



Research Paper

A Study of Chromium (VI) Ions Fixation and Transport using Polymer Inclusion Membrane Containing D2EHPA as Complexing Agent

S. Bensaadi ¹, N. Draï ¹, O. Arous ^{*1}, Y. Berbar ¹, Z.E. Hammache ¹, M. Amara ¹, B. Van der Bruggen ²

¹ Laboratory of Hydrometallurgy and Inorganic Molecular Chemistry, Faculty of Chemistry, USTHB, P.O. Box 32 El Alia, BabEzzouar, 16111, Algiers, Algeria

² ProcESS - Process Engineering for Sustainable Systems, Department of Chemical Engineering, Leuven, Belgium

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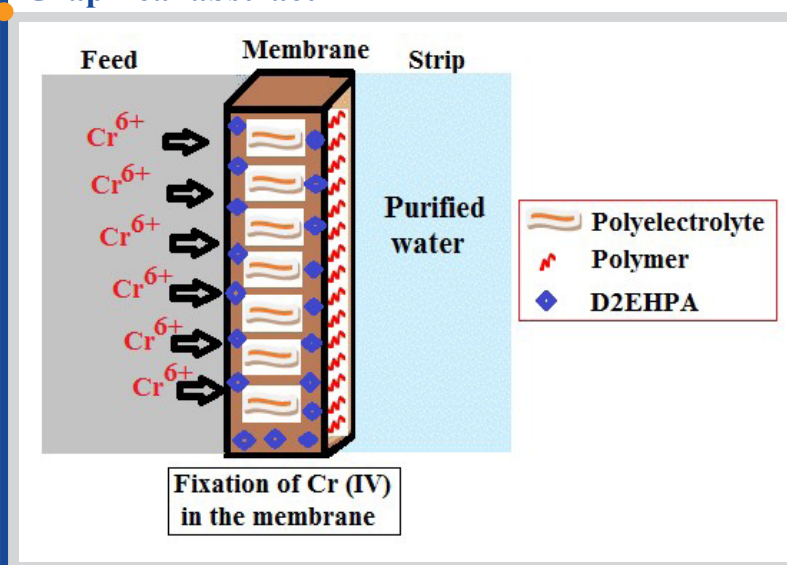
Keywords

Membrane
Fixation
Polymers
D2EHPA
Chromium

Highlights

- Homogeneous thin films containing a mixture of polymers have been synthesized under a new method and using a new experimental condition.
- All synthesized membranes were efficaciously elaborated from binary polymers and plasticized by NPOE.
- Membrane filters show suitable thermal, structural and morphological properties.
- The synthesized polymeric membranes exhibited considerably enhanced permeability to chromium ions.

Graphical abstract



Abstract

In this paper, polymeric inclusion membranes (PIMs) containing cellulose triacetate (CTA) and polycaprolactone (PCL) as polymer matrix and di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a specific carrier were prepared by solution casting followed by solvent evaporation. Different polymeric membranes were modified by the addition of polyelectrolytes: polyvinylpyrrolidone (PVP), polyacrylamide (PAA), and polyethylene imine (PEI). 2-Nitrophenyl octyl ether (NPOE) was added to the different membranes as the plasticizer. All synthesized membranes were characterized by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Transfer of chromium through selective membranes is accomplished by using a specific compound, called carrier. A study of the fixation and transport of Cr (VI) across a polymer inclusion membrane PIMs has shown a good removal from the treated solution. The Cr (VI) removal efficiency reached 42% after 8 hours of transport using the membrane containing (CTA + PCL + PATSA + D2EHPA) and 43% for only 2 hours using the membrane containing (CTA + PCL + PATSA+ NPOE).

