH PLASTICIZED POLYMERIC MEMBRANES PREPARED FROM HYBRID ORGANIC–INORGANIC MATERIALS

HAYAT BRIKI,* NAIMA ABDELLAOUI,* OMAR AROUS,** FARID METREF*
and DJAMEL EDDINE AKRETCHE**

*USTHB, Laboratory of Polymer Materials, Faculty of Chemistry, PO Box 32,
El Alia Bab Ezzouar 16111, Algiers, Algeria

**USTHB, Laboratory of Hydrometallurgy and Inorganic Molecular Chemistry, Faculty of
Chemistry, PO Box 32, El Alia Bab Ezzouar 16111, Algiers, Algeria

✉ Corresponding author: O. Arous, omararous@yahoo.fr

Received August 22, 2022

In this work, the development of polymeric inclusion membranes for elimination of toxic ions is reported. The effect of a local clay additive on the structure and performances of the membranes was studied. The membrane was made up of cellulose triacetate (CTA) and polysulfone (PSu), plasticized by dioctylphthalate (DOP) and modified by local clay and di-(2-ethylhexyl) phosphoric acid (D2EHPA) incorporated into the polymer as metal ions carrier. The transport of lead (II) and cadmium (II) ions through two kinds of polymer inclusion membrane (PIM) systems, with and without clay, was investigated. The membranes (polymers/plasticizer/carrier/clay) were synthesized using a new method and characterized by various techniques, including Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and contact angle determination. A study of Pb(II) and Cd(II) retention using the synthesized membranes was realized. Dialysis experiments of lead and cadmium ions transfer across the polymer inclusion membranes have proved their good performance.

Keywords: clay, polymers, heavy metals, polymeric membranes, water purification

INTRODUCTION

Water is an essential element for the life and functioning of any terrestrial ecosystem. Unfortunately, pure water is gradually becoming scarce, as human activities release increasing amounts of organic and mineral species that are not completely removed before their discharge into the nature. Water pollution, accidental or deliberate, is a source of environmental degradation and is currently a major concern that is fully justified at the international level. Heavy industries, chemical industries and some metal processing industries can be the source of toxic and persistent pollution. Some rejected products have a long shelf life before they can be biodegraded. Food manufacturing industries mainly release organic matter and fertilizers.¹ Heavy metals, solvents, resins, pigments, monomers and plastics, nitrates, pesticides, fertilizers and antibiotic residues can also pollute water. One of the most serious water pollutants are metal ions. Indeed, heavy metals, although natural elements of the earth, are among the most toxic pollutants in high concentrations in fresh water resources.² Some heavy metals are essential, in very small quantities, for the metabolism of living beings, but harm their health when in high doses. This is the case with iron (II, III), copper (II) and zinc (II) ions. Others, which are not essential, are on the contrary toxic, even at low doses. This is the case with lead (II), cadmium (II) and mercury (II) ions. The latter, entering the food chain, cause pathologies, such as lead poisoning, increased blood pressure, kidney problems, neurological disorders and various cancer forms.

The toxicity of heavy metals has led the public authorities to regulate their emissions by setting alert or intervention limit levels and maximum admissible concentrations (C.M.A.). The maximum allowable concentration set by the WHO for lead (II) is 10 µg/L for water for domestic consumption and 1 mg/L for industrial discharges. In order to recycle and reuse wastewater, one of the solutions that seems very promising is the installation of membrane filtration systems capable of ensuring the treatment and disinfection of effluents. The majority of these processes uses organic membranes based on several polymers.³⁻⁵

Liquid membrane processes have become an attractive alternative to conventional solvent extraction for selective separation and concentration of compounds, such as metals and acids, from dilute aqueous solution, because they combine into a single stage an extraction and a stripping operation. In order to reduce the amounts of reactants and energy needed for separation and to decrease the environmental and economic impact of solvent extraction separations, several membranes have been proposed in the past three decades based on separation techniques.⁶⁻¹¹

