LOW-COST TREATMENT OF REAL EFFLUENT WASTEWATER CONTAINING LEAD IONS USING CARBOXYMETHYL CELLULOSE AND POLYMETHYL METHACRYLATE BASED MEMBRANES

OMAR AROUS,[*] WALID MANSOUR,[*] KENZA LAMRI[*] and OUARDA MERDOUD[*,**]

[*]*Laboratory of Hydrometallurgy and Inorganic Molecular Chemistry (LHCIM), Faculty of Chemistry, USTHB, PO Box 32 El Alia, Bab Ezzouar, 16111, Algiers, Algeria*
[**]*Center of Research in Physical and Chemical Analysis (CRAPC), Bousmail, Tipaza, Algeria*
✉ *Corresponding author: O. Arous, omararous@yahoo.fr*

Received December 26, 2024

Membrane technologies have emerged as a great possibility in wastewater treatment, exhibiting high selectivity, resulting in high-quality effluent and low sludge production, with reduced equipment size and low energy requirements, being low cost and allowing to merge several treatment processes into one. The aim of this work has been the synthesis of new polymeric membranes for water purification, especially for the removal of various toxic pollutants, such as lead (II) ions. One of the most promising solutions for recycling and reusing wastewater is the installation of membrane filtration systems that can guarantee water purification. During this work, a new class of organic membranes for ions elimination was developed. The membranes were synthesized using carboxymethyl cellulose (CMC) and poly-methyl methacrylate (PMMA), plasticized by dioctyl phtalate (DOP) or glycerol, and modified by the incorporation of D2EHPA using as a selective carrier. All synthesized membranes were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and contact angle measurements. A study of Pb(II) retention using the synthesized membranes was realized. Dialysis experiments of Pb(II) transfer across the polymer inclusion membranes have proved their good performance. The treatment of an industrial effluent containing 56.5 mg.L^{-1} of lead gave very satisfactory results, where it was noticed that the membranes based on DOP eliminated practically 58% of lead.

Keywords: carboxymethyl cellulose, heavy metals, membranes, water purification, dialysis

INTRODUCTION

Water resources are continuously decreasing, while the demand for water is constantly growing. The rainfall deficit and pollution recorded over the last decade have had an impact on available water reserves. The water, which is essential to the needs of living beings, must comply with certain minimum quality standards. Water resources, threatened by human, industrial and agricultural activities, have become of a major concern on a global level.[1]

Among the many chemical substances that can contaminate aquatic environments, organic dyes and heavy metals are the most frequently encountered. The former are used in many industrial sectors, such as textile, paper, leather dyeing, and cosmetic industries.[2] Dyes have the reputation of being toxic and persistent in the environment,[3] sometimes requiring the combination of several techniques to eliminate or degrade them. Also, heavy metals present in many industrial liquid effluents pose a serious problem for the environment in general and public health in particular. Indeed, heavy metals are toxic even at low concentrations and have the capacity to accumulate throughout the food chain.[9] Lead is one of these metals; it is actually a by-product of the metallurgical processing of zinc.[10] It has certain properties capable of being incorporated into the biomass whose enzymatic system it disrupts.[11]

Several physical, chemical and biological techniques have been developed and tested for the treatment of effluents loaded with toxic pollutants. These processes include flocculation, precipitation, ion exchange, membrane filtration, irradiation and ozonation.[4-5] However, these processes are expensive and lead to the generation

of large quantities of sludge or the formation of sometimes more toxic derivatives.[6] The adsorption process, especially on activated carbon, can constitute a better alternative, which has proven itself through numerous research works carried out in this direction. An excellent adsorbent must generally have a large specific surface area and a short equilibrium time, so that it can easily remove a large quantity of pollutants in a very short time, and it must also generate few secondary materials and therefore have good regeneration efficiency.[7-8] Thus, activated carbon is by excellence a material with high adsorbent power.

Many researchers have focused their attention on the advanced treatment of secondary effluents from wastewater treatment plants for reuse. Liquid membrane (LM) processes were successfully used to obtain water of recyclable quality. However, LMs present some difficulties for industrial applications, such as low fluxes, poor mechanical properties and leaching of carriers at membrane interfaces, limiting the long term stability of the membranes.[12-13] Common problems of LMs, such as the loss of membrane solvent and/or carrier to both aqueous phases, have led to LM-based processes not to be exploited industrially. Recently, facilitating transport membranes have been applied more frequently for ion separation.

