

Research Article

Polyurethane-Keratin Membranes: Structural Changes by Isocyanate and pH, and the Repercussion on Cr(VI) Removal

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Keratin has the capacity to interact with metal ions. In order to take advantage of this potential, a novel membrane with polyurethane and keratin has been developed and studied for removal of Cr(VI) from aqueous solution. Physicochemical and morphological properties of these hybrid membranes were studied, varying synthesis parameters such as the type of isocyanate and pH in keratin solution. The effects of using diphenyl-methane-diisocyanate or toluene-diisocyanate and modifying the pH in keratin solutions were evaluated by scanning electron microscopy, Fourier transform infrared spectroscopy, and dynamical mechanical analysis. Results show that pH has a strong influence on morphology and on Cr(VI) removal efficiency. When pH in keratin solution is low (2.5), the protein separates from water, and a more closed cell in the membrane is obtained affecting its mechanical properties. The removal efficiency of Cr(VI) was also assessed at different pH values of chromium solutions. These results show that when pH of the Cr solution is acidic (at 1.5), the Cr(VI) removal percentages increase significantly, reaching up to a 58%. Thus this paper demonstrates the successful combination of synthetic and natural polymers depending on the process parameters to be applied in the critical purpose of remediation of Cr(VI) contamination.

1. Introduction

Polymeric membranes to remove high toxic contaminants have attracted highly the attention of a large sector of scientific community, since innovative materials with more potential are needed due to the increasing in pollution problems. New materials to remove pollution comprise polymer inclusion membranes and activated composites membranes, which have been developed using different active agents supported by diverse polymers as substrate. Thus, synthetic ion carriers such as tri-*n*-octylamine,

dibenzo-21-crown-7, tertbutyl-dibenzo-21-crown-7 [1], methyltricaprylammonium chloride [2], and among others have been studied to remove anionic or cationic metal species. In spite of the successful results with this kind of membranes, other efforts including more ecofriendly materials must be developed. In this sense, natural materials have attracted also great attention as biosorbents due to their low cost and important efficiency as metallic ions receptors [3–5].

Recently, keratin from chicken feathers has been proposed as biosorbent, considering that it has abundant amino acid groups that have demonstrated good potential to attract

heavy metals [4, 6]. However, one limitation concerning the use of biosorbents is their handling; this is particularly true for feather keratin fibers, since one of their most important features is their low density [7–9]. Due to this inconvenience, new materials have been studied in order to improve the ability to support and obtain special physical characteristics that could give high interaction with pollutants, durability, and resistance to water flow [10–12]. Our research group has developed new polyurethane-keratin membranes with the aim of taking advantage of the natural affinity of keratin towards metals with the adequate porous support to act as membrane during separation processes [6, 7].

Polyurethane (PU) has been chosen due to the chemical compatible groups with keratin, because it is very important that the biosorbent could be strongly attached to the substrate and has the capacity to capture metal ions from the wastewater flow. In addition, different systems have used successfully polyurethane as membrane matrix or support foam [13–16].

Thus, in this work, we use keratin solutions extracted from chicken feathers as suitable biosorbents to remove Cr(VI); PU foams were synthesized with two types of isocyanates: diphenyl-methane-diisocyanate (MDI) and toluene-diisocyanate (TDI), which were mixed separately with polyol and keratin in order to study their effect on the membrane microstructure. The influence of pH is also evaluated, since it is one of the most important parameters as ionic charges on the biosorbent surface, responsible for metal ion attachment [7, 17, 18]. Besides, the isoelectric point of keratin (pH 4.0) [19] plays an important role, since water and amino hydrolysis depend on pH value, and isocyanates are very sensitive to their presence.

Chromium (VI) was chosen to be removed from water with these novel PU-keratin membranes due to the contaminant problems caused by this. Chromium is one of the most abundant hazardous metals on earth. As for Cr(VI), it is highly toxic and represents a threat for living organisms because it is a strong oxidant and soluble at all pH values. The ionic species of Cr(VI) depends strongly on the pH. When pH is from 1.0 to 6.0, $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- coexist in equilibrium; if pH is higher than 8.0, CrO_4^{2-} is the predominant species. Different kinds of membranes have been probed to separate Cr(VI) from water; for instance, Alguacil et al. studied the transport of Cr(VI) from hydrochloric acid medium by pseudoemulsion membrane strip dispersion using a phosphonium salt as ionophore; with this system, a 95% extraction was obtained and by using NaOH solution, the system reaches 60% of removal [20]. Similar results removing Cr(VI) from hydrochloric acid aqueous solutions were reported using polymer inclusion membranes based on organic solvents: cellulose triacetate as the support, tri-n-octylamine as the ionic carrier, and o-nitrophenyl pentyl ether as plasticizer [21]. Alpaydin et al. studied the transport of Cr(VI) from aqueous solution by a bulk liquid membrane using p-tert-butylcalix[4]arene 3-diethylaminopropyl diamide derivative as a carrier; they observed the highest transport efficiency (around 96%) at pH 2.0 in the donor phase and at pH 5.0 in the acceptor phase [22]. These membranes reach high efficiency, but are completely based in synthetic supports and carriers. Efforts in using biosorbents

