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Metal Ions Removal from Contaminated Water Using Membranes Functionalized with Ionic Liquids

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Abstract: The present work studies the efficiency of new innovative quaternized polysulfone (PSFQ)/ionic liquid (IL) membranes in the treatment process of water containing cadmium ions (Cd(II)). The design and development of the polysulfone membranes with morphology tailored by the use of ILs (Cyphos 101 IL and Aliquat 336) was based on the rheological study of the casting solutions that dictated the optimal compositions of ILs and facilitated the preparation of the membranes for performance tests. Thus, according to the variation of the rheological functions obtained (G' , G''), it was demonstrated that Aliquat 336 has better compatibility with PSFQ, facilitating the workability of the solution and improving the final properties of the membranes relative to Cyphos 101 IL. However, the casting solutions consisting of 5 wt.% Ph-IL and 15 wt.% Am-IL content produce membranes with superior physico-chemical properties. Also, the surface chemistry and morphology analysis of the membranes obtained were investigated in order to understand the relationship between the PSFQ and ILs, as well as their surface properties, as indicators for their future applications. Additionally, the results obtained from the kinetic studies regarding Cd(II) removal from aqueous solutions and the amount of Cd(II) accumulated onto the membranes showed that the ILs enhance the filtration efficiency of the membranes studied and underlined the positive effect of IL in the structure of the quaternized polysulfone membranes. A content of 15 wt.% Aliquat 336 in PSFQ membranes shows the best properties for Cd(II) removal from aqueous solutions; the maximum amount of Cd(II) accumulated on the membrane studied was 3300 mg/m². This behaviour was maintained for two cycles of washing/filtration, and then the efficiency decreased by 20%. The results obtained showed that the membranes functionalized with ionic liquid could be used efficiently in the treatment of water containing trace concentration of cadmium.

Keywords: polysulfone membranes; ionic liquids; rheological parameters; removal degree; water treatment; cadmium removal



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1. Introduction

One of the major concerns of the 21st century is to maintain high standards for the quality of water sources. This desire has become more and more difficult due to the increase in world population and the development of industrial activities. The most widespread and problematic pollutants are heavy metals. They are not biodegradable and have the disadvantage of accumulating in different living organisms [1,2]. In this sense, cadmium is one of the most toxic heavy metals, which can spread in the environment from industry discharges of different processes, namely the manufacturing of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating [3–7].

Additionally, cadmium exists naturally as a minor constituent of base metal ores and coal deposits. According to the World Health Organization (WHO), the allowable limit for

cadmium in drinking water is set at 0.005 mg/L [3]. Ingested above this limit, cadmium causes kidney failure, nervous system damage, and bone damage, as well as other serious diseases [8]. For this reason, the removal of this heavy metal from contaminated water attracts the attention of researchers and has become an extremely important task. Therefore, great efforts have been made over time to develop different methods for the treatment and purification of water containing heavy metal ions. These methods include precipitation, coagulation-flocculation, ion-exchange, electrodialysis, liquid-liquid extraction, etc. Each method has its advantages and disadvantages. The selection of water treatment technology depends on many factors, such as: water composition, destination, knowledge in the field, operational costs, etc. If it is necessary to remove trace amounts of pollutants and to recover the useful elements from the effluents, the membrane separation processes represent a good choice in terms of technical and economic feasibility [2,9,10]. Thus, the applicability of the membrane techniques in the environmental field involves several advantages in terms of low consumption of energy, no requirement of chemical substances to be added, ease of increasing the capacity in a modular system, separation in the continuous mode, possibility to easily join the membrane processes with other unit processes, and separation performed under mild environment conditions [11,12].

The challenge in the membrane separation processes is to develop new materials with a wide range of structures, chemistries, increased selectivity, and stability. In this context, the quaternized polysulfones (PSFQ) represent a new generation of membrane materials with controlled properties (hydrophilicity, antimicrobial properties, higher permeability [13,14]) which improve performance in the water treatment technologies [15,16]. Therefore, the purpose of this paper is to study the efficiency of new innovative polysulfone/ionic liquid membranes in the treatment process of water containing cadmium ions. Compared with the conventional methods of water treatment, such as adsorption, ion exchange, chemical precipitation, and solvent extraction processes, the use of new membranes represents a green, compact, and economical alternative system. Thus, polymer inclusion membranes (PIM), which consist of PSFQ and different ionic liquids (ILs), i.e., Cyphos 101 IL—triethyl (tetradecyl) phosphonium chloride (Ph-IL) and Aliquat 336—methyltrialkylammonium chloride (Am-IL), and that act not only as carriers but also as plasticizers, were developed and studied as a membrane filtration system in the treatment process of cadmium-containing water.

The problem that occurs in the removal of heavy metal ions by membrane filtration is the fact that the dissolved metallic salts have small sizes, so it is necessary to use membranes with very small pore diameters (for example, reverse osmosis). This involves the use of very high pressures, implying an increase in operating costs. To eliminate these disadvantages, it is necessary to complex the metal ions to achieve a much easier retention through a simple ultrafiltration process [7,17]. That was the reason why the quaternized polysulfone was functionalized with different quantities of selected ILs (Am-IL and Ph-IL). Generally, the studied ionic liquids have had very good efficiency in the liquid-liquid extraction of cadmium ions from aqueous solutions [18], but a great quantity of ionic liquid is lost in the aqueous phase, which is a disadvantage of this method. Therefore, the use of PIM membranes avoids these shortcomings and combines the properties of the functionalized polysulfones with those of the ionic liquids [19–23]. The method to obtain the membrane, inclusion, presents the advantage of the ionic liquids bonding in the membrane structure, which avoids the loss of ionic liquid in the aqueous phase. In addition to the fact that they are environmentally, the use of ILs as an extractant in this technique ensures the efficiency and selectivity of the obtained membranes. The main purpose of this work is to highlight the influence of the ionic liquid present in the membrane structure on the removal efficiency of cadmium ions from aqueous solutions. Another goal is to determine if the nature and amount of ionic liquid has an influence on the process of cadmium ions removal.

2. Materials and Methods

The quaternized polysulfone, PSFQ, ($M_n = 28,000$ g/mol) was obtained by the substitution reaction of the chlorine atoms of chloromethylated polysulfone (CMPSF, $M_n = 29,000$ g/mol) with tertiary amines, namely *N,N*-dimethylbutylamine [24]. The detailed procedure of reactions for obtaining PSFQ was presented in previous studies [24,25]. Ionic liquids used in the present study, trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) and methyltrialkylammonium chloride (Aliquat 336), were purchased from Sigma-Aldrich (Germany). The selection of ionic liquids was made based on their strong electrostatic characteristics and solvation forces. In order to obtain membranes with improved performance, only certain contents of ILs were selected, an aspect imposed by the presence of the precipitation phenomenon. This phenomenon, that occurs at a certain mixing ratio and depends on the nature and size of the alkyl chain of the ionic liquid, limits and establishes, at the same time, the range of compatibility (Figures S1 and S2, Supplementary Materials). The polymeric inclusion membranes, PIM, used in the present study were obtained by the solution casting method. This procedure was presented in detail in a previous study [16].