Facilitated transport across polymeric membranes has been applied for ions separation.¹²⁻¹⁹ These membranes utilize a carrier dissolved in an organic solvent, but this solution is contained in a polymeric matrix as a plasticizer or within the pores of a polymer membrane. Diffusion of metal ions in liquid membranes is governed by complex formation with the carrier at the aqueous/organic interface, so that selectivity is generally very high, whereas the fluxes in these membranes are very low, because they are limited by the convection of the carrier in the organic phase.²⁰⁻²³ Facilitated transport of metal ions through plasticized polymeric membranes (PPMs) has resulted in good stability over liquid membranes and polymer-stabilized liquid membranes. Polymer membranes with grafted crown ether groups have been reported by Gherrou *et al.*²⁴ and Radzaminska-Lenarcik *et al.*²⁵ A similar variation on the solvent-free membrane is detailed in a paper by Lacan *et al.* A sol-gel matrix with grafted crown ethers was produced for the facilitated transport of potassium ions (K^+) over lithium ions (Li^+).²⁶ A synthetic receptor, with the ability to bind sodium or potassium chloride as a contact ion-pair, was shown to effectively transport either salt across organic membranes and significant transport was observed.²⁷

The objective of this work is the development of composite membranes based on cellulose triacetate (CTA) and polysulfone (PSu) as a polymeric matrix plasticized by dioctylphthalate (DOP) and the insertion of lamellar filler, *i.e.*, yellow clay from Maghnia region, located in the west part of Algeria. To ensure good cohesion between the organic and inorganic materials, a carrier was added, *i.e.*, D2EHPA. The synthesized membranes were applied for the purification of polluted water containing a mixture of cadmium (II) and lead (II) ions. A further objective of this work is the valorization of local clay for the treatment of water resources polluted by heavy metals.

EXPERIMENTAL

Materials

The clay used as a solid support was an Algerian montmorillonite (MMT) extracted from the bentonite category from Roussel in Maghnia (Algeria). It was supplied by ENOF Chemical Ltd. Research Company for non-ferrous matters (Algeria). All chemicals (highest purity grade) were used as received, without any further purification. Chloroform ($CHCl_3$) ($GC \geq 99\%$), tetrahydrofuran (THF) (99.99%), pure cellulose triacetate (CTA), polysulfone (PSu) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) were purchased from Fluka; dioctylphthalate (DOP), $Pb(NO_3)_2$ and $Cd(NO_3)_2$ were obtained from Carlo Erba Co. Aqueous solutions were prepared with ultrapure water obtained by a Millipore purification unit (Millipore B.V., Amsterdam, the Netherlands).

Preparation of composite membranes

The natural clay was washed with distilled water to remove iron hydroxide, carbonates and other metallic oxides. It was dispersed in distilled water and the clay fraction was recovered by centrifugation, dried at 105 °C for 48 hours and sieved through a set of ASTM standard sieves. The fraction of an average diameter of 0.075 mm was used for membrane preparation.

Composite membranes were prepared using the procedure described by Sugiura.²⁸ In this method, 0.2 g of cellulose triacetate (CTA) was dissolved in 30 mL of chloroform and stirred for 4 hours. After that, 0.014 g of clay was dispersed in the first solution (CTA- $CHCl_3$) and 0.2 g of polysulfone (PSu) was separately dissolved in 30 mL of tetrahydrofuran (THF). Then, 0.1 mL of DOP (as plasticizer) and 0.1 mL of D2EHPA (as carrier) were added, respectively, to the first solution (CTA-Clay- $CHCl_3$) under vigorous stirring during 2 h. The homogeneous solution was transferred to a circular glass container and left for slow evaporation during 24 h. The resulting membrane was extracted by addition of distilled water and dried at 40 °C.

The plasticizer used in the preparation of the composite membranes must be compatible with both the polymer and the clay component, and also must be miscible with the solvent. Plasticizers with high lipophilicity are preferred.

Characterization of membranes

FTIR spectra of the different prepared membranes were recorded using a Perkin Elmer spectrophotometer (Spectrum One model), in the range of 400-4000 cm^{-1} , with a resolution of 4 cm^{-1} , and a total of 32 scans were accumulated for each spectrum along with the background. The surface morphologies of the synthesized

membranes were observed using SEM imaging via a Philips Scanning Electron Microscope XL30 FEG (the Netherlands), with a voltage of 20 keV. The contact angle measurements were carried out as the tangent angle of the drop with the membrane surface. Water contact angles were recorded with an OCA20 Data-Physics Instruments, with a syringe to control the droplet size. The average of three arbitrarily selected locations for each sample represents the reported contact angle measurements. Conventional TGA was performed using 10 mg of each membrane, using a TA instruments TGA-Q 500 thermogravimeter, under nitrogen atmosphere, with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Characterization of membranes by TGA