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1. Introduction

The industrial revolution brought many toxic metal contaminants using heavy metals in various fields [1]. These heavy metals cause risks to human health, including effects on the nervous system, carcinogenic effects, and kidney disorders [2,3]. Hexavalent chromium (Cr (VI)) is a principal heavy metal ion in a regular environment and is highly toxic even at insignificant concentrations (50 µg/L) in water. Chromium is used in industrial processes such as the electroplating industry, textiles, and tanneries [4-6]. Due to its critical effect on the environment and human health, industrial emissions containing Cr (VI) must be eliminated. Some physicochemical and biological technologies have been established and tested for Cr (VI) remediation [7-14]. Most effluent treatment processes containing Cr (VI) are based on

the reduction of chromium (VI) to chromium (III) [15-18]. This category of treatment was confirmed to be ineffective because it does not meet the required standards for the Cr (VI) remaining in the treated liquid effluent. Membrane processes such as dialysis are among the new technologies that can play an important part in Cr (VI) removal [19-23].

Thus, currently, polymer inclusion membranes (PIM) are considered materials that act as a sink for the contaminant and immobilize it [24-26]. Due to their great adaptability and low cost compared to mineral membranes, polymeric membranes are usually the greatest materials used in desalination and water purification. Various polymers are used as the basic matrix for the development of these membranes such as cellulose acetate (CA) [27],

* Corresponding author: omararous@yahoo.fr (O. Arous)

cellulose triacetate (CTA) [28], polyvinylidene fluoride (PVDF) [29], polyethersulfone (PES) [30]. Different polymers and polyelectrolytes with different proportions are commonly mixed for the synthesis of PIMs in order to eliminate the undesirable morphology change of the membranes during the surface modifications. In this sense, membranes containing polyvinylpyrrolidone PVP [31], polyethyleneimine (PEI) [32], polyethylene (PE) [33], polyvinyl alcohol (PVA) [34], or poly-4-vinylpyridine (P4VP) [35] were developed. A performance study of CTA-based membranes with the presence of PVP and PEG as additives was accomplished in our previous study [36]. The results show a good selectivity of this type of membrane for Cu^{2+} , Ni^{2+} , Cd^{2+} , and Zn^{2+} ions. In another work, the behavior of CTA-based membranes in the presence of PVP, PEI, PEG as additives, and TEHP as plasticizer was studied [37]. The results showed also a certain selectivity of these membranes for Cu^{2+} , Ni^{2+} , Zn^{2+} . In the same work, the combination of two processes, the dialysis process and the photo-deposition process using the prepared membranes and semiconductors used as electrodes allowed to remove Cu^{2+} , Ni^{2+} , and Zn^{2+} satisfactorily. The application of CTA membranes with the presence of trioctyl amine (TOA) and *o*-nitrophenylpentyl ether (NPPE) as plasticizers has proven to be a current and selective technique for recovering 99 % of Chromium from acid solution [38].

Numerous polymers are commercially accessible, but the choice of the adequate polymer is not fortuitous. Chains rigidity, chains interactions, and functional groups polarity are the most important characteristics of the polymer involved in membrane formation [36,37]. The selection of the constituents of each membrane was made according to their affinity towards Cr (VI) via complexation reactions. Therefore, in this work hydrophilic cellulose triacetate (CTA) with high crystallinity and semi-crystalline and hydrophobic polycaprolactone (PCL) were used as the basic polymeric matrix. Polyvinylpyrrolidone (PVP K30), polyanetholsulfonic acid (PATSA), and polyethylene imine (PEI) were added as polyelectrolytes additives. 2-Nitrophenyl octyl ether (NPOE) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) were used as plasticizer and carrier, respectively. The aim of this paper is to investigate the influence of the membrane composition and process conditions guaranteeing an effective elimination of Cr(VI) ions by fixation in the polymer inclusion membrane containing D2EHPA as a selective barrier. FTIR, TGA, and SEM were used as characterization techniques for all synthesized membranes. The transport of chromium ions in an aqueous solution was studied using different elaborated polymeric supports.

2. Experimental

2.1. Materials

Cellulose triacetate (CTA) purchased from Fluka and polycaprolactone (PCL) purchased from Solvay Chemicals sector-SBU (Belgium) were used as the basic polymeric matrix. Polyvinylpyrrolidone (PVP K30), polyanetholsulfonic acid (PATSA), and polyethyleneimine (PEI) purchased from Fluka were used as polyelectrolytes to improve the properties of the membranes. 2-Nitrophenyloctyl ether (NPOE) and D2EHPA (obtained from Aldrich) were used as plasticizer and carrier respectively. Chloroform (GC \geq 99%) was purchased from Fluka. Hexavalent chromium solution was prepared using potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) purchased from Merck. All the chemicals were analytical grade. All aqueous solutions were prepared using deionized water.