The rheological tests of PSFQ/ILs blends in *N,N*-dimethylformamide (DMF) were performed using a CS50 Bohlin rheometer manufactured by Malvern Instruments (Worcestershire, UK) equipped with cone-plate geometry (cone angle of 4° and diameter of 40 mm). Fourier transform infrared spectroscopy (FTIR, Bruker FTIR Spectrometer (VERTEX 70), Bruker Optics, Ettlingen, Germania) equipped with a DLaTGS detector) and scanning electron microscopy (SEM, Verios G4 UC field-emission scanning electron microscope (ThermoFisher Scientific, Prague, Czech Republic)) coupled with an energy dispersive X-ray detector (EDX) and a Quanta FEG 250 microscope, equipped with an EDAX/ZAF quantifier, were used for microstructural and surface membrane characterization. Also, the obtained membranes were tested in the ultrafiltration (UF) process of water with cadmium content using the system shown in Figure 1, which consists of: feed tank, peristaltic pump, support for the membrane, permeate reservoir, and a vacuum pump. The concentration of Cd(II) ions before and after the membrane filtration process was measured through atomic absorption spectrometry using a Varian Spectra AA 280 FS spectrometer (Agilent Technologies, Santa Clara, CA, USA).

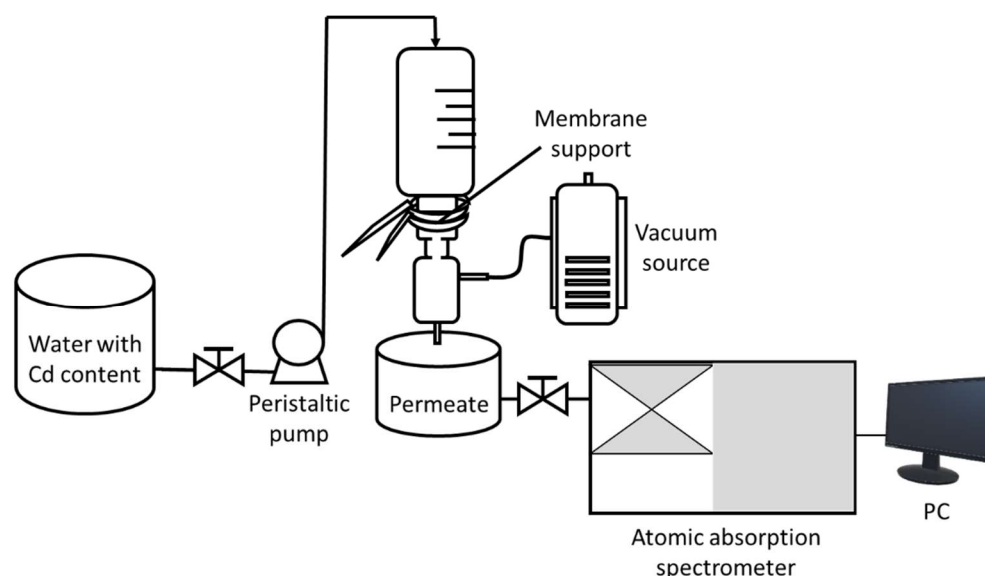


Figure 1. Schematic representation of the ultrafiltration test cell of water with cadmium content.

To evaluate the filtration efficiency of the membranes in the process of Cd(II) ion removal from aqueous solutions, the prepared membranes were initially well washed and cut into the desired size, $d = 1$ cm, and loaded into the UF test cell. The surface area of the

membranes was 0.785 cm². The membranes were used in ultrafiltration experiments using a pressure of 30 mBa. After compaction, the membranes were subjected to pure water flow estimation at a transmembrane pressure of 3 kPa. The flux of pure water was determined using the expression [17,26,27]:

$$J_w = \frac{V}{\Delta t \cdot A} \quad (1)$$

where J_w is the flow of pure water (L/m²h), V is the amount of permeate collected (L), Δt is the collection time (h), and A is the membrane surface (m²).

The water content of the membranes was obtained after soaking in water for 24 h. They were weighed after being previously wiped with filter paper. The wet membranes were placed in an oven at 75 °C for 48 h, then cooled at room temperature in a desiccator for 8 h and weighed again. The percentage of water content was calculated using Equation (2) [26]:

$$WC = \frac{w_1 - w_2}{w_1} 100 \quad (2)$$

where w_1 is the mass of the wet membrane, w_2 is the mass of the dry membrane, and WC is the percentage of water retained by the membrane (%).

The overall porosity (ε) was determined by the gravimetric method as defined in the following equation [28]:

$$\varepsilon = \frac{w_1 - w_2}{A \cdot l \cdot \rho} \quad (3)$$

where w_1 , w_2 , and A are the same as before, ρ is the density of water (0.998 g/cm³), and l is the membrane thickness (m).

To evaluate the filtration efficiency in removing cadmium ions from the feed solution, the degree of rejection defined by equation 4 [17,26] was used:

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) 100 \quad (4)$$

where C_p and C_f are the Cd(II) ion concentrations in the permeate and feed solution, respectively.

The amount of Cd(II) accumulated in the membrane was determined using the following equation:

$$Q_{ac} = \sum \frac{(C_f - C_p)V}{A} \quad (5)$$

where C_f , C_p , and A are the same as before, and V is the volume of the solution passed over the membrane (L).

The removal degree of Cd(II) ions, respectively the amount of Cd(II) accumulated in the membrane were determined as a function of time and as a function of the permeate volume. A volume of 100 mL of aqueous solution containing 10 mg/L Cd(II) was used. Samples were collected every 5 min using a feed solution flow rate of 2 mL/min. The concentration of 10 mg/L Cd was chosen because classical treatment methods used to treat industrial wastewater, such as precipitation, fail in most cases to reach a residual concentration below 10 mg/L, even if they develop yields of over 90% [5,29]. Thus, this treatment technique is an advanced method that claims to be used for the treatment of water with trace concentrations of Cd, a content which could nevertheless have negative effects on the environment.