As can be seen in Figures 1 and 2, all the synthesized membranes exhibited good thermal stability until 170 °C. Firstly, the PSu+CTA+DOP+D2EHPA membrane decomposes in two steps. In the first step (52%), from 193 °C to 300 °C, the volatilization of the mixture (DOP, CTA and D2EHPA) occurs. The second step, at 500 °C, represents the degradation of PSu polymer chains. However, the PSu+CTA+DOP+D2EHPA+Clay membrane decomposes in three steps. The first step (28%), occurring at 300 °C, represents the thermal degradation of the plasticizer DOP and of the carrier D2EHPA. The second one, starting at around 340-390 °C, represents the main thermal degradation of the polymeric chains of CTA. The third step, starting at 520 °C, corresponds to the degradation of PSu and clay. Based on these figures, we can confirm that the two synthesized membranes exhibit good thermal stability.

Characterization of synthesized membranes by FTIR

Figures 3 and 4 show the FTIR spectra of the PSu+CTA+DOP+D2EHPA and, respectively, PSu+CTA+DOP+D2EHPA+Clay membranes.

The main features of the spectrum in Figure 3 are an absorption band located around 1730 cm^{-1} , which is attributed to the stretching vibrations of the carbonyl group (C=O) of CTA polymer and DOP plasticizer. The band detected at around 1589 cm^{-1} corresponds to the elongation vibrations of the (C=C) bond of the benzene groups. The bands at 1243 and 1018 cm^{-1} correspond to the stretching modes of asymmetric and symmetric C-O-C of CTA, respectively. Three other bands characteristic of the elongation vibration bonds of SO₂, S=O and C-S, detected at 1373 cm^{-1} , 1104 cm^{-1} and 553 cm^{-1} , respectively, were also observed.

The FTIR spectrum of the PSu+CTA+DOP+D2EHPA+Clay membrane (Fig. 4) showed two bands at 2931 and 2858 cm^{-1} , attributed to the elongation vibrations of the asymmetric and symmetric C-H bonds, respectively. The presence of carbonyl groups of the ester function of CTA was evidenced by the existence of a band located around 1732 cm^{-1} . The acetate groups (COO⁻) were detected at 1574 cm^{-1} .