to remove Cr(VI) were reported by several authors [17, 23–25], identifying as a key factor the pH of chromium solutions. This fact is an important parameter that has not been studied in the PU-keratin system. Thus, this paper is focused on both, the adsorption of Cr(VI) at different pH values and the improvement of the characteristics of new PU-keratin membranes through modification of their processing conditions, taking into account the behavior caused by keratin's isoelectric point.

2. Experimental

2.1. Materials. Keratin biofibers from chicken feathers were kindly supplied by Walter Schmidt and were obtained according to a patented process by Schmidt (US 5750030). Toluene diisocyanate (TDI) was provided by Poliformas Plásticas (Mexico), whereas diphenylmethane-diisocyanate (MDI) and polyol were purchased from Polioles (Mexico). Dehydrated (ethylenedinitrile) tetraacetic acid disodium salt (EDTA) was acquired from J. T. Baker. Urea, 2-mercaptoethanol, tris (hydroxymethyl) aminomethane (Tris), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and 1,5-diphenylcarbazide were purchased from Sigma-Aldrich. All substances were of analytical grade. The dialysis membrane (Spectra/Por MWCO6-8000) was purchased from Cole Palmer.

2.2. Preparation of Keratin. In order to prepare membranes, keratin was used as solution, which was obtained by dissolving chicken feather biofibers according to the procedure described by Schrooyen et al. [26]. 30 g of keratin biofibers was solubilized in 750 cm^3 of water with 8 M urea, 3 mM EDTA, 125 mM 2-mercaptoethanol, and 200 mM tris, maintaining the pH at 9.0. After that, salt residues were separated from the keratin solution through a dialysis membrane. 10 cm^3 of keratin salt solution was dialyzed with 1 L of distilled water, which was replaced completely after 16 and 24 hrs. The dialysis process was stopped after 48 hrs. Dialyzed keratin solution was preserved at 4°C. The pH of the dialyzed keratin solution was adjusted by using H_2SO_4 or NaOH to 2.5, 6.0, and 9.5; these solutions were used in each PU-keratin membrane formulation as shown in Table 1.

2.3. Synthesis of Hybrid Polyurethane-Keratin Membranes. Polyurethane-keratin (PU-keratin) membranes were produced by *in situ* polymerization between isocyanate and polyol. Control membranes using distilled water (at pH 7.0) instead keratin solutions were produced using both TDI and MDI. The synthesis of PU-keratin membranes made with TDI includes dialyzed keratin solutions with a specific pH (2.5, 6.0, or 9.5) and polyol; they were mixed in a polypropylene flask for one minute. After that, TDI was poured in the mixture and stirred for 15 s. The mixture foams during the polymerization reaction producing the internal cells in membranes. For those membranes made with MDI, 2.3 cm^3 of dialyzed keratin solution was centrifuged at 2033 rpm; this produces 0.2 g of hydrated keratin that

TABLE 1: Nomenclature and components of polyurethane-keratin membranes.

Isocyanate type	Dialyzed keratin solution	Water	pH of keratin solution	Membrane nomenclature
TDI 3 g	—	2.3 cm ³	—	TPH
TDI 3 g	2.3 cm ³	—	6.0	TPKN
TDI 3 g	2.3 cm ³	—	2.5	TPKAc
TDI 3 g	2.3 cm ³	—	9.5	TPKAl
MDI 5.7 g	—	0.2 cm ³	—	MPH
MDI 5.7 g	2.3 cm ³	—	6.0	MPKN
MDI 5.7 g	2.3 cm ³	—	2.5	MPKAc
MDI 5.7 g	2.3 cm ³	—	9.5	MPKAl