3. Results and Discussion

3.1. Rheological Parameters: Impact of ILs on Viscoelastic Behaviour

To induce a surface model with improved characteristics and increased efficiency in the ultrafiltration processes, the preliminary study of the casting solutions has an important role in defining the properties of the final product and, consequently, the surface properties of the membranes. In this context, rheological functions such as storage (G') and loss (G'')

moduli are parameters that, aside from dynamic viscosity and flow activation energy [16], are involved in the polymer solution processing by informing on physical and structural changes. Thus, the storage modulus (G') is correlated with the elasticity or energy stored in the material during deformation, while loss modulus (G'') offers information concerning the viscous character or dissipated energy into the environment.

Based on these findings, it is necessary to study the solution dynamics of the quaternized polysulfone/ionic liquids blends to obtain an overview of the many processes underlying the generation of membranes with the specific properties required for their application in water treatment processes. In this sense, the viscoelastic properties of the studied PSFQ/ILs blends, evidenced by the dependence of storage (G') and loss (G'') moduli on the frequency, provide information on the dynamics and architecture of macromolecular chains, as well as on the impact of ionic liquids addition (Aliquat 336—Am-IL and/or Cyphos 101 IL—Ph-IL) to PSFQ solutions (Figures 2 and 3).

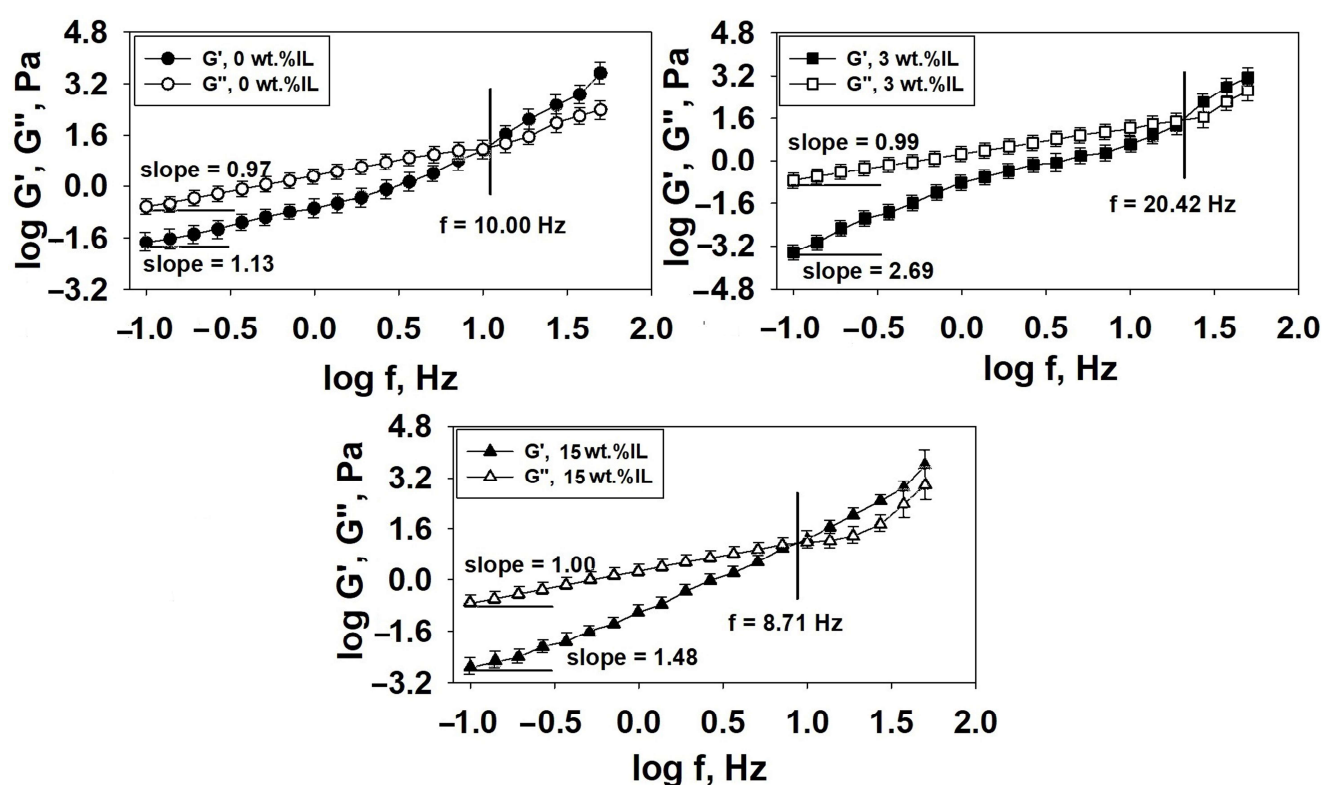


Figure 2. Logarithmic plot of storage (G') and loss (G'') moduli versus frequency for the PSFQ/Am-IL 336 blend at different compositions.

As can be observed, the curves obtained for PSFQ/ILs blends at different compositions of ILs show that in the range of low frequencies, $G' < G''$, which means that a viscous behaviour prevails, while at high frequencies, the response is mostly elastic ($G' > G''$). The G' and G'' curves indicate a characteristic behaviour typical of a viscous liquid, which could be related to the polymer's topological entanglements and association phenomena exhibited in studied systems [30]. Furthermore, G' and G'' obey a power law of $G' \cong G'' \sim f^x$ form, where x represents the slope values of the two moduli. For PSFQ/ILs blends in different mixing ratios, the x exponent is higher for G' than for G'' , indicating a viscoelastic behaviour. An exception occurs in the case of the PSFQ/Ph-IL blend with 15 wt.% concentration of ionic liquid, where the value of x for G' decreases compared to that of G'' , a behaviour generated by the interactions or entanglements/association among the molecules [31,32]. Therefore, the variation in the slope values as the content of IL changes suggests that structural transformations occur in the polysulfonic solutions.