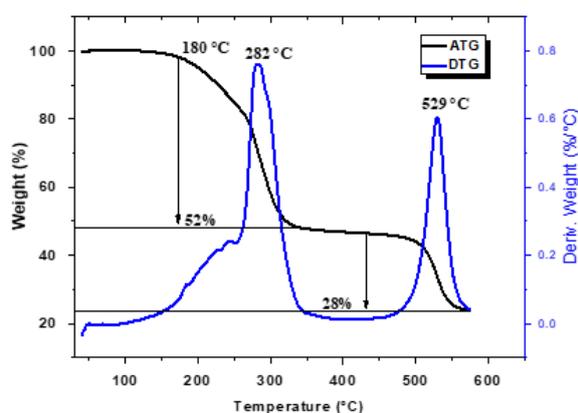


Figure 1: TGA and DTG of PSu+CTA+DOP+D2EHPA membrane

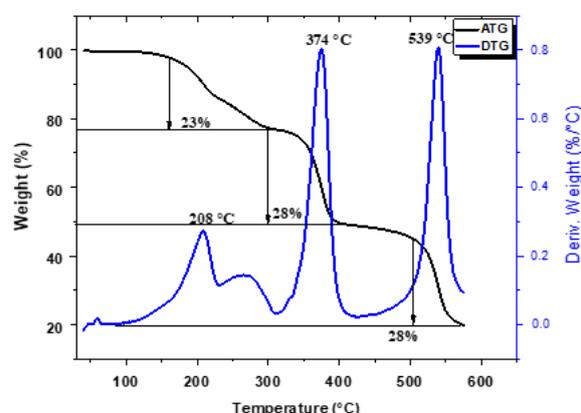


Figure 2: TGA and DTG of PSu+CTA+DOP+D2EHPA+Clay membrane

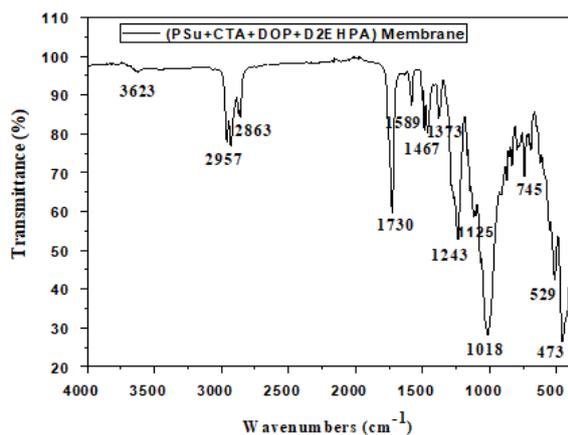


Figure 3: FTIR spectrum of synthesized polymeric membrane PSu+CTA+DOP+D2EHPA

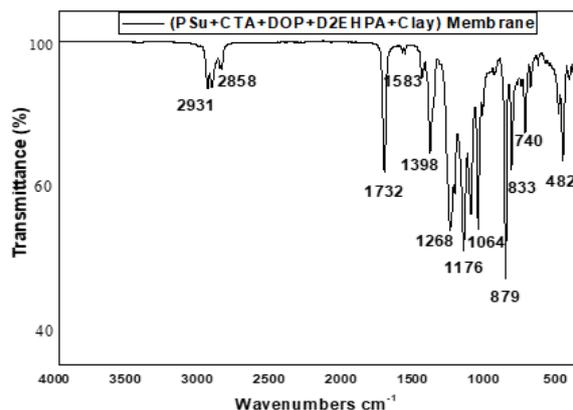


Figure 4: FTIR spectrum of synthesized polymeric membrane PSu+CTA+DOP+D2EHPA+Clay

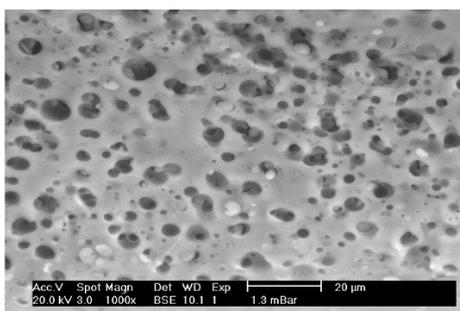
We also noted that the CTA absorbed around 1268 and 1064 cm^{-1} , characterizing the asymmetric and symmetric elongation vibrations of (C-O-C) groups. An absorption band located around 879 cm^{-1} is attributed to the angular deformation of the Si-O-Al group of clay. The band at 833 cm^{-1} corresponds to the stretching mode of (Si-O) single bonds. The same figure also shows the presence of Fe_2O_3 bonds detected at 482 cm^{-1} .

Characterization of synthesized membranes by SEM

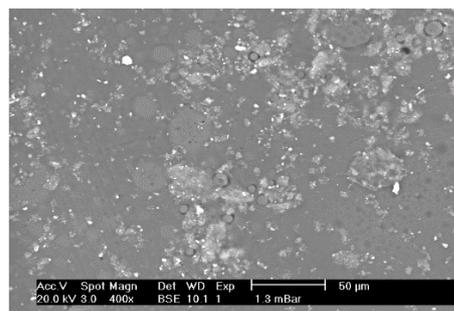
An important aspect of polymeric membranes is their microstructure, which determines the distribution of nanoparticles in the polymer matrix and ultimately affects the membrane filtration efficiency. SEM provides excellent qualitative information (dense or porous membranes) and quantitative capability in measuring important subsurface features, such as porosity and layer thickness. SEM images of surface sections of the synthesized polymeric membranes are given in Figure 5. It can be observed that the morphologies of the PSu+CTA+DOP+D2EHPA+Clay composite membrane has a uniform surface and appears dense, with no apparent porosity. However, the PSu+CTA+DOP+D2EHPA membrane displays a porous structure, the distribution of the pores is nearly uniform. This is probably due to the fact that the presence of D2EHPA leads to more spaces or pores that may be generated after the interactions developed between the different compounds of the membrane.

Contact angle measurements

A comparison of the hydrophobicity of the synthesized composite membranes by measuring their water contact angles is shown in Figure 6. Compared with the PSu+CTA+DOP+D2EHPA control membrane ($68.2^\circ \pm 0.2^\circ$), the water contact angles of the composite membranes were found to decrease noticeably. Lower water contact angles correspond to more hydrophilic surfaces. The average contact angle of the PSu+CTA+DOP+D2EHPA+Clay membrane is lower than that of the control membrane. The improved hydrophilicity of the synthesized composite membranes can be attributed to the presence of hydrophilic clay, arising from the hydroxyl functional groups on their surface. At the same time, a decrease in the average contact angles indicates successful incorporation of the clay into the polymer matrix.