In recent years, membrane techniques have been increasingly used for wastewater treatment. Generally, their performance meets water quality objectives, as they can effectively remove microparticles and macromolecules, which generally give rise to inorganic particles and organic colloids (*i.e.* microorganisms from dissolved organic matter).[6]

The use of macroporous polymer supports, with a high surface area and good mechanical stability, has been found to be more suitable for the removal of toxic elements from dilute solutions, due to their faster kinetics, ease of regeneration and high adsorption capacity. The development and application of these systems in metal extraction processes have been intensively investigated for applications on metal separation and recovery processes.[14-30]

This work was focused on studying the purification of water polluted by an inorganic contaminant (lead (II) ions), coming from a real effluent, using newly developed polymeric membranes. The membranes based on PMMA and CMC polymers were modified by the addition of a carrier – 2-di-ethyl hexyl phosphoric acid (D2EHPA), and by a plasticizer – dioctyl phthalate (DOP) or glycerin, to make them more flexible and more resistant.

EXPERIMENTAL

Materials

CMC (pure), polymethyl methacrylate (PMMA), chloroform (GC ≥ 99%), glycerin and di-(2-ethylhexyl) phosphoric acid (D2EHPA) were purchased from Fluka. Dioctyl phtalate (DOP) was obtained from Carlo Erba. The aqueous solutions were obtained by dissolving the different reagents in deionized water. All reagents were used as received, without any further purification.

Preparation method of membranes

Membranes were prepared via phase inversion. In this method, carboxymethyl cellulose (CMC) was dissolved in deionized water at 1% w/v concentration by 24 h of magnetic stirring, until achieving a moderately viscous and transparent solution. In parallel, 0.2 g of PMMA was dissolved in 30 mL of chloroform ($CHCl_3$) for two hours. Then, the plasticizer DOP and a carrier D2EHPA were added to the polymeric solution under vigorous stirring for 3 hours. The two solutions were mixed, then transferred into a circular glass container and degassed in an ultrasonic cleaner for 15 min to remove air bubbles and allow the formation of a homogeneous and stable solution. After degassing, the casting solution was allowed to slowly evaporate for 24 hours. The resulting membrane was extracted by the addition of distilled water.

Transport experiments were carried out in a dialysis cell made of Teflon, in which the membrane film was tightly clamped between two cell compartments, as shown in Figure 1. The membrane consists of 0.2 g of CMC, 0.2 g of PMMA, 0.1 mL of DOP and 0.1 mL of D2EHPA, the average thickness of membrane is 100 μm, and specific surface area is 9.6 cm^2.

Characterization of membranes

FTIR spectroscopy was used to observe the frequency changes of the functional groups. This technique was used to detect the presence of the different bonds of constituents used in the initial mixture and final polymeric membranes. The FTIR spectra were registered with a Perkin-Elmer spectrometer (Spectrum One). The instrument was calibrated before analysis, using 60 scans at a resolution of 2 cm^{-1} in the wavenumber range of 4000–400 cm^{-1}.

Thermogravimetric analysis is considered a simple and suitable method to evaluate the thermal stability of different materials. TGA allows observing the effects of thermal decomposition, evaporation, reduction, desorption, sublimation, oxidation and absorption. TGA analyses were realized using a TGA Q500, TA Instrument, automated from 50 to 600 °C at a rate of 10 °C/min. All samples were purged with nitrogen gas at a flow rate of 60 mL/min. The sample weights were approximately 10 mg.

The contact angle measurements were given 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 five arbitrarily selected locations for each sample represents the reported contact angle measurements.

Wastewater sampling and analysis

Industrial wastewater was sampled from an area located about 13 km east of Algiers, which is known for being a highly industrialized area, especially with battery manufacturing factories. Samples were stored in obscurity at 4 °C, transported to the laboratory and kept in the fridge to avoid degradation until treatment.

A large range of water quality parameters were measured. Standard methods were used for the determination of chlorides, nitrates, nitrites and water hardness.[31] Turbidity (T) was measured using a Hanna Instruments HI88703 Turbidimeter. Biochemical oxygen demand (BOD_5) was assessed using a Velp Scientifica BOD sensor system. Conductivity (C), potential hydrogen (pH) and total dissolved solids (TDS) were measured using a Consort multi-parameter analyzer, while chemical oxygen demand (COD) was determined using a QuickCODultra.

Water pretreatment and treatment experiments

In order to avoid rapid fouling of the membranes, we carried out a pretreatment using two adsorbents (activated carbon and sand). The solution pretreated with the two adsorbents was subsequently treated using the dialysis process.