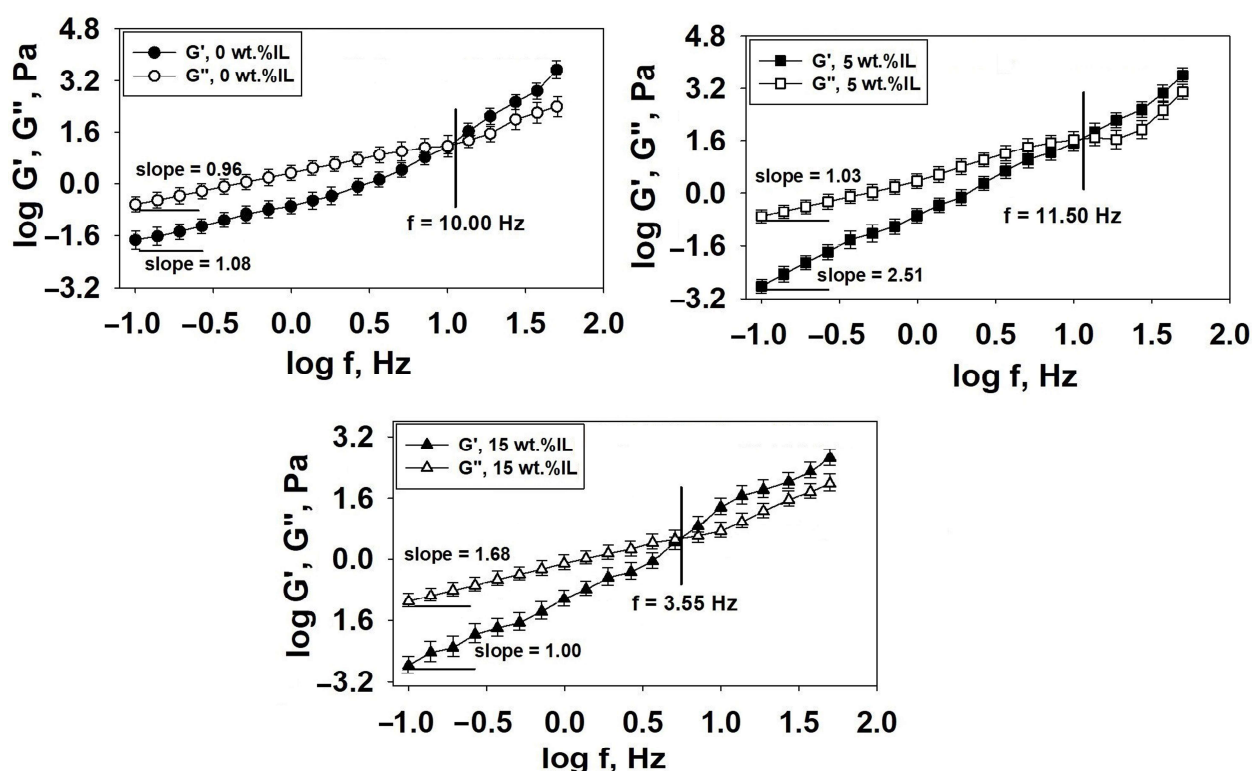


Figure 3. Logarithmic plots of storage (G') and loss (G'') moduli versus frequency for the PSFQ/Ph-IL blend at different compositions.

This aspect is much better reflected in the overlap frequency values that delimit the viscous flow from the elastic one. The crossover point, which corresponds to $G' = G''$, varies depending on the IL content of the system. Thus, this transition from the viscous to the elastic state occurs sooner or later as the systems are enriched in alkyl groups. As can be seen in Figures 2 and 3, a low content of ionic liquid, regardless of its nature (Ph-IL or Am-IL), makes the transition from viscous to elastic to occur at a higher frequency, while a high content of IL makes it occur at a lower frequency. This happens as a consequence of the combination of effects generated by the different alkyl chain lengths of the two ILs and their cationic and anionic nature- that affect the distribution of the ionic liquid molecules and their interactions with the quaternized polysulfone chain. In other words, as the content of Am-IL increases, the PSFQ-based systems are characterized by reduced entanglement density and an enhanced number of oriented segments. In agreement with previous data [16], the higher orientation of the PSFQ chains in the presence of Am-IL represents the major cause of the pseudoplastic behaviour [33,34]. This feature, obtained by the investigation of flow curves [16], evidenced a non-Newtonian behaviour (shear thickening behaviour for compositions varying between 3 and 15 wt.% Am-IL), which occurs under the action of shearing associations or granules packages which are mobile in the liquid phase.

Instead, for high compositions of Ph-IL with longer alkyl chains relative to Am-IL, the obtained viscoelastic parameters were associated with a disruption in the interactive forces of ionic liquid [35]. Therefore, based on the data obtained, we can state that the polysulfonic system containing Am-IL shows a better compatibility with PSFQ and acts as plasticizer, leading to an increase in the workability and improving the system elasticity regardless of its composition. On the other hand, the results also confirm the applicability of polysulfonic systems with low contents of Ph-IL (i.e., 5 wt.%) to obtain membranes with superior physico-chemical properties (improved morphology, mechanical and thermal stability) that could be successfully used in water treatment technology, unlike those with a high ionic liquid content. Consequently, the results allow us to claim that the structural

properties of PSFQ (e.g., the charge density and the size of polycation) and the ionic liquids used significantly influence rheological parameters, which have a major role in choosing the optimal compositions suitable for future investigations. Thus, we affirm that successful application of a polymeric material in any field, such as the environmental field, is determined by its bulk and surface properties, and is also mediated by the combination of the solution and surface specific characteristics that are required for specific applications.

3.2. Surface Chemistry and Morphological Analysis

The presence of ionic groups from the chemical structure of the functionalized polysulfone, through their size and nature, as well as the hydrophobicity, polarity, and length of the alkyl chain of the selected ILs, affects the solution properties of the mixtures (see Figures S1 and S2 from Supplementary Materials, and also Figures 2 and 3). As has already been shown in the rheological analysis, the nature of the used ionic liquids generates differences in PIM membranes as a result of the orientation of the PSFQ and IL functional groups during the solution processing. This tendency to change the membrane structure by addition of ionic liquids as plasticizers to the polysulfone matrix was evaluated by comparison of FTIR spectra recorded from PSFQ and PSFQ/IL blends membranes (Figure 4). Thus, it was possible to demonstrate the way in which the used ILs are distributed among the PSFQ chains and modify the strength of some bonds between the atoms of the host polymer.

Upon analysis of the FTIR spectra, the characteristic bands of pure PSFQ were found (Figure 4a), confirming the PSFQ structure [15]: the absorption bands around $2990\text{--}2940\text{ cm}^{-1}$ and $2894\text{--}2850\text{ cm}^{-1}$, attributed to vibrations of the aliphatic units —CH₃ and —CH₂; the bands from the $1590\text{--}1480\text{ cm}^{-1}$ domain specific to the aromatic structure; the bands at 1300 and 1240 cm^{-1} , characteristic of the asymmetric stretching of —SO₂; those corresponding to the symmetric stretching of —SO₂ around 1150 cm^{-1} ; and the absorption band around 1670 cm^{-1} . In the PSFQ/Ph-IL blend (Figure 4b), we found more pronounced bands around 1488 , 1099 , and 1006 cm^{-1} , corresponding to P—C stretching, and at 727 cm^{-1} , for C—H and P—C deformation out of the plane. Instead, in the FTIR spectrum of the PSFQ/Am-IL blend (Figure 4c), the peak at 1465 cm^{-1} is characteristic of the quaternary amine (CH₃) — N⁺; the one at approximately 1238 cm^{-1} corresponds to the C—N stretching vibration; and the one at 1377 cm^{-1} corresponds to the C—H deformation vibration. In addition, the broad absorption band at 3411 cm^{-1} may be caused by the stretching vibration of the —OH of water, soluble in Aliquat 336 [36]. Therefore, the FTIR results show the way in which the ILs are stabilized in the membrane structure and confirm their role in the process of PIM formation. In addition, the differences observed in the surface chemistry analysis, in agreement with the study in solution, can be attributed to the ionic liquid's nature.