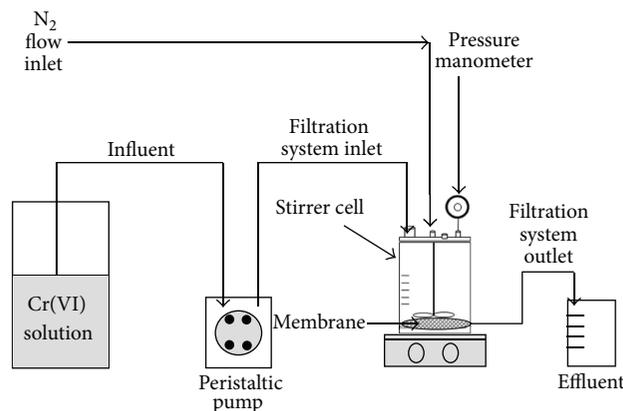


FIGURE 1: Filtration system by continuous flow.

was mixed with polyol and MDI in order to introduce the biopolymer during the polymerization process, analogous to TDI. Centrifugation of dialyzed keratin solution was realized in order to minimize the amount of water. This last procedure was carried out with systems using MDI. Table 1 shows the different conditions for the synthesized membranes, only 5.5 g of polyol remain constant in all membranes. When polymerization reaction was complete, the membranes were cut according to the filtration reactor geometry (diameter 47 mm, thickness 3 mm).

2.4. Preparation of Cr(VI) Solutions. Cr(VI) solutions were prepared by dissolving $K_2Cr_7O_2$ in distilled water; the influent concentration was 20 mg/L. The chromium solution was adjusted to 5.7, 2.5, and 1.5 by H_2SO_4 or NaOH solutions in order to study the effect of ionic species of Cr(VI) in the membrane efficiency.

2.5. Adsorption Experiments. The filtration experiments were performed in a Millipore filtration cell by continuous flow. The equipment, shown in Figure 1, consists in a solvent-resistant stirred cell, with the following characteristics: cell capacity 50 cm³, stirred minimum volume 2.5 cm³, membrane diameter 4.7 cm, effective membrane area 17.3 cm², and maximum operating pressure 6.2 bar. In order to equilibrate the system, first, deionized water was fed for 30 to 60 min. Once the filtration cell operated at equilibrium conditions, Cr(VI) aqueous solution was fed. This is considered the initial

point of the continuous flow inlet. Feed solution (influent Cr(VI) aqueous solution at 20 mg/L) was injected with a peristaltic pump at 60 cm³/min. The outlet flow (effluent of filtrated water) was maintained constant together with cell internal pressure (controlled between 0.7 and 2.8 bar) by a nitrogen gas flow injected into the cell. The cell is provided with an agitator system that operates at 150 rpm to maintain a homogenous solution. PU-keratin membranes were fixed at the bottom of the cell. Dimensions of the membranes were adjusted to 4.7 cm of diameter and 0.4 cm of thickness. The Cr(VI) aqueous solution is filtrated through PU-keratin membranes; the maximum feed velocity across the membrane surface was around 0.06 cm/s, maintaining contact between the influent and membranes for 36 s. The system was operated for 270 min, taking samples every 30 min.

The concentrations of Cr(VI) for the initial solution and the effluent were determined with UV-vis spectrophotometer equipment (Spectronic Genesis 2PC) at a wavelength of 540 nm using the 1,5-diphenylcarbazide complexation method, according to the Mexican Official Standard NMX-AA-044-SCFI-2001.

The removal percentage of Cr(VI) was determined by these simple equations:

$$P_t = \frac{C_t \cdot 100}{C_i}, \quad (1)$$

$$\text{Removal percentage of Cr(VI)} = 100 - P_t,$$

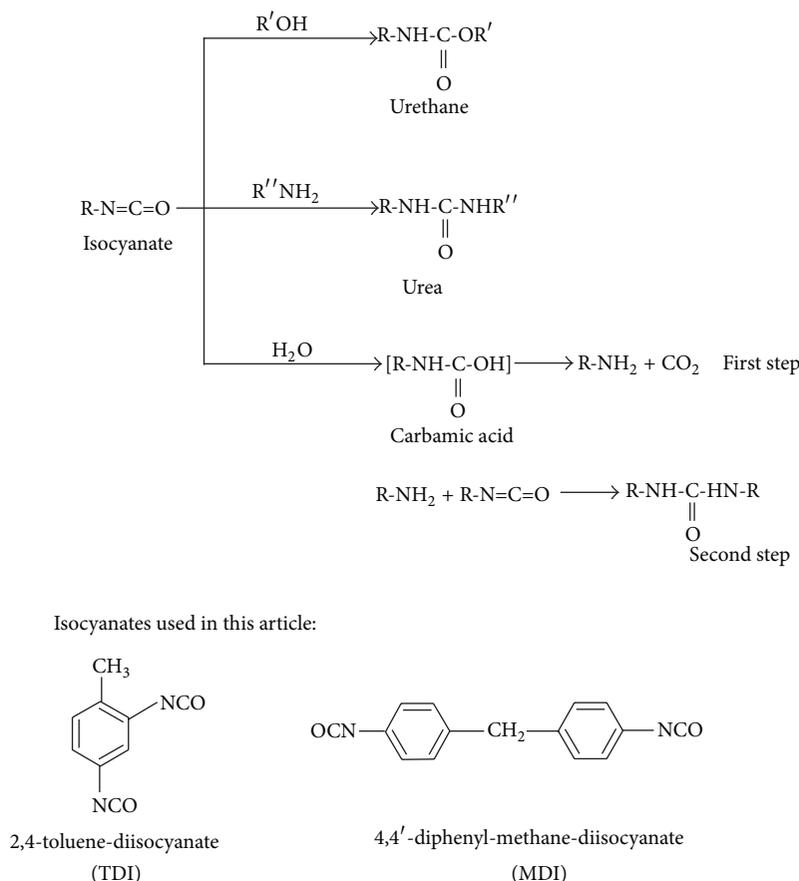


FIGURE 2: Scheme of possible reactions of isocyanates with moieties of polyethylene glycol-keratin-water system.

where C_i indicates the initial concentration of Cr(VI): 20 mg/L; C_t corresponds to the effluent concentration at predetermined time, the latter is obtained from a calibration curve according to the UV-Vis spectrophotometric method.

2.6. Membrane Characterization. The membrane morphology was studied before and after the filtration process by scanning electron microscopy (SEM) in a JEOL JSM 6510LV microscope at 20 kV and high vacuum. The membranes were characterized by SEM after filtration in order to observe any surface damage after flow. All the samples were gold-coated to prevent surface charging during SEM analysis. Functional groups of PU-keratin membrane and interactions between Cr(VI) and PU-keratin were studied by infrared spectroscopy using an IR Prestige-21 Shimadzu Corporation spectrometer on the attenuated total reflectance mode (ATR), in the range of $4000\text{--}500\text{ cm}^{-1}$. In order to study the thermomechanical properties of the membranes, dynamic mechanical analysis was carried out in a DMA 2980 instruments equipment using a multifrequency model-dual cantilever; the heating rate used was $3^\circ\text{C}/\text{min}$ using 1 Hz of frequency and a temperature range from 30 to 200°C .

3. Results and Discussion

3.1. SEM Characterization. One of the most important features of PU-keratin membranes is the cell conformation,

since it influences the properties of flexible PU foams. The cell conformation is determined by the polymerization process in the first step of PU reaction. This involves the isocyanate group reacting with water to yield an unstable carbamic acid, which decomposes quickly in amine and carbon dioxide (Figure 2). The carbon dioxide production is proportional to the added water quantity and is related to the formation of cells and “foam” porous in PU. In order to observe some structural details and internal size cell, SEM images of TDI- and MDI- based PU-keratin membranes are shown in Figure 3. The nomenclature for each membrane is described in Table 1. There are some morphological differences mainly in the opening of the cells, where the TDI-based membranes (Figures 3(a)–3(d)) have a greater number of open cells compared to MDI-based membranes (Figures 3(e)–3(h)).

The TDI membranes have higher water content; this causes less homogeneity and greater amount of open cells, as can be observed in Figures 3(a)–3(d). Figure 3(e) shows the MDI membrane without keratin (MPH), where only 0.2 cm^3 of water was used instead of keratin solution. This membrane has nonuniform open cells similar to TPH and TPKAl (Figures 3(a) and 3(d), resp.). These three types of membranes have an irregular cell boundary, whereas TPKN, TPKAc, MPKN, and MPKAc (Figures 3(b), 3(c), 3(f), and 3(g)) have well-defined cell frames, no matter the diameter of the open cells. This fact indicates that keratin protein and pH on