The cell used for water treatment experiments consisted of two compartments, made of Teflon with a maximum filling volume of 100 mL and separated by the polymeric membrane (Fig. 1). The feed compartment contained the wastewater and the strip compartment contained distilled water. Both the feed and strip aqueous phases were stirred at 800 rpm using a magnetic stirrer. The metal concentration was determined by samplings at different time interval aliquots (0.5 mL) from both the feed and strip solutions, and analyzed using the atomic absorption spectroscopy technique (AAS) with a Perkin-Elmer Analyst 700 model for Pb^{2+} ions. The membrane surface area was 9.61 cm^2. Three independent experiments were realized to determine the lead concentration.

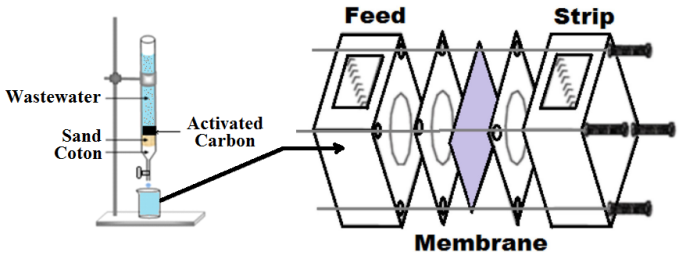


Figure 1: Experimental procedure comprising (a) pretreatment; and (b) treatment by dialysis of wastewater

RESULTS AND DISCUSSION

Characterization of polymers (CMC and PMMA) and polymeric membranes by FTIR

An appropriate quantity of the polymer dissolved in chloroform at a concentration of 10% (weight/volume) was prepared and then spread on a Teflon plate. A film was then generated after the evaporation of the solvent. The sample was dried at room temperature, protected from dust, then in a vacuum oven at a constant temperature of 40 °C and under reduced pressure for several days to eliminate all traces of solvent and humidity.

The FTIR spectrum of CMC, shown in Figure 2, mainly displays several absorption bands characteristic of the functional groups of this polymer: a band at 1730 cm^{-1}, characteristic of the free C=O groups of the ester; a band at 3438 cm^{-1} attributed to the OH hydroxyl groups of CMC; a band relating to acetate groups (COO-) located at 1608 cm^{-1}; two bands located around 1274 cm^{-1} and 1036 cm^{-1}, respectively, characterizing the elongation vibrations of the asymmetric and symmetric groups (C-O-C). The bands relating to the stretching vibrations of the symmetric and asymmetric C-H bond are easily identified in this spectrum at 2926 cm^{-1} and 2882 cm^{-1}.

Figure 3 shows the FTIR spectrum of PMMA. In addition to the bands, relating to the stretching vibrations of asymmetric (2992 cm^{-1}) and symmetric C-H bonds (at around 2846 cm^{-1}), the examination of the FTIR spectrum of poly(methyl methacrylate) (PMMA) has revealed the existence of several characteristic bands relating to the functional groups of this polymer. The presence of methyl methacrylate groups is highlighted by the vibration band specific to the carbonyl groups of the ester function located around 1733 cm^{-1}.

Figures 4 and 5 represent the FTIR spectra of the synthesized polymeric membranes.