More information concerning the importance of the presence of the ILs in the PIM structure was obtained by SEM microscopy (Figure 5). Also, the results mentioned above were sustained by the analysis of the chemical structure and the identification of all elements characteristic of PSFQ and the studied ionic liquids from the EDX spectra (Figure 5). Thus, the morphology of the PSFQ membrane (P0) and of the PIMs functionalized with the ionic liquids studied, PIM-Am 15 wt.% and PIM-Ph 5 wt.%, can be seen on the SEM images obtained at two different magnitudes (500 and $2000\times$) shown in Figure 5.

The PSFQ membrane (P0) has a smooth, compact, and uniform surface, free of porosities. The use of ionic liquids to obtain PIMs has a substantial impact on the surface morphology. When using Ph-IL, the membrane looks like a fibrous network and the pores appear as branched “veins”. When Am-IL is used, the surface of the membrane is much more porous, and it presents a uniform porosity over the entire surface in the form of spheres. Therefore, we can conclude that these blends represent the optimal compositions for which the distribution of ILs among the polysulfonic chains is appropriate, suggesting a perfect match in the membrane structure.

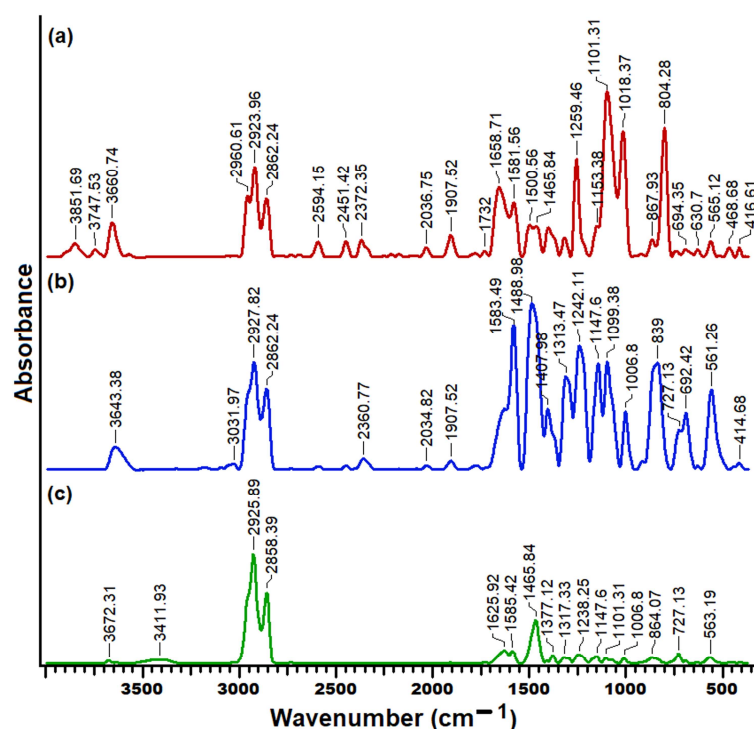


Figure 4. FTIR spectra recorded from membranes obtained from casting solutions: (a) PSFQ (P0), (b) PSFQ/Cyphos 101 IL (PIM-Ph 5 wt.%), and (c) PSFQ/Aliquat 336 (PIM-Am 15 wt.%).

3.3. Evaluation of the Membranes Performance: Removal of Cd(II) Ions from Aqueous Solutions

As observed in the SEM and FTIR analysis, the functionalization of membranes with the ionic liquids studied changes their morphology and consequently the performance in the filtration process. To evaluate the filtration efficiency of the membranes in the process of Cd(II) ions removal from aqueous solutions, the PIMs obtained were characterized in terms of the pure water flux, the water content of the membranes, and the overall porosity. The characteristics of the membranes studied are presented in Table 1.

Pure water flux, percentage of water content, and overall porosity increase with increasing IL content in the membrane. Higher values of the parameters studied were obtained when using methyl trialkyl ammonium chloride (Aliquat 336) compared to membranes functionalized with trihexyltetradecyl phosphonium chloride (Chyphos 101 IL). Based on the characteristics of the membranes studied, it is assumed that the membrane that will develop the best filtration efficiency will be PIM-Am-15 wt.%. The studied membranes presented a higher water flux than other studied membranes in the literature, such as: bleached and unbleached RSNF membranes (150 and 600 $\text{L}/\text{m}^2\text{h}$, respectively) [37], PES UF membrane (1643 $\text{L}/\text{m}^2\text{h}$) [38], and PEG-Ag functionalized with PANCMACDAMN (poly (acrylonitrile co maleic acid co di-amino maleio-nitrile) (1050.2 $\text{L}/\text{m}^2\text{h}$) [39]. Once again, this underlines the benefit brought by ionic liquids through their incorporation into the membrane structure.

The experimental data regarding the dependence of the removal degree and the amount of Cd(II) accumulated onto the membranes studied as a function of the treatment time and the permeate volume are presented in Figure 6. For all the membranes studied, as the time and permeate volume increase, the removal degree of Cd(II) ions decreases but the accumulated amount increases.

In the case of the P0 membrane, the decrease in the removal degree of Cd(II) ions with increasing treatment time is almost linear. In the case of the PIMs functionalized with the ionic liquids studied, there is a decrease in the first 30 min of treatment and then the efficiency remains constant. This initial decrease in efficiency is attributed to an increase in membrane resistance and a lesser chance for Cd(II) ions to bind to the functional group of

the membrane [7]. The advantage of the porous membranes obtained is that they combine adsorption, extraction, and stripping in one step.