2.2. Membranes preparation method

Five polymer inclusion membranes (PIMs) were prepared using the same

procedure described by Sugiura [39-41]. In this method, 200 mg of CTA was dissolved in 40 mL of chloroform and stirred for 4 hours. Then, 100 mg of PCL was added to the solutions under stirring for 2 hours. After a homogeneous mixture was obtained, PVP, PATSA, or PEI was introduced in solutions still under stirring for 2 hours. Finally, NPOE or D2EHPA was poured into solutions with continuous stirring for 2 hours. After that, the homogeneous and miscible solution was transported in a glass container, and chloroform was slowly evaporated until obtaining polymeric thin films with a smooth surface. The membranes were abbreviated MB1, MB2 MB3, MB4, and MB5. It is very important to note that all sticky and breakable membranes were eliminated. Only the membranes exhibiting good mechanical strength were selected for this study. The different combinations between the polymers, plasticizer, and carrier used for the preparation of the different membranes are reported in Table 1.

2.3. Characterization techniques

2.3.1. Characterization of the synthesized PIMs by FTIR

FTIR spectroscopy was used to detect the frequency variations of the functional groups [42]. 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 standardized before analysis using 60 scans at a resolution fixed to 2 cm^{-1} in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$.

2.3.2. Characterization of the synthesized PIMs by SEM

SEM was used to determine qualitative characteristics (porosity and homogeneity) and quantitative characteristics such as layer thickness [43]. The morphologies of the different membranes were obtained by SEM analysis using a JEOL JSM 6301FFEG with a voltage of 20 kV.

2.3.3. Characterization of the synthesized PIMs by TGA

Thermogravimetric analysis (TGA) is the best and most consistent technique able to estimate the thermal stability of all constituents. TGA allows observing the effects of thermal decomposition, evaporation, reduction, desorption, sublimation, oxidation, and absorption [44]. TGA analyses were realized using a TGA Q500, TA Instrument, automated from 50 to 600°C at a rate of $10^\circ\text{C}/\text{min}$. All samples were purged with N_2 gas at a flow rate of $60\text{ ml}/\text{min}$.

2.4. Process of water treatment and chromium elimination

The cell used for all experimentations consisted of two compartments, made of Plexiglas with a maximum filling volume of 1000 mL and separated by the synthesized membrane as shown in Figure 1. The feed phase contained the chromium solution at a concentration of 5 ppm of metal salt and the strip phase contained distilled water, hydrochloric acid (HCl , 10^{-2} M), sodium chloride (NaCl , 10^{-2} M), or sodium hydroxide (NaOH 10^{-2} M) as different receiver medium and counter transport forces. The active membrane area was 49 cm^2 . Both the feed and strip phases were moderately stirred using a multi-point magnetic stirrer.

Three different experimentations were realized to determine the chromium concentration. The experimental standard deviation was determined to be $\pm 0,05$.

Table 1
Membranes composition.

	CTA (g)	PCL (g)	PVP (g)	PATSA (g)	PEI (g)	NPOE (mL)	D2EHPA (ml)
MB1	0.2	0.1	0.1	-	-	0.2	-
MB2	0.2	0.1	-	-	0.1	0.2	-
MB3	0.2	0.1	-	0.1	-	0.2	-
MB4	0.2	0.1	0.1	-	-	-	0.2
MB5	0.2	0.1	-	0.1	-	-	0.2

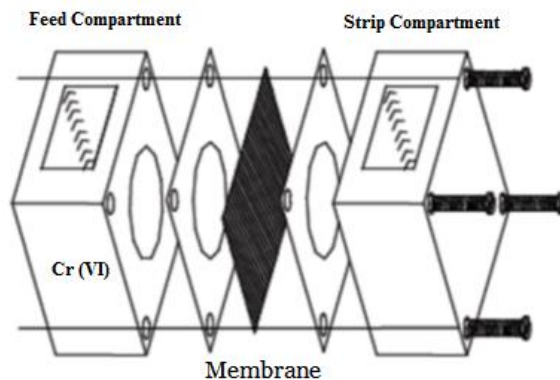


Fig. 1. Transport cell scheme.