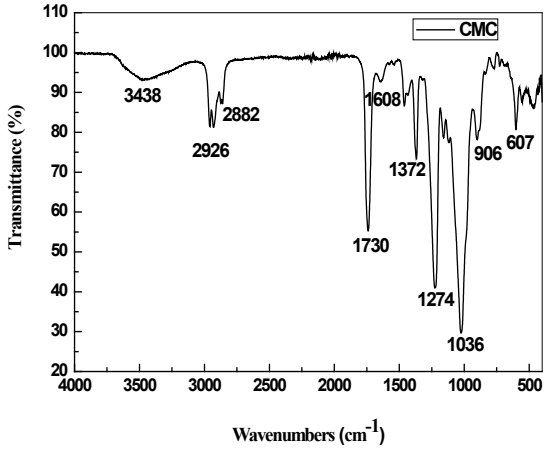


Figure 2: FTIR spectrum of CMC

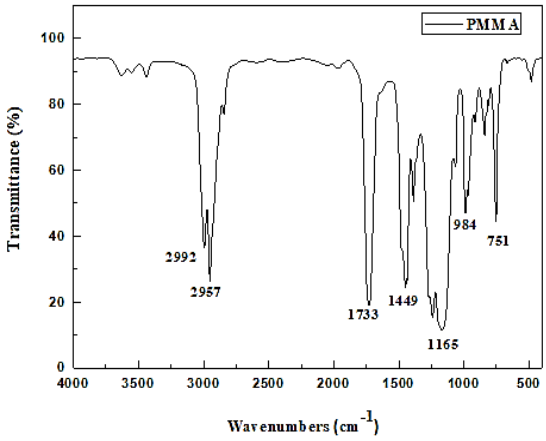


Figure 3: FTIR spectrum of PMMA

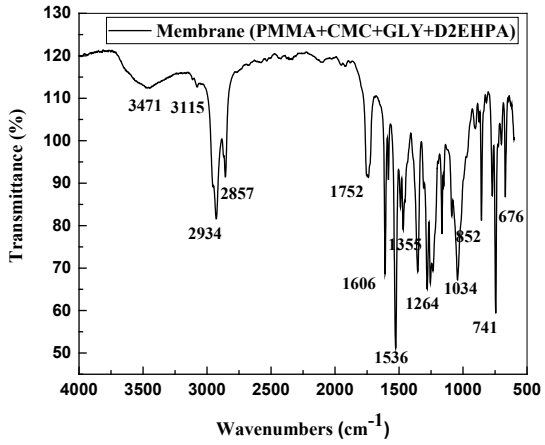


Figure 4: FTIR spectrum of PMMA+CMC+Glycerin+D2EHPA membrane

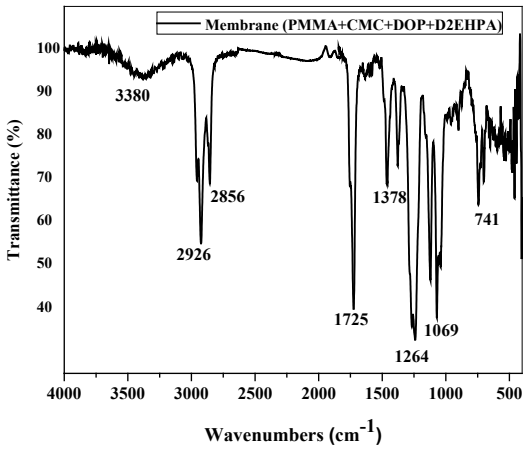


Figure 5: FTIR spectrum of PMMA+CMC+DOP+D2EHPA membrane

It may be remarked that the FTIR spectra of the membranes mainly display several absorption bands characteristic of vibrations of elongation and angular deformations of the functional groups of the polymers, carrier (D2EHPA) and the plasticizer (DOP). Namely, the band at 1725 cm^{-1} is characteristic of the free C=O groups of the ester of the CMC base polymer; the band around 1755 cm^{-1} is characteristic of the free C=O groups of the ester of the DOP plasticizer; the band relating to the COO^- acetate groups of CMC is located at 1580 cm^{-1}; two bands located around 1231 cm^{-1} and 1040 cm^{-1}, respectively, characterize the elongation vibrations of the asymmetric and symmetric groups (C-O-C). The presence of DOP within the PMMA+CMC+DOP+D2EHPA membranes produced is highlighted by the appearance of several bands detected at 1608 cm^{-1}, corresponding to the elongation vibration of the C=C groups of phenyls.

Ultimately, the results obtained highlight that, in all the membranes developed, the interconnected chains of the PMMA and CMC base polymers include the plasticizer and the complexing agent (D2EHPA). The presence of elongation vibration bands of O-H, C-H, C=O, C=C, asymmetric C-O-C and symmetric C-O-C was detected in the different membranes synthesized in this study.

Characterization of membranes by TGA

As part of this work, the thermal stability of the different membranes developed was studied by thermogravimetric analysis (TGA). This technique allowed examining the behavior of the different constituents within the mixtures and their influence on the thermal stability of the membranes developed.

The TGA weight loss thermograms and the corresponding derivative d(TGA) curves of the PMMA+CMC+DOP+D2EHPA membrane are

shown in Figure 6. It may be clearly noticed that membrane PMMA+CMC+DOP+D2EHPA degrades in three stages. During the first stage, a mass loss of around 14% is recorded in the temperature range of 180-240 °C, with a maximum degradation around 238 °C. This mass loss is attributed to the volatilization of the complexing agent D2EHPA. During the second degradation stage, between 250 °C and 290 °C, the membrane loses only 8% of its mass, due to the degradation of the DOP. The last mass loss, of 32%, occurs from 360 °C to 430 °C, which is related to the degradation of the two polymers PMMA and CMC. During this stage, the maximum degradation temperature is recorded at 386 °C.