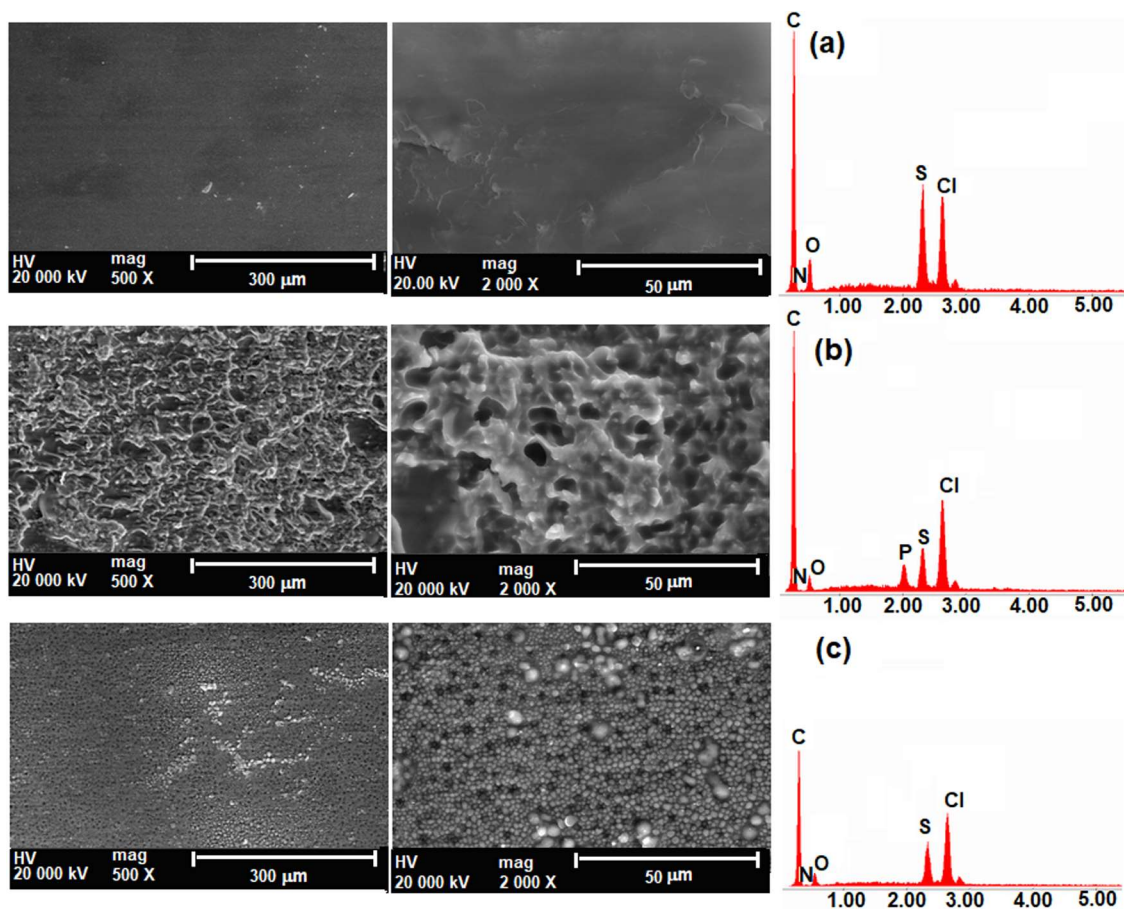


Figure 5. SEM images and EDX spectra of the membranes studied: (a) P0, (b) PIM-Ph 5 wt.%, and (c) PIM-Am 15 wt.%.

Table 1. Characteristics of the membranes studied.

Membrane Code	ILs Studied	IL, wt. %	Jw, L/m ² h	w ₁ , g	w ₂ , g	WC, %	ε, %
P0	-	-	1529	0.0232	0.0308	24.7	2.43
PIM-Ph-3	Cyphos 101 IL	3	1592	0.0228	0.0319	28.5	2.90
PIM-Ph-5		5	1698	0.0245	0.0615	60.2	11.8
PIM-Am-3		3	1663	0.0288	0.0492	41.5	6.51
PIM-Am-5	Aliquat 336	5	1779	0.0242	0.0636	61.9	12.6
PIM-Am-10		10	1819	0.0251	0.0689	63.6	13.9
PIM-Am-15		15	1930	0.0254	0.0760	66.5	16.2

The kinetics of cadmium ion removal by the membranes studied was described by the first order kinetic model presented in equation 6 [40–42]:

$$\ln\left(\frac{C_f - C_p}{C_p}\right) = -kt \quad (6)$$

where k is the speed constant (min^{−1}) and t is the time of treatment (min).