2.5. Solutions analysis

The chromium (VI) concentrations in both feed and strip solutions were determined at different time intervals (1 hour) using the atomic absorption spectroscopy method (AAS) with a Perkin-Elmer spectrometer Analyst AA-700 model at 357.9 nm. The concentrations of chromium (VI) retained in the membranes were determined by the calculation of the difference between the concentration transferred to the strip compartment and the concentration remaining in the feed compartment.

3. Results and discussion

3.1. FTIR characterization

Figure 2 shows the FTIR spectra of MB1, MB2, MB3, MB4, and MB5 membranes. The FTIR spectra of all synthesized membranes show two bands at 2930 and 2860 cm^{-1} attributed to elongation vibrations of the asymmetric and symmetric C-H bonds respectively. The presence of CTA and PCL polymers within all membranes is confirmed by the presence of several bands detected at 1725-1750 cm^{-1} and a large band at around 3450 cm^{-1} , characteristic of carbonyl and hydroxyl groups of these two polymers. It was noted that the CTA absorbed at around 1270 and 1040 cm^{-1} characterizing the asymmetric and symmetric elongation vibrations of (C-O-C) groups respectively. A peak at 1583 cm^{-1} related to the acetate groups (COO^-) of CTA can also be detected. The band corresponding to the carbonyl group of PVP in MB1 and MB4 appeared at 1660 cm^{-1} . This peak initially present at 1654 cm^{-1} in the pure component shifted to higher wavenumbers in these two membranes. The FTIR spectra of the membranes MB1, MB2, and MB3 revealed the presence of two bands at 1608 and 1526 cm^{-1} corresponding to the stretching vibrations of C=C and $-\text{NO}_2$ bonds of the plasticizer (NPOE). In contrast, the spectra of the membranes MB4 and MB5 confirmed the presence of D2EHPA by the appearance of bands at 1635, 1212, and 1032 cm^{-1} characterizing the elongation vibrations of HO-P=O, P=O, and P-O-C groups of the carrier D2EHPA. A large peak is also detected at 3433 cm^{-1} related to the hydroxyl groups of this carrier.

Thus, in the light of these results, it was concluded that the different components of the synthesized membranes develop specific interactions such as Van der Waals, electrostatic, and/or hydrogen bonding type [45].

The presence of intermolecular hydrogen bonding interactions in the synthesized polymeric membranes is proved by the perturbation of some characteristic bands principally the shift and the widening of the carbonyl groups band (Figure 3).

Macromolecular complexes are generally formed by hydrogen bonding, electrostatic forces, π -acid to π -base interaction, and van der Waals attractive forces [46,47]. Some interactions between the different components of the synthesized membranes are shown in Figure 4.

3.2. SEM characterization

The microstructure of membrane materials is one of the important characteristics of PIMs, which determines the distribution of the carrier in the polymer matrix. Figure 5 shows the morphology of the different synthesized membranes.

The morphology of the synthesized membranes (surface view) shows that the membranes constituted by different polymers and plasticized by NPOE (MB1, MB2, and MB3) have a dense structure. However, MB4 and MB5 have a heterogeneous and porous structure characterized by micropores with the irregular distribution. This is probably due to the addition of the carrier D2EHPA.