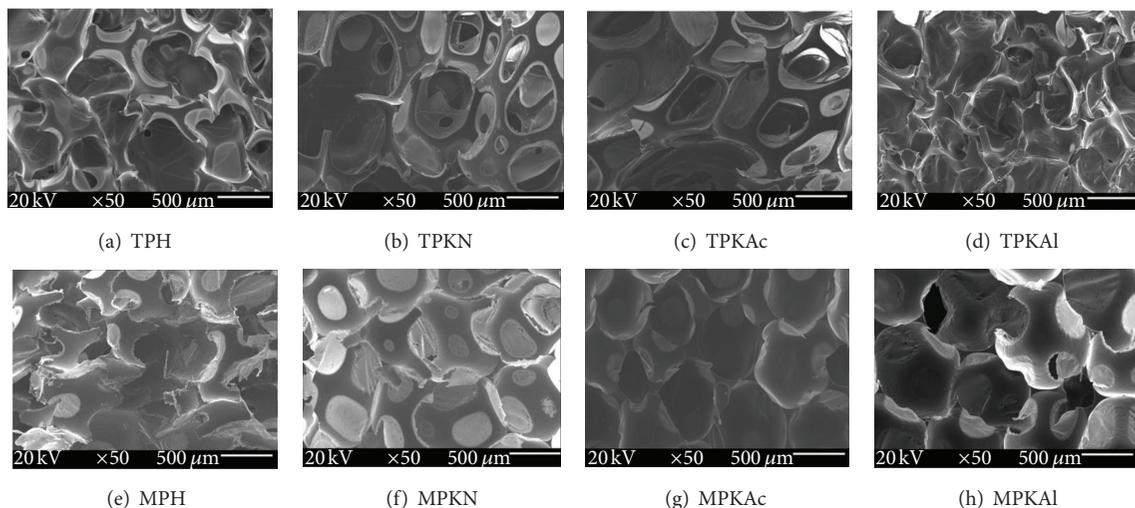


FIGURE 3: SEM images of PU-keratin membranes; ((a)–(d)) with TDI; ((e)–(h)) with MDI.

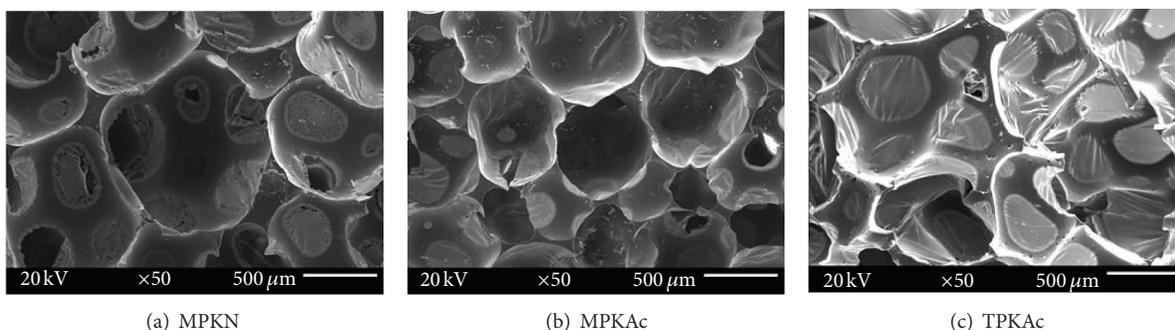


FIGURE 4: SEM images of PU-keratin membranes after the removal process.

keratin solution have an effective role in the polymerization process, since the morphological characteristics of PU have been affected. In addition, as MDI membranes contain lower levels of hydration, they have most of their cells closed because of the lower production of CO_2 as well as fewer urea microdomains which are partly responsible of the open cells [32]. As it can be observed the internal cells measure between 100 and 500 μm ; with these open pore arrangements an easy accessibility of Cr(VI) ions is expected to interact with immobilized active sites of keratin.

Figure 4 shows SEM images of selected membranes after the removal process. As it can be observed, there are only few morphological changes that could reveal damage on the cell opening or over the surface throughout the membrane during the filtration process. The cells in tested MPKN membrane (Figure 4(a)) are almost unaltered, whereas those in tested MPKAc and TPKAc membranes (Figures 4(b) and 4(c), resp.) show only small ruptures in the cell borders compared to non-used MPKAc and TPKAc membranes (Figures 3(g) and 3(c), resp.). This demonstrates that the PU-keratin membranes remain almost unaltered after the removal process and cells do not undergo a severe collapse that could impede their use in additional cycles of removal. This structural integrity is due to open cells allowing

water flux without high pressure conditions and preserving an effective contact between Cr(VI) ions and keratin amino acids.