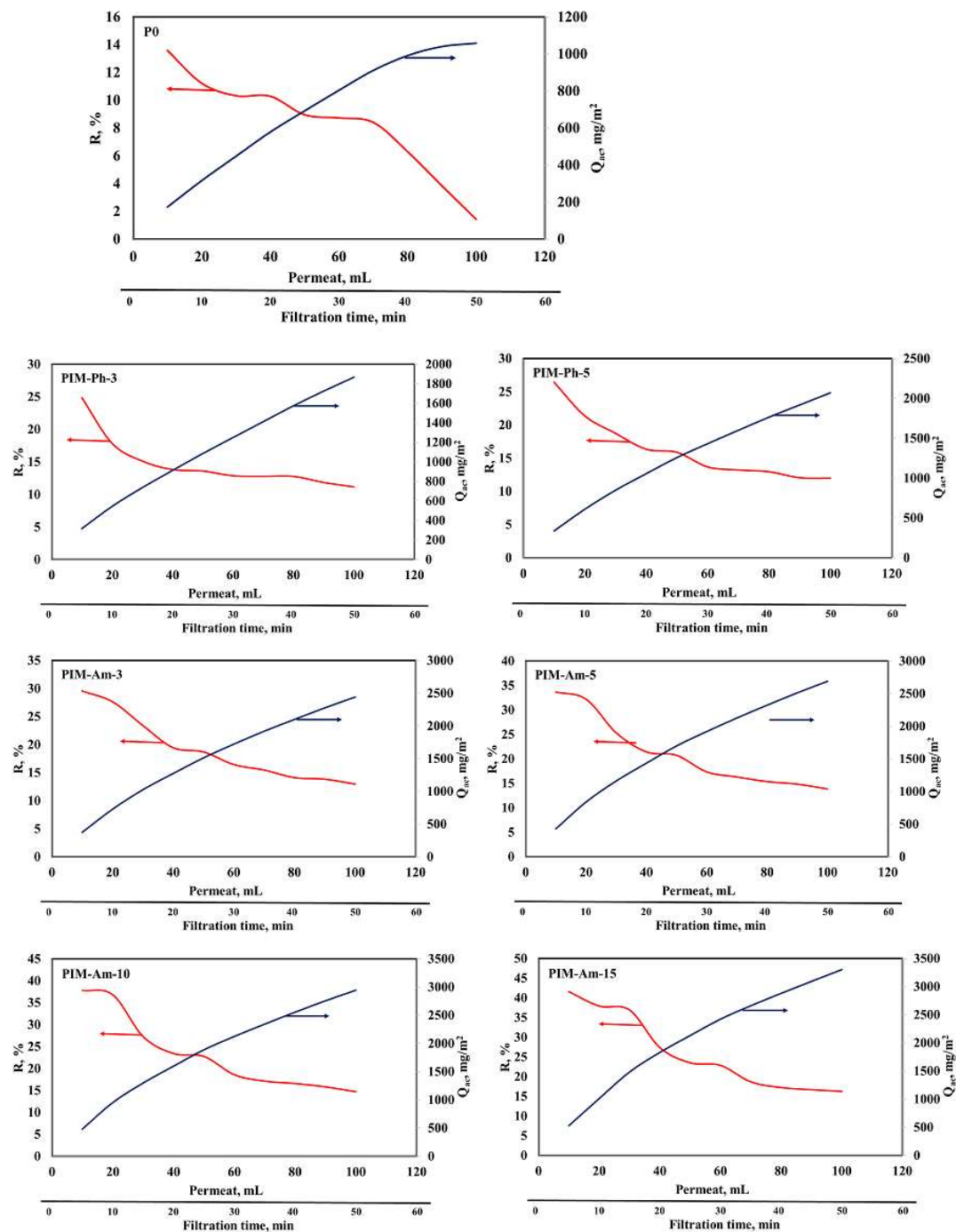


Figure 6. Dependence of the removal degree (red lines) and the amount of Cd(II) accumulated in the membrane (blue lines) as a function of the treatment time and the permeate volume.

The linear dependency of $\ln(C_f - C_p)$ versus time, for all the studied membranes, is presented in Figure 7, which allowed the determination of the rate constant of the cadmium removal process from the slope. Table 2 presents the values obtained for k and for the correlation coefficients.

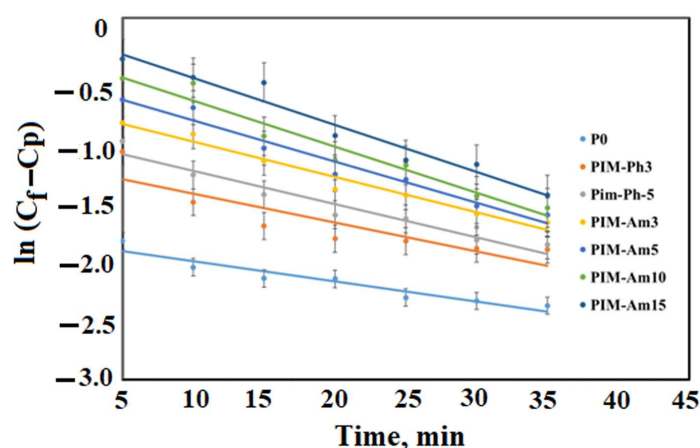


Figure 7. Kinetics of Cd removal through filtration onto the membranes studied.

Table 2. The rate constant of cadmium removal for the studied membranes.

Membrane Code	k, min^{-1}	R^2
P0	0.0167	0.9132
PIM-Ph-3	0.0261	0.8991
PIM-Ph-5	0.0276	0.9453
PIM-Am-3	0.0292	0.9701
PIM-Am-5	0.0342	0.9818
PIM-Am-10	0.0382	0.9915
PIM-Am-15	0.0390	0.9815

The data in Table 2 are presented only for the linear range until 35 min of function. After this time, the P0 membrane and the membranes functionalized with Ph-IL do not present linearity due to membrane clogging. Instead, the correlation between $\ln(C_f - C_p)$ and time was linear for the membranes based on Am-IL, which was confirmed by the high values obtained for the correlation coefficient (R^2) ranging from 0.9741 to 0.9905. The apparent rate constant of Cd removal through filtration onto the membranes studied increases with increasing ionic liquid content in the structure of the membranes studied. These results suggest a more rapid retention of cadmium ions, underlining the positive effect of the ionic liquid present in the membrane structure for the filtration process of Cd ions.

Comparing the maximum amount of Cd(II) accumulated onto the studied membrane (Figure 8), it is observed that it increases with the increase of IL content in the membrane. Membranes based on Am-IL show a higher filtration efficiency compared to membranes based on Ph-IL. These results are in accordance with the conclusions raised from the material characterization step and from the kinetic studies.

The better performance of the membranes based on Am-IL could be explained by the formation of more stable complexes between Cd ions and the quaternary ammonium functional group compared with the interactions between Cd ions and the phosphonium functional group. The interaction between Cd ions and the quaternary ammonium functional group leads to the formation of more stable and hydrophobic complexes, which increase the accumulation of cadmium ions on the membrane surface, therefore enhancing the filtration efficiency [43–46].

The membrane with the most efficient removal degree of Cd ions from aqueous solutions was used at different volume flows of the feed. The results are presented in Figure 9. It was observed that by applying a lesser flow and longer time of contact between the feed solutions with Cd content and the membrane, a higher removal degree of Cd ions from aqueous solutions is obtained. At each volume flow, the removal degree of Cd ions decreases with increasing filtration time. The use of a flow rate of 0.5 mL/min leads to an

increase in the removal degree, but in this case it is necessary to use the filtering equipment for a long time and to treat a much smaller volume of water. This is not economically advantageous. Decreasing the flow rate from 2 mL/min to 1 mL/min does not lead to a significant improvement of the removal efficiency. Therefore, the optimum flow rate was considered to be 2 mL/min.

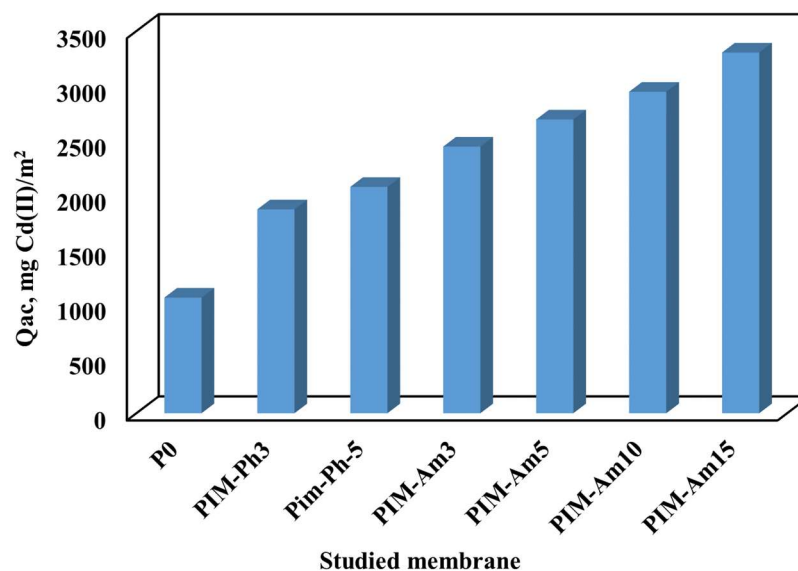


Figure 8. The filtration efficiency of the membranes studied in the treatment process of water with Cd(II) ion content.