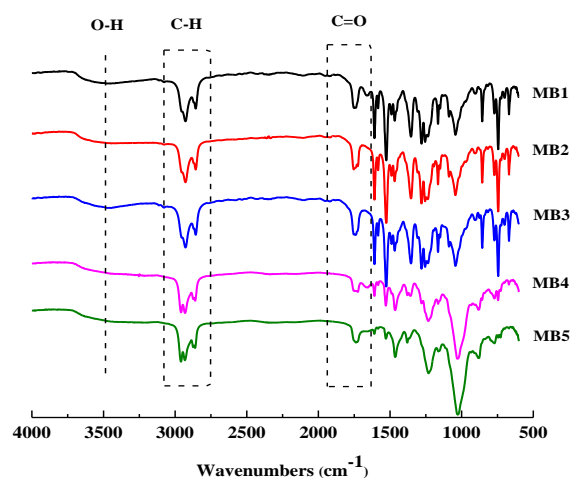
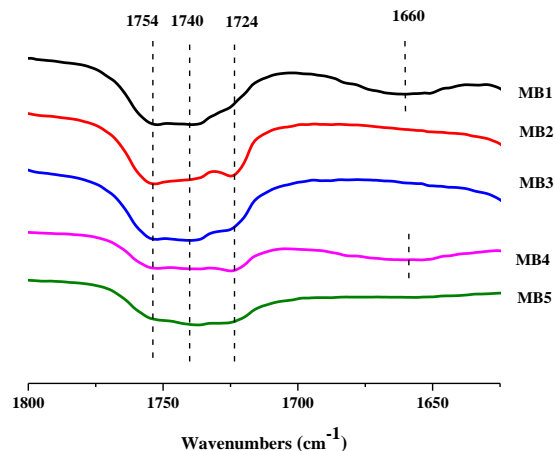


Fig. 2. FTIR Spectra of different synthesized membranes.

Fig. 3. FTIR Spectra of different synthesized membranes in 1800-1600 cm^{-1} region.

CTA-based membranes are known for their high porosity [24] while PCL, PEI, or PATSA membranes are dense [25,26]. The porosity of CTA is due to the rod form of its polymeric chains caused by the gluco-pyranose cycle steric hindrance. In contrast, the polymeric chains of PCL and PATSA are in the form of spherical pellets which suppress the pores and yield dense membranes. In the SEM images of MB4 and MB5 membranes (without plasticizer NPOE), large pores of CTA polymer associated with carrier D2EHPA can be indeed detected. Some pores of CTA/D2EHPA were filled by NPOE, PATSA, and PEI while the others remained empty.

3.3. TGA characterization

Weight loss thermograms TGA and the corresponding derivative d(TGA) curves of the different synthesized membranes (MB1, MB2, MB3, MB4, and MB5) obtained by conventional TGA are shown in Figures 6a,b. As can be seen from Figure 6, all the membranes exhibited thermal stability until 130°C. All synthesized membranes decomposed in two steps. The first step occurs at 150 °C and represents the volatilization of the plasticizer (NPOE) or the carrier (D2EHPA), which have an ebullition temperature of 198°C and 155°C, respectively. The other stages of degradation of the synthesized membranes are attributed to the main thermal degradation of the polymeric chains of CTA, PCL, PVP, PEI, and PATSA. It can be concluded that specific interactions between the different polymers take place [48]. This conclusion confirms the FTIR results.

3.4. Membranes application for Chromium (VI) removal

3.4.1. Effect of membrane composition

Table 2 shows the chromium concentration in the feed compartment, strip compartment, and the concentration in all synthesized membranes.

It can be seen that (CTA+PCL+PVP+D2EHPA) and (CTA+PCL+PATSA+D2EHPA) membranes have a good performance by fixing 24.5 % and 41.6 % of chromium, respectively. This is probably due to the acidic character of D2EHPA used as the carrier in MB4 and MB5 membranes. These results confirm the affinity between D2EHPA and Cr (VI) caused by the presence of the phosphoric acid function. These results are in accordance with the literature [49]. Furthermore, the presence of PATSA containing the sulfonic acid function can promote the fixation of Cr (VI) in the MB5 membrane. Figure 7 shows the chromium (VI) removal efficiency versus time using all synthesized membranes.