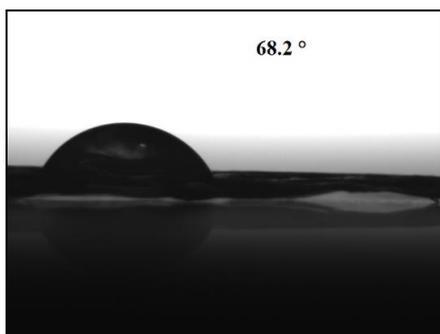


PSu+CTA+DOP+D2EHPA membrane

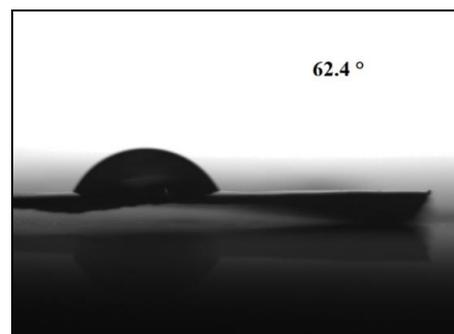


PSu+CTA+DOP+D2EHPA+Clay membrane

Figure 5: SEM images of synthesized membranes



PSu+CTA+DOP+D2EHPA membrane



PSu+CTA+DOP+D2EHPA+Clay membrane

Figure 6: Average contact angle of synthesized membranes

Cadmium and lead ions transport across synthesized polymeric membranes

The porous, homogeneous and mechanically resistant membrane (PSu+CTA+DOP+D2EHPA) was used in the transport experiments in comparison with the dense membrane (PSu+CTA+DOP+D2EHPA+Clay). Tables 1 and 2 represent, respectively, the evolution of the concentration and the yield of Pb^{2+} and Cd^{2+} ions transferred to the stripping phase, not transferred and fixed in the membranes as a function of time.

From the two tables, we can note that the quantities of Pb(II) and Cd(II) ions decreased significantly in the feeding compartment versus time, while they increased in the stripping one and a plateau region is reached after 5 h using all the prepared membranes. The results also show that the concentration of Pb(II) and Cd(II), transferred to the stripping compartment, attained a maximum of 43.2% and 23.5%, respectively, using the membrane without clay, while 28.4% and 25% were transferred after 5 hours in the case of the composite membrane.

The obtained results clearly show that the two elaborated membranes are more suitable for the transport of cadmium, with amounts of 24.9% and 20.6% in the feeding compartment, compared to lead ions, with 42.1% and 47.9%. This is probably due to the ionic radius of cadmium (II) (0.97 Å), which is smaller than that of lead (II) (1.2 Å). This allows the cadmium ions to cross the membranes more easily. It is also shown that the transport of cadmium in the composite membrane is better than that in the membrane without clay, while the permeation of lead with bigger ionic radius is more efficient in the membrane without clay. This can be attributed to the barrier effect caused by the presence of the natural adsorbent.

Additionally, the obtained results show that the quantities of Pb(II) fixed in the membrane are very low (23.7%). However, a maximum of 54.35% yield was obtained in the case of Cd(II) using the composite membrane, thus confirming that there is an active transport of metallic ions (combination between complexation and adsorption), where both carrier and clay play an important role in the separation process. These results are in accordance with the literature²⁹⁻³² and confirm the positive role of a mixture of carrier and adsorbent. The experimental results reported by Fontas *et al.* showed that after 300 min of experimentation, all the Cd initially present in the feed phase was transported to the stripping phase, whereas only 8.5% of Pb was transported.³³ It has been reported that polymer inclusion membranes have low permeabilities, relative to other membranes, despite their significant stabilities. Several studies have been conducted on the stability of this type of membranes, *e.g.*, Tayeb *et al.*³⁴ have studied the influence of Lasalocid A on the stability of a membrane with CTA as a

polymeric support and NPOE as plasticizer. Show *et al.*³⁵ have demonstrated that a polymer inclusion membrane, with CTA as a support and DC18C6 as a carrier, is stable for 100 days. The authors proposed the development of a new type of membrane (a pore-filled membrane [PFM]), which could be stable over 3 months.