The PIM-Am15 was backwashed with distilled water using a higher pressure and used for three filtration/washing cycles. The maximum amount of Cd(II) accumulated on the membrane at different washing/filtration cycles is shown in Figure 10. It was observed that for the first two cycles, the efficiency is almost the same. In the third cycle, the efficiency decreases by 20%, probably due to inadequate removal of Cd(II) ions during the washing step.

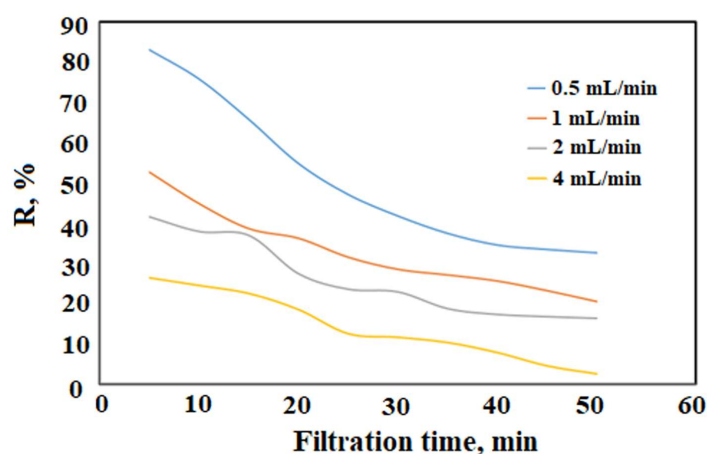


Figure 9. The filtration efficiency of the PIM-Am15 in the treatment process of water with Cd(II) ion content at different volume flows.

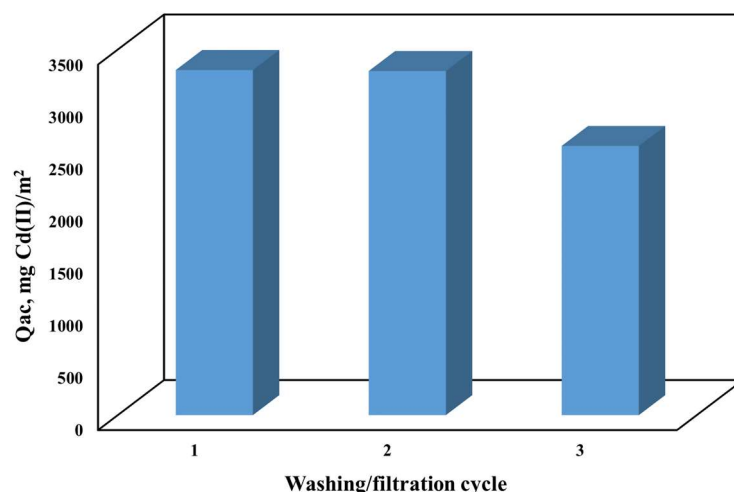


Figure 10. The filtration efficiency of the PIM-Am15 in the treatment process of water with Cd(II) ion content at different washing/filtration cycles.

4. Conclusions

The present paper, through the analyses undertaken, indicates a way to improve the membrane's technological processes, in terms of efficiency and selectivity in filtration/separation, by using ionic liquids (Cyphos IL 101—Ph-IL and Aliquat 336—Am-IL) to obtain more environmentally friendly polysulfone membranes. In this context, the membranes obtained by processing the PSFQ/ILs solutions (in various mixing ratios) were tested to analyse their surface properties and performance for their subsequent application in the metal's removal, in particular of cadmium ions from aqueous solutions. The results obtained from the tests in solution and solid state have confirmed the compatibility of PSFQ with the selected ionic liquids and indicated their good integration/stabilization in the structure of polysulfonic PIMs. Moreover, the surface characteristics of the studied membranes have confirmed the important role played by the ILs in the processing of the solution, in the structure of PIMs, and consequently in the filtration efficiency of water with cadmium content. In this context, it was observed that the membranes based on Am-IL had a better filtration efficiency in the removal process of cadmium ions from aqueous solutions compared with the membranes based on Ph-IL. The apparent speed constant of Cd removal through filtration and the amount of Cd accumulated onto the membrane studied increased with an increase in the ionic liquid content in the membranes studied, underlining the positive effect of the ionic liquid present in the membrane structure upon the filtration process of Cd ions. All these characteristics have an impact on their performance, and for this reason, these membranes can be considered potential candidates for efficient use in the water treatment process.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14244105/s1>, Figure S1: Solutions of quaternized polysulfone (PSFQ) with Aliquat 336 ionic liquid (ILQ) in different mixing ratios of 25 g/dL concentration: 0 wt.% content of Aliquat 336 (PSFQ), 3 wt.% content of Aliquat 336 (PSFQ/ILQ1), 5 wt.% content of Aliquat 336 (PSFQ/ILQ2), 10 wt.% content of Aliquat 336 (PSFQ/ILQ3), 15 wt.% content of Aliquat 336 (PSFQ/ILQ4), 20 wt.% content of Aliquat 336 (PSFQ/ILQ5), 25 wt.% content of Aliquat 336 (PSFQ/ILQ6). Visualization of the compatibility limit for the studied systems (3 wt.% content of Aliquat 336 (PSFQ/ILQ1) compared with 25 wt.% content of Aliquat 336 (PSFQ/ILQ6)); Figure S2: Solutions of quaternized polysulfone (PSFQ) with Cyphos IL 101 ionic liquid (ILP) in different mixing ratios of 25 g/dL concentration: 0 wt.% content of Cyphos IL 101 (PSFQ), 3 wt.% content of Cyphos IL 101 (PSFQ/ILP1), 5 wt.% content of Cyphos IL 101 (PSFQ/ILP2), 10 wt.% content of Cyphos IL 101 (PSFQ/ILP3), 15 wt.% content of Cyphos IL 101 (PSFQ/ILP4), 20 wt.% content of Cyphos IL 101 (PSFQ/ILP5). Visualization of the compatibility limit for the studied system (20 wt.% content of Cyphos IL 101 (PSFQ/ILQ5)).

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