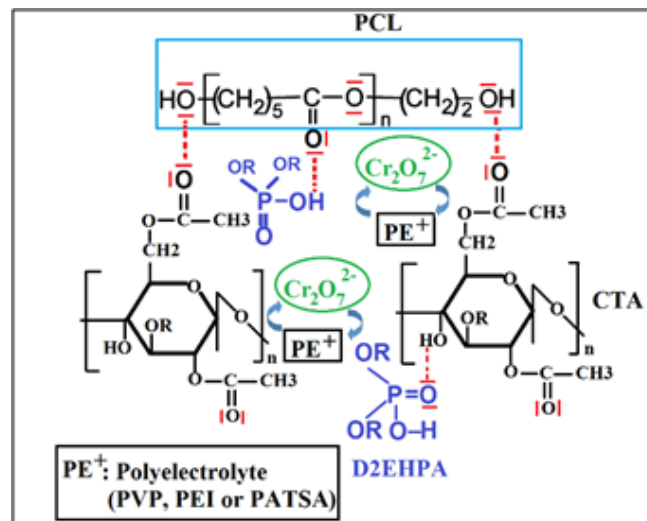


Fig. 4. Schematic representation of the electrostatic interactions and hydrogen bonding formation mechanism.

Table 2

Variation of chromium (VI) concentrations in feed and strip compartments and fixed in the membrane versus the membrane nature. T: 25°C, [Cr (VI)]₀ = 5 mg/L, t=8h.

Membrane	[Cr(VI)] in Feed compartment (mg/L)	[Cr(VI)] in strip compartment (mg/L)	[Cr(VI)] in Membrane (mg/L)
MB1	4.289	0.044	0.667
MB2	4.031	0.077	0.892
MB3	4.169	0.141	0.690
MB4	3.294	0.482	1.224
MB5	2.832	0.089	2.079

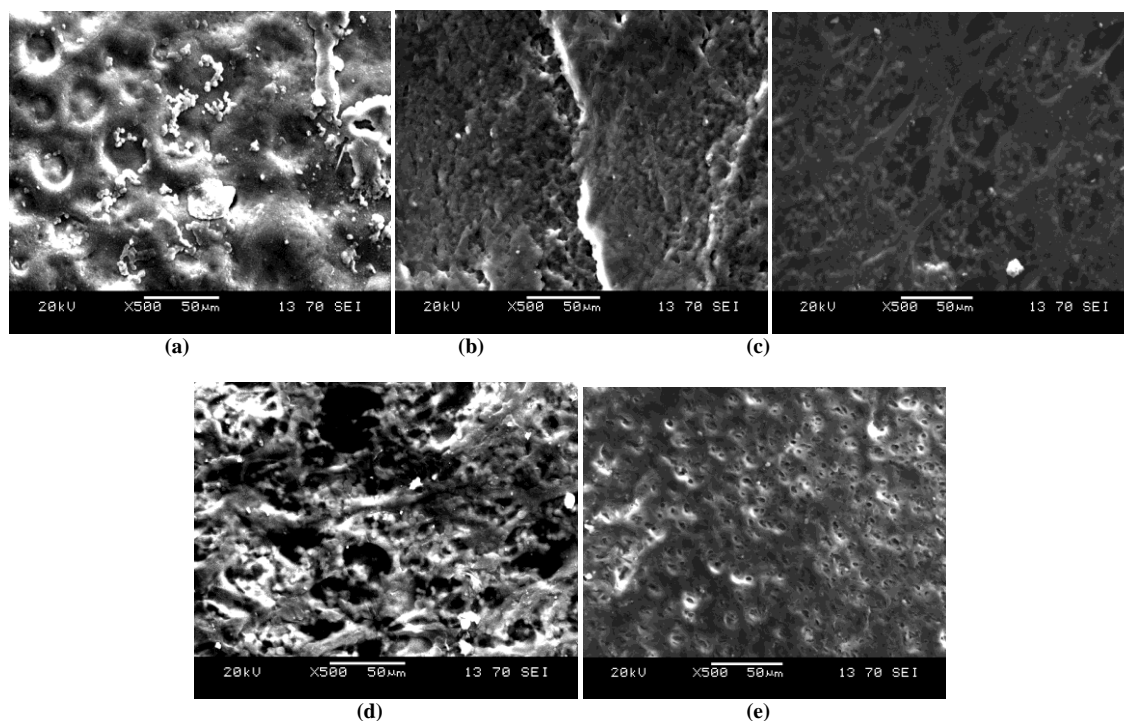


Fig. 5. SEM images of all synthesized membranes. (a): MB1, (b): MB2, (c): MB3, (d): MB4, (e): MB5.