Figure 7, illustrating the evolution of the mass loss and the first derivative of membrane PMMA+CMC+Glycerin+D2EHPA as a function of temperature, allows the conclusion that the degradation process also follows three main stages. This confirms the existence of interactions between the different constituents of this membrane. The first stage of degradation extends over a temperature range of 135-180 °C, where the membrane loses only 6% of its mass. The maximum degradation temperature is 157 °C; this mass loss is attributed to the degradation of the D2EHPA complexing agent. The mass loss of the PMMA+CMC+Glycerin+D2EHPA membrane during the second degradation step occurred at a temperature ranging from 240-280 °C. A mass loss of 38% was detected at 264 °C, which is attributed to the volatilization of the DOP plasticizer. Furthermore, the mass loss recorded during the last degradation stage, ranging from 340 °C to 440 °C, reached 50%; this stage is related to the degradation of the polymer mixture (PMMA + CMC). During this stage, the maximum degradation temperature is recorded at 396 °C. The obtained results are summarized in Table 1. Ultimately, the thermogravimetric study carried out during this work on the membranes allowed highlighting the following: very good thermal stability of the two base polymers (CMC and PMMA) up to 386 °C and 396 °C, respectively; and acceptable thermal stability of the membranes – up to a temperature of 135 °C.

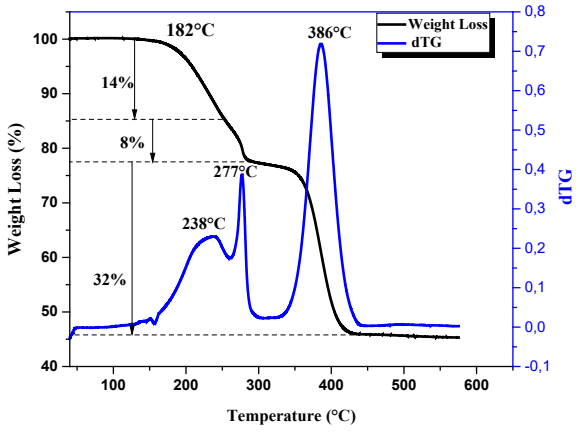


Figure 6: Thermogravimetric (TG) and d(TGA) curves of PMMA+CMC+DOP+D2EHPA membrane

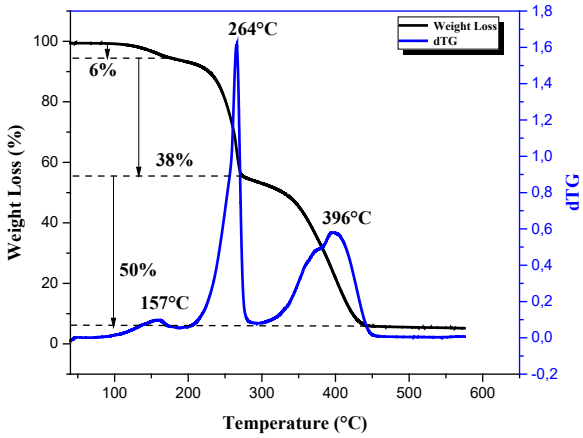


Figure 7: Thermogravimetric (TG) and d(TGA) curves of PMMA+CMC+Glycerin+D2EHPA membrane

Table 1
Thermogravimetric data of the synthesized membranes

Membrane	T_{onset} (°C)	T_{max} (°C)	Weight loss (%)	Residue (%)
PMMA+CMC+DOP+D2EHPA	182	238	14	46
		277	8	
		386	32	
PMMA+CMC+Glycerin+D2EHPA	148	157	6	6
		264	38	
		396	50	

Table 2
Contact angles of the synthesized membranes and the polymers

Sample	Contact angle (°)	Reference
Poly(methyl methacrylate) (PMMA)	70.9	[3]
Carboxymethyle cellulose (CMC)	33.5	[4]
PMMA+CMC+DOP+D2EHPA membrane	64.24 ± 0.04	This work
PMMA+CMC+Glycerin+D2EHPA membrane	54.30 ± 0.01	This work

This limiting temperature is much higher than that used in membrane processes on an industrial scale.

Contact angle measurements

A comparison of the hydrophobicity of the synthesized membranes by measuring their water contact angles is shown in Table 2. Compared with the PMMA control membrane (70.9°), the water contact angles of the elaborated membranes were found to decrease noticeably. Lower water contact angles correspond to more hydrophilic surfaces. The average contact angles of the PMMA+CMC+DOP+D2EHPA and PMMA+CMC+Glycerin+D2EHPA membranes are lower than that of the control membrane. The higher hydrophilicity of the synthesized membranes can be attributed to the presence of hydrophilic glycerin and carrier, 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 plasticizer into the polymer matrix.