Table 1
[Pb²⁺] ions in the feeding and stripping compartments and fixed in the membrane

Time (h)	[Pb ²⁺] in membrane, stripping and feeding compartments (ppm)					
	PSu+CTA+DOP+D2EHPA membrane			PSu+CTA+DOP+D2EHPA+Clay membrane		
	[Pb ²⁺] in stripping	[Pb ²⁺] in feeding	[Pb ²⁺] in membrane	[Pb ²⁺] in stripping	[Pb ²⁺] in feeding	[Pb ²⁺] in membrane
0	0	207.2 (100%)	0	0	207.2 (100%)	0
1	28.1 (13.6%)	137.1 (66.2%)	42 (20.3%)	17.4 (8.4%)	133.1 (64.2%)	56.7 (27.4%)
2	59.3 (28.6%)	120.8 (58.3%)	27.1 (13.1%)	34.6 (16.7%)	125.3 (60.7%)	47.3 (22.8%)
3	66.8 (32.2%)	101.6 (49.0%)	38.8 (18.7%)	48.2 (23.3%)	110.3 (53.2%)	48.7 (23.5%)
4	78.1 (32.2%)	96.9 (46.8%)	32.2 (15.5%)	55.9 (27%)	105.4 (50.9%)	45.9 (22.2%)
5	89.6 (43.2%)	87.2 (42.1%)	30.4 (14.7%)	58.8 (28.4%)	99.3 (47.9%)	49.1 (23.7%)
24	97.4 (47%)	85.4 (41.2%)	24.4 (11.8%)	63.1 (30.5%)	97.8 (47.2%)	46.3 (22.4%)
25	98.6 (47.6%)	86.0 (41.5%)	22.6 (10.9%)	64.8 (31.3%)	97.9 (47.3%)	44.5 (21.5%)

Table 2
[Cd²⁺] ions in the feeding and stripping compartments and fixed in the membrane

Time (h)	[Cd ²⁺] in membrane, stripping and feeding compartments (ppm)					
	(PSu+CTA+DOP+D2EHPA) membrane			(PSu+CTA+DOP+D2EHPA+Clay) membrane		
	[Cd ²⁺] in stripping	[Cd ²⁺] in feeding	[Cd ²⁺] in membrane	[Cd ²⁺] in stripping	[Cd ²⁺] in feeding	[Cd ²⁺] in membrane
0	0	112.41 (100%)	0	0	112.4 (100%)	0
1	12.34 (11%)	63.58 (56.6%)	36.49 (32.5%)	16.9 (15.0%)	49.9 (44.4%)	45.6 (40.6%)
2	15.29 (13.6%)	41.63 (37.0%)	55.49 (49.4%)	19.3 (17.2%)	35.3 (31.4%)	57.8 (51.4%)
3	17.88 (15.9%)	33.19 (29.5%)	61.34 (54.6%)	21.8 (19.4%)	31.7 (28.2%)	58.9 (52.4%)
4	23.16 (20.6%)	30.37 (27.0%)	58.88 (52.4%)	26.7 (23.8%)	25.1 (22.3%)	60.7 (54%)
5	26.37 (23.5%)	27.95 (24.9%)	58.09 (51.7%)	28.1 (25.0%)	23.2 (20.6%)	61.1 (54.4%)
24	27.55 (24.5%)	25.84 (23.0%)	59.02 (52.5%)	29.2 (26.0%)	22.9 (20.4%)	60.3 (53.6%)
25	27.79 (24.7%)	25.72 (22.9%)	58.9 (52.4%)	28.8 (25.6%)	22.1 (19.7%)	61.5 (54.7%)

CONCLUSION

In this work, we synthesized a new type of polymeric membranes, using a mixture of polymers, and prepared them by solution casting, followed by solvent evaporation. Membranes were successfully synthesized using two polymers (CTA and PSu), modified by a local clay and plasticized by DOP. D2EHPA was used as a selective mobile carrier. These composite membranes were characterized using physical-chemical methods, such as Fourier transform infrared spectroscopy (FTIR),

thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and contact angle measurements. The degradation of the membranes occurred via two- or three-step processes, with the main loss starting at 190 °C, due to the thermal degradation of the plasticizer. This result confirmed that all the synthesized membranes exhibited good thermal stability. The SEM observation of the membranes revealed a dense or porous and homogeneous structure. Further analyses of membrane surface properties were performed by means of contact angle measurements. A study of the metal ions transport across the polymer inclusion membrane has shown that the retention efficiency for lead and cadmium ions was increased when using Algerian clay as adsorbent.