Figure 7 shows that the best Cr (VI) elimination efficiency was achieved after 2 hours of transport using MB2 and MB3 membranes; it was in the order of 40% and 43%, respectively. After that, the number of transferred ions decreased. This phenomenon was observed only in the case of membranes elaborated without D2EHPA. On the other hand, the best removal efficiency was obtained after 8 hours for MB4 and MB5 membranes; it was in the order of 33% and 42%, respectively. It can be concluded that the presence of D2EHPA in the pores of the synthesized membranes promotes the elimination of Cr (VI) when a long time of transport was applied.

It should be noted that the Cr (VI) removal efficiency does not exceed 50%. This is mainly due to the process used, but also to the fact that NPOE and/or D2EHPA which fixes Cr(VI) may not be retained by the membrane in solution causing a decrease in the membrane performance [50-51].

3.4.2. Influence of the strip phase nature

The influence of the receiving medium nature on chromium (VI) removal using the MB5 membrane was studied. Figure 8 shows the chromium (VI) removal efficiency for different mediums using the MB5 membrane.

Figure 8 shows that the best Cr (VI) removal efficiency was obtained after 8 hours of transport, 43% and 29% of Cr (VI) was removed in the presence of H₂O (pH = 6,4) and NaCl (pH = 7) respectively, in the feed compartment. The best results were obtained using MB5 (CTA + PCL + PATSA + D2EHPA) membranes at 6 < pH < 7. This result is comparable with the literature [49]. It suggests that the presence of Cl⁻ (at pH = 2) or OH⁻ (at pH = 12) in the receiving solution slows down the diffusion of Cr(VI) across the PIM. This is probably due to the diffusion of the anions for the same types of receiving solutions. Moreover, these results suggest that the

membrane MB5 is losing its properties over time in contact with acidic conditions. This is possibly due to the Donnan dialysis effect [52]. In fact, the transfer of Cl⁻ and OH⁻ ions from the receiving compartment to the feed compartment causes the transfer of the Cr (VI) ions in the opposite direction.

4. Conclusions

In this work, new polymeric membranes have been synthesized using a mixture of polymers and polyelectrolytes (CTA, PCL, PEI, PATSA, and PVP), plasticizer (2-NPOE), and carrier (D2EHPA). All elaborated membranes were characterized by FTIR, TGA, and SEM techniques. The application of the elaborated membranes for Cr (VI) removal shows that the Cr (VI) elimination efficiency depends on the membrane composition. The best results were obtained using MB5 (CTA + PCL + PATSA + D2EHPA) membranes, it was near 43% at 6 < pH < 7. Furthermore, counter-ion transport is the preferred transport mechanism through the synthesized membranes when different reception phases (ultrapure water, NaCl, NaOH, HCl) are used. It is assumed that the membrane deteriorates and loses its properties due to the hydrolysis of CTA under acidic conditions. Thus, the highest efficiency was obtained when the reception phase was ultrapure water.

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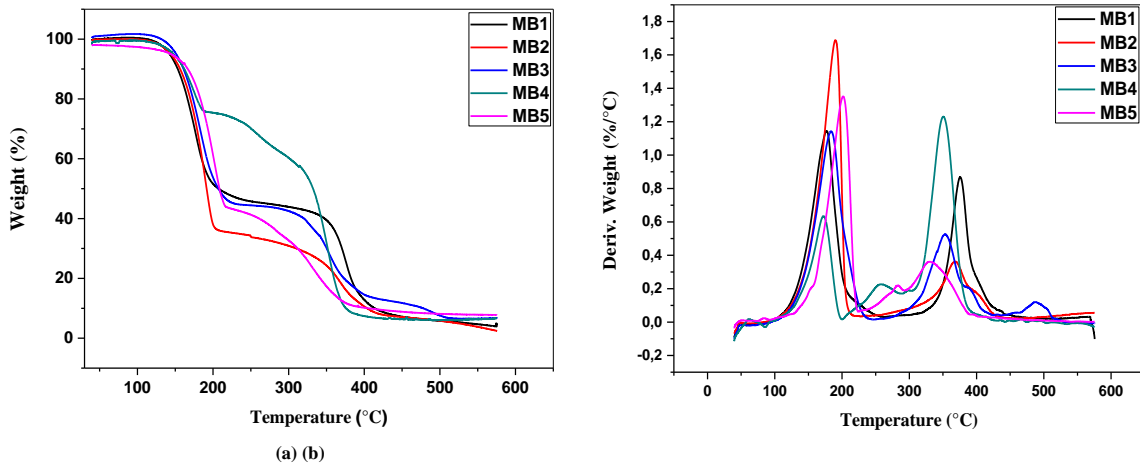