Table 2 groups the contact angle values of the different polymers and membranes. It is noted that carboxymethyl cellulose (CMC) is hydrophilic, while polymethyl methacrylate (PMMA) is slightly hydrophobic. It should be noted that the two polymers (CMC and PMMA), with one plasticizer (DOP or glycerin), and the same complexing agent D2EHPA form both membranes. Therefore, the wettability of the different membranes developed depends strongly on the nature of the plasticizer. It is noted from Table 2 that both membranes developed are moderately hydrophilic ($54.30° < \theta < 64.24°$). It is also observed that the substitution of glycerin by dioctyl phthalate increases the contact angle (with water as solvent). This is related to the very hydrophilic nature of glycerin.

Pretreatment and treatment of wastewater

The problem of water pollution has become very worrying. Heavy metals are among the most commonly released pollutants into wastewater, either dissolved or associated with suspended solids. Pretreatment of wastewater can effectively improve the service life of the filtration system by removing contaminants that can block or damage membranes.

We have used adsorption to remove various macro-pollutants from aqueous media using low-cost adsorbents. The determination of heavy metal concentrations from the industrial wastewater before pretreatment was accomplished using atomic absorption spectrometry (AAS). Table 3 shows the obtained results of the heavy metals analysis by AAS. According to Table 3, the AAS analysis showed the total absence of cadmium ions in the sample of industrial wastewater studied, and the concentrations of zinc and copper ions fall within the limit values required by the World Health Organization (WHO). However, the concentration of lead (II) ions (56.5 mg/L) is very high and did not conform to the standards established by the WHO.

Table 3
AAS results of heavy metal ions concentration before pretreatment

Heavy metals	Content in wastewater (mg/L)	According to WHO norms (mg/L)
Copper II	0.148	1
Lead II	56.5	0.5
Cadmium II	00	0.1
Zinc II	0.561	3
Iron II	5.307	3

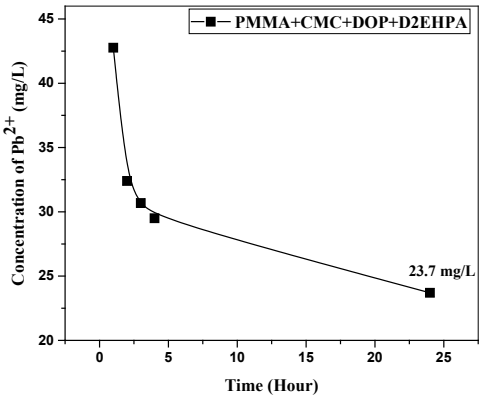


Figure 8: Variation of lead (II) ions concentration *vs* time in feed compartment for membrane PMMA+CMC+DOP+D2EHPA ($[Pb^{2+}]_0$ = 55.82 mg/L)

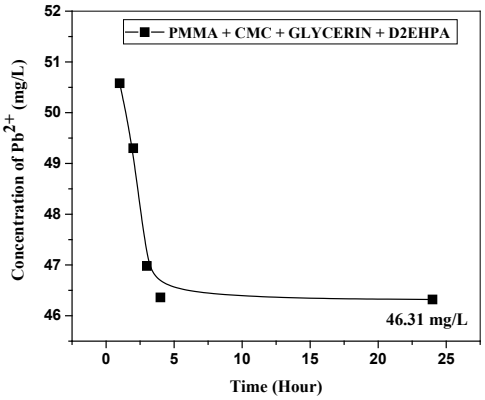
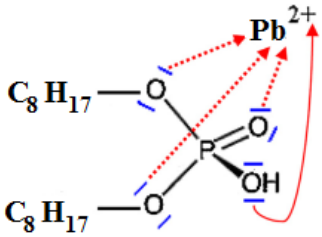


Figure 9: Concentration of lead (II) ions *vs* time in feed compartment for membrane PMMA+CMC+ Glycerin+D2EHPA ($[Pb^{2+}]_0$ = 55.82 mg/L)



Scheme 1: Electrostatic interactions between D2EHPA and Pb^{2+}

Table 4
Some quality indicators of wastewater after pretreatment and treatment stages

Quality indicator	Initial	After pretreatment	After treatment
Temperature (°C)	38	24	24
pH	8.67	6.89	6.98
BOD_5	119	32	29
COD	682	429	397
TDS	4540	2238	2225
Conductivity (µS/cm)	2866	2846	1592
Turbidity (NTU)	202	4	3
Chlorides, Cl^-	586	435	435
Lead (mg/L)	56.51	55.82	23.70

Figures 8 and 9 represent the variation of the lead concentration as a function of time in the feed compartment using the prepared membranes: PMMA+CMC+DOP+D2EHPA and PMMA+CMC+Glycerin+D2EHPA. The initial concentration of lead in the real effluent is equal to 55.82 mg/L (obtained after pretreatment).