REFERENCES

- ¹ S. D. Faust and O. M. Aly, "Chemistry of Water Treatment", 2nd ed., Lewis Publishers, 1998, <http://www.crcpress.com>
- ² S. E. Manahan, "Environmental Chemistry", 10th ed., CRS Press, 2017, <https://doi.org/10.1201/9781315160474>
- ³ D. Y. Takigawa, *Sep. Sci. Technol.*, **27**, 325 (1992), <https://doi.org/10.1080/01496399208018883>
- ⁴ A. Troupis, E. Gkika, A. Hiskia and E. Papaconstantinou, *C.R. Chim.*, **9**, 851 (2006), <https://doi.org/10.1016/j.crci.2005.02.041>
- ⁵ P. J. James, T. J. Mc Master, J. M. Newton and M. J. Miles, *Polymer*, **41**, 4223 (2000), [https://doi.org/10.1016/S0032-3861\(99\)00641-2](https://doi.org/10.1016/S0032-3861(99)00641-2)
- ⁶ Y. Berbar, Z. E. Hammache, S. Bensaadi, R. Soukeur, M. Amara *et al.*, *J. Water Process Eng.*, **32**, 100953 (2019), <https://doi.org/10.1016/j.jwpe.2019.100953>
- ⁷ C. A. Nogueira and F. Delmas, *Hydrometallurgy*, **52**, 267 (1999), [https://doi.org/10.1016/S0304-386X\(99\)00026-2](https://doi.org/10.1016/S0304-386X(99)00026-2)
- ⁸ R. A. Bartsch and J. Way, "Chemical Separation with Liquid Membranes", ACS Symposium, Washington DC, **642**, 575 (1996), <https://doi.org/10.1021/bk-1996-0642.ch001>
- ⁹ S. Bensaadi, O. Arous, H. Kerdjoudj and M. Amara, *J. Env. Chem. Eng.*, **4**, 1545 (2016), <https://doi.org/10.1016/j.jece.2016.02.003>
- ¹⁰ A. Ammi Said, O. Arous, A. Yahia Cherif, Y. Berbar, M. Amara *et al.*, *Polym. Bull.*, **76**, 3659 (2019), <https://doi.org/10.1007/s00289-018-2568-7>
- ¹¹ N. Abdellaoui, F. M. Laoui, H. Cerbah and O. Arous, *J. Appl. Polym. Sci.*, **135**, 46592 (2018), <https://doi.org/10.1002/app.46592>
- ¹² D. Zioui, O. Arous, N. Mameri, H. Kerdjoudj, M.S. Sebastian *et al.*, *J. Hazard. Mater.*, **336**, 188 (2017), <https://doi.org/10.1016/j.jhazmat.2017.04.035>
- ¹³ E. Radzimska-Lenarcik and M. Ulewicz, *Sep. Sci. Technol.*, **47**, 1113 (2012), <https://doi.org/10.1080/01496395.2011.646378>
- ¹⁴ L. D. Nghiem, P. Mornane, I. D. Potter, J. M. Perera, R. W. Cattrall *et al.*, *J. Membr. Sci.*, **281**, 7 (2006), <https://doi.org/10.1016/j.memsci.2006.03.035>
- ¹⁵ A. Yahia Cherif, O. Arous, M. Amara, S. Omeiri, H. Kerdjoudj *et al.*, *J. Hazard. Mater.*, **227-228**, 386 (2012), <https://doi.org/10.1016/j.jhazmat.2012.05.076>
- ¹⁶ M. Ulewicz, U. Lesinska, M. Bochenska and W. Walkowiak, *Sep. Sci. Technol.*, **54**, 299 (2007), <https://doi.org/10.1016/j.seppur.2006.09.018>
- ¹⁷ O. Arous, M. Amara, M. Trari, A. Bouguelia and H. Kerdjoudj, *J. Hazard. Mater.*, **180**, 493 (2010), <https://doi.org/10.1016/j.jhazmat.2010.04.057>
- ¹⁸ D. Zioui, L. Aoudjit, H. Aburideh and Z. Tigrine, *Cellulose Chem. Technol.*, **56**, 353 (2022), <https://doi.org/10.35812/CelluloseChemTechnol.2022.56.31>
- ¹⁹ H. Aburideh, Z. Tigrine, D. Zioui, S. Hout, D. Tassalit *et al.*, *Cellulose Chem. Technol.*, **55**, 697 (2021), <https://doi.org/10.35812/CelluloseChemTechnol.2021.55.59>
- ²⁰ E. L. Cussler, R. Aris and A. Brown, *J. Membr. Sci.*, **43**, 149 (1998), [https://doi.org/10.1016/S0376-7388\(00\)85094-2](https://doi.org/10.1016/S0376-7388(00)85094-2)
- ²¹ R. D. Noble, *J. Membr. Sci.*, **75**, 121 (1992), [https://doi.org/10.1016/0376-7388\(92\)80011-8](https://doi.org/10.1016/0376-7388(92)80011-8)
- ²² Y. S. Kang, J.-M. Hong, J. Jang and U. Y. Kim, *J. Membr. Sci.*, **109**, 149 (1996), [https://doi.org/10.1016/0376-7388\(95\)00190-5](https://doi.org/10.1016/0376-7388(95)00190-5)
- ²³ J. M. Hong, Y. S. Kang, J. Jang and U. Y. Kim, *J. Membr. Sci.*, **109**, 159 (1996), [https://doi.org/10.1016/0376-7388\(95\)00189-1](https://doi.org/10.1016/0376-7388(95)00189-1)
- ²⁴ A. Gherrou, H. Kerdjoudj, R. Molinari and P. Seta, *Mater. Sci. Eng. C*, **25**, 436 (2005), <https://doi.org/10.1016/j.msec.2004.11.002>
- ²⁵ E. Radzimska-Lenarcik, I. Pyszka and M. Ulewicz, *Membranes*, **10**, 88 (2020), <https://doi.org/10.3390/membranes10050088>