Fig. 6. TGA (a) and dTGA (b) thermogravimetric analysis curves of the different synthesized membranes.

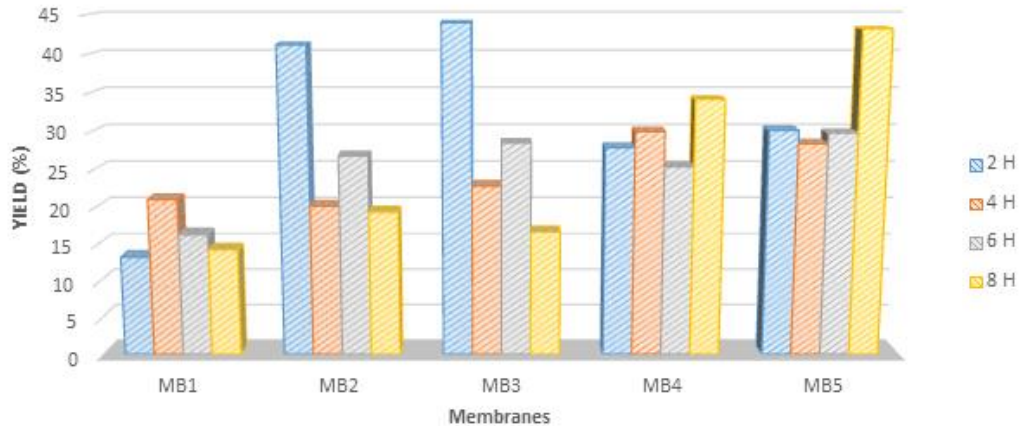


Fig. 7. Chromium (VI) removal efficiency versus time for different membranes. T=298K, [Cr (VI)]₀= 5 mg/L.

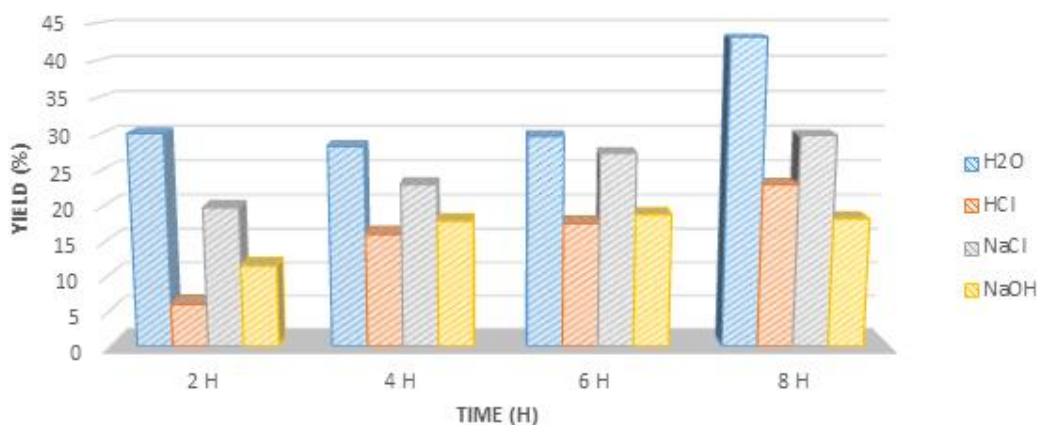


Fig. 8 Chromium (VI) removal efficiency versus time for different medium. $T=298\text{K}$, $[\text{Cr (VI)}]_0 = 5 \text{ mg/L}$.

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