It may be noted that, in the case of both synthesized membranes, the lead (II) ions concentration decreases over time in the feed compartment, to reach a minimum level after 4 hours of transport. It should also be remarked that the membrane PMMA+CMC+DOP+D2EHPA is more efficient, as it recorded a remaining concentration in the feed compartment equal to 23.7 mg/L, which represents 58% purification. This acceptable value for a real sample, extremely polluted with lead ions, confirms that the membrane process is very effective for the elimination of this toxic metal ion. It is important to note that the selectivity of the interface is much higher, when the metal cation interacted more with organo-phosphorus compounds according to the electrostatic interactions (Scheme 1).

Table 4 shows some quality parameters of wastewater after pretreatment and after the membrane treatment. It is clear that the results exhibited high removal efficiency of the membrane/adsorbent combination for industrial effluents. The obtained results confirmed a significant reduction in turbidity (98.51%), lead (57.54%) and electrical conductivity (EC)

(44.45%). According to the results obtained, the values of BOD_5 measured varied between 32 mg/L and 29 mg/L. These results do not meet the standard value required by the WHO, which is 25 mg/L. Overall, our results are in accordance with the findings of other researchers using other techniques.[32-34]

CONCLUSION

In this study, we developed novel plasticized polymer membranes, whose transporter (D2EHPA) is fixed in the matrix of carboxymethyl cellulose (CMC) and polymethyl methacrylate (PMMA). The synthesized membranes were characterized by different techniques, such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and contact angle measurements. The membranes developed were applied for the purification of a real effluent from the battery industry, highly loaded with highly toxic lead species, using the dialysis technique. A pretreatment was carried out using activated carbon and sand to avoid blockage of the membranes. FTIR spectroscopy confirmed the composition of the developed membranes. The obtained TGA results showed that all the elaborated membranes have good thermal stability and resist up to a temperature of 160 °C. The treatment of an industrial effluent containing 56.5 $mg.L^{-1}$ of lead (II) ions gave very satisfactory results, as the polymeric membranes were successful in eliminating 58% of lead.

REFERENCES

[1] S. Veli and B. Alyuz, *J. Hazard. Mater.*, **149**, 226 (2007), https://doi.org/10.1016/j.jhazmat.2007.04.109

[2] M. Safarpour, A. Safikhani and V. Vatanpour, *Sep. Purif. Technol.*, **279**, 119678 (2021), https://doi.org/10.1016/j.seppur.2021.119678

[3] L. C. Lin and R. S. Juang, *Chem. Eng. J.*, **112**, 211 (2005), https://doi.org/10.1016/j.cej.2005.07.009

[4] C. A. Nogueira and F. Delmas, *Hydrometallurgy*, **52**, 267 (1999), https://doi.org/10.1016/S0304-386X(99)00026-2

[5] B. Wassink, D. Dreisinger and J. Howard, *Hydrometallurgy*, **57**, 235 (2000), https://doi.org/10.1016/S0304-386X(00)00116-X

[6] S. Memon and M. Yilmaz, *Sep. Purif. Technol.*, **36**, 473 (2001), https://doi.org/10.1081/SS-100102939

[7] B. Gupta, A. Deep and P. Malik, *Hydrometallurgy*, **61**, 65 (2001), https://doi.org/10.1016/S0304-386X(01)00157-8

[8] K. Takeshita, K. Watanabe, Y. Nakano and M. Watanabe, *Hydrometallurgy*, **70**, 63 (2003), https://doi.org/10.1016/S0304-386X(03)00046-X

[9] L. C. A. Oliveira, E. Pereira, I. R. Guimaraes, A. Vallone, M. Pereira *et al*., *J. Hazard. Mater.*, **165**, 87 (2009), https://doi.org/10.1016/j.jhazmat.2008.09.064

[10] A. Namane, A. Mekarzia, K. Benrachedi, N. Belhaneche-Bensemra and A. Hellal, *J. Hazard. Mater.*, **119**, 189 (2005), https://doi.org/10.1016/j.jhazmat.2004.12.006

[11] B. Benguella and H. Benaissa, Water Res., **36**, 2463 (2000), https://doi.org/10.1016/S0043-1354(01)00459-6