- ²⁶ P. Lacan, C. Guizard, P. L. Gall, D. Wettling and L. Cot, *J. Membr. Sci.*, **100**, 99 (1995), [https://doi.org/10.1016/0376-7388\(94\)00259-2](https://doi.org/10.1016/0376-7388(94)00259-2)
- ²⁷ A. Koulov, J. M. Mahoney and B. D. Smith, *Org. Biomol. Chem.*, **1**, 27 (2003), <https://doi.org/10.1039/B208873H>
- ²⁸ M. Sugiura, M. Kikkawa and S. Urita, *Sep. Sci. Technol.*, **22**, 2263 (1987), <https://doi.org/10.1080/01496398708068612>
- ²⁹ M. F. San Roman, I. Ortiz Gandara, R. Ibanez and I. Ortiz, *J. Membr. Sci.*, **415**, 616 (2012), <https://doi.org/10.1016/j.memsci.2012.05.063>
- ³⁰ Q. Chen, J. Zheng, L. Wen, C. Yang and L. Zhang, *Chemosphere*, **224**, 509 (2019), <https://doi.org/10.1016/j.chemosphere.2019.02.138>
- ³¹ R. Ahmad and A. Mirza, *J. Mol. Liq.*, **249**, 805 (2018), <https://doi.org/10.1016/j.molliq.2017.05.125>
- ³² D. Hamane, O. Arous, F. Kaouah, M. Trari, H. Kerdjoudj *et al.*, *J. Env. Chem. Eng.*, **3**, 60 (2015), <https://doi.org/10.1016/j.jece.2014.11.003>
- ³³ N. Pont, V. Salvado and C. Fontas, *J. Membr. Sci.*, **318**, 340 (2008), <https://doi.org/10.1016/j.memsci.2008.02.057>
- ³⁴ R. Tayeb, C. Fontas, M. Dhahbi, S. Tingry and P. Seta, *Separ. Purif. Technol.*, **42**, 189 (2005), <https://doi.org/10.1016/j.seppur.2004.07.006>
- ³⁵ A. J. Schow, R. T. Peterson and J. D. Lamb, *J. Membr. Sci.*, **111**, 291 (1996), [https://doi.org/10.1016/0376-7388\(95\)00295-2](https://doi.org/10.1016/0376-7388(95)00295-2)