[12] P. Venkateswaran and K. Palanivelu, *J. Hazard. Mater.*, **131**, 146 (2006), https://doi.org/10.1016/j.jhazmat.2005.09.025

[13] N. Drai, N. Abdellaoui, F. Saib, O. Arous and M. Trari, *Des. Water Treat.*, **255**, 185 (2022), https://doi.org/10.5004/dwt.2022.28340

[14] M. Amara, H. Kerdjoudj, A. Bouguelia and M. Trari, *J. Membr. Sci.*, **312**, 125 (2008), https://doi.org/10.1016/j.memsci.2007.12.047

[15] 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

[16] A. Yahia Cherif, O. Arous, M. Amara, S. Omeiri, H. Kerdjoudj *et al*., *J. Hazard. Mater.*, **227**, 386 (2012), https://doi.org/10.1016/j.jhazmat.2012.05.076

[17] M. Sugiura, M. Kikkawa and S. Urita, *J. Membr. Sci.*, **42**, 47 (1989), https://doi.org/10.1016/S0376-7388(00)82364-9

[18] F. J. Alguacil, *Hydrometallurgy*, **61**, 177 (2001), https://doi.org/10.1016/S0304-386X(01)00168-2

[19] A. C. Ahmia, M. Idouhar, O. Arous, K. Sini, A. Ferradj *et al*., *J. Surfact. Det.*, **19**, 1305 (2016), https://doi.org/10.1007/s11743-016-1884-x

[20] S. Azzoug, O. Arous and H. Kerdjoudj, *J. Env. Chem. Eng.*, **2** 154 (2014), https://doi.org/10.1016/j.jece.2013.11.028

[21] Y. Sedkaoui, N. Abdellaoui, O. Arous, H. Lounici, N. Nasrallah *et al*., *J. Polym. Eng.*, **41**, 127 (2020), https://doi.org/10.1515/polyeng-2020-0165

[22] H. Briki, N. Abdellaoui, O. Arous, F. Metref and D. E. Akretche, *Cellulose Chem. Technol.*, **56**, 1109 (2022), https://doi.org/10.35812/CelluloseChemTechnol.2022.56.99

[23] F. Saib, O. Arous, A. Mazari and M. Trari, *Macromol. Symp.*, **386**, 1 (2019), https://doi.org/10.1002/masy.201800245

[24] N. Abdellaoui and O. Arous, *Macromol. Symp.*, **386**, 1800244 (2019), https://doi.org/10.1002/masy.201800244

[25] N. Abdellaoui, F. M. Laoui, H. Cerbah and O. Arous, *J. App. Polym. Sci.*, **135**, 46592 (2018), https://doi.org/10.1002/app.46592

[26] N. Abdellaoui, Z. Himeur and O. Arous, *Macromol. Symp.*, **386**, 1800240 (2019), https://doi.org/10.1002/masy.201800240

[27] H. Briki, N. Abdellaoui, F. Metref, D. E. Akretche and O. Arous, *J. Biotech. Biores.*, **2**, 1 (2020), https://doi.10.31031/JBB.2020.02.000539

[28] O. Arous, A. Gherrou and H. Kerdjoudj, *Sep. Purif.*

Technol., **39**, 1681 (2005), https://doi:10.1081/SS-120030792
[29] F. Benhacine, N. Abdellaoui, O. Arous and A. S. Hadj-Hamou, *Environ*. *Technol*., **41**, 2049 (2020), https://doi:10.1080/09593330.2018.1555283
[30] F. Smail, O. Arous, M. Amara and H. Kerdjoudj, *Comptes Rendus Chim*., **16**, 605 (2013), https://doi.org/10.1016/j.crci.2013.04.003
[31] AWWA, Standard Methods for the Examination of Water and Wastewater, 20th Ed., APHA, AWWA, WEF, Washington, D.C., (1998), https://www.scirp.org.reference
[32] C. Zaharia and D. Suteu, in "Organic Pollutants Ten Years after the Stockholm Convention - Environmental and Analytical Update", edited by T. Puzyn and A. Mostrag, InTech, 2012, http://doi.org/10.5772/32373
[33] I. Samai, S. Nebbache, F. Chalane, Z. Meghlaoui and H. Ramdani, *Egypt*. *J*. *Aquat*. *Biol*. *Fish*., **27**, 531 (2023), https://doi.10.21608/ejabf.2023.303529
[34] T. E. Oladimeji, M. Oyedemi, M. E. Emetere, O. Agboola, J. B. Adeoye *et al*., *Heliyon*, **10**, e40370 (2024), https://doi.org/10.1016/j.heliyon.2024.e40370