3.2. Dynamic Mechanical Analysis. This analysis was used to determinate the viscoelastic properties: storage modulus (E') and loss factor ($\text{Tan}\delta$) of flexible PU-keratin membranes. Figure 5 shows storage modulus versus temperature for the membranes synthesized with MDI and TDI, and Figure 6 shows the values of $\text{Tan}\delta$ for these membranes.

It is observed for the storage modulus curves, that there is a similar slope between 35 and 100 $^\circ\text{C}$ for all MDI membranes (Figure 5(a)). The fall of these curves is related to thermal transitions of hard segments of PU [33], which have been modified according to the keratin solution. The higher E' (0.91 MPa at 40 $^\circ\text{C}$) for MPKAc indicates a more restricted mobility; therefore, this membrane has a more rigid behavior than the other MDI membranes.

On the other hand, E' for TDI membranes (Figure 5(b)) shows that TPH membrane (with E' of 0.59 MPa at 40 $^\circ\text{C}$) is more rigid than the other TDI membranes. However, this characteristic diminishes quickly as the temperature is increased around 100 $^\circ\text{C}$, whereas TPKAc and TPKN have a similar slope in E' decreasing. It is reported that the

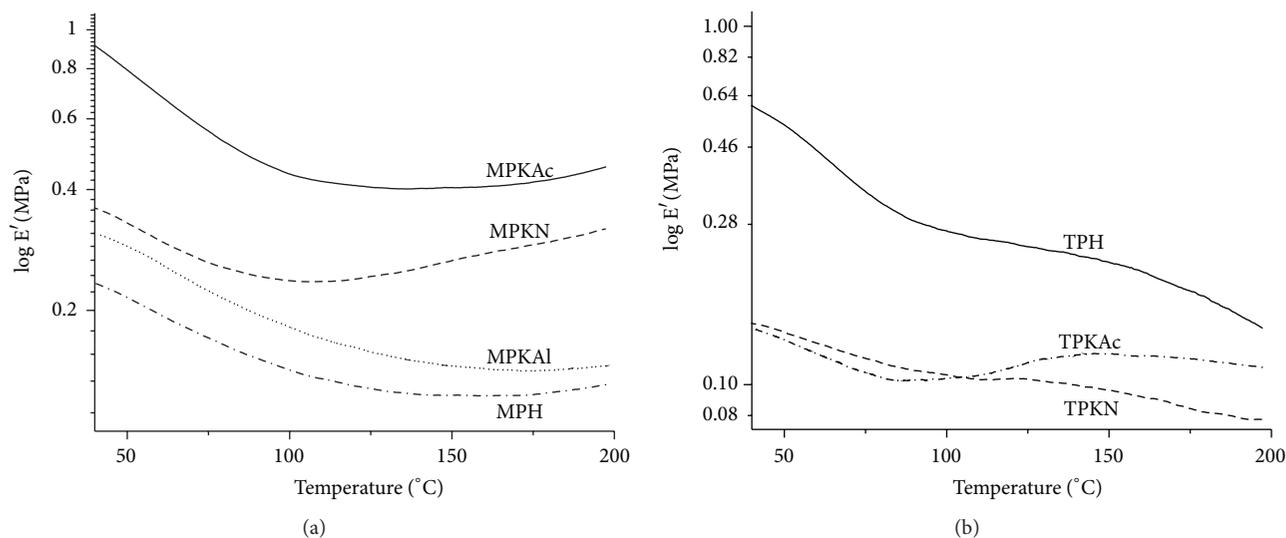


FIGURE 5: Storage modulus of PU-keratin membranes; (a) for MDI and (b) for TDI.

modulus in this region is proportional to either the number of crosslinks or the chain length between entanglements [34]. Thus, keratin, in this kind of PU membranes, produces more flexible membranes in the opposite behavior to MDI membranes. In addition, it is important to mention that E' values are in agreement with SEM results, where the most rigid membranes (with high values of E') show more closed cells than the membranes with less rigid behavior.

The transitions observed near 100°C are attributable to the presence of high concentration of hydrogen-bonded urethane groups and hard-segment domains which act as macroscopic crosslink. Hard and soft segments for MDI and TDI are shown in Figure 7. The segmented structure of PU explains the differences between storage modulus curves of MDI and TDI membranes, since MDI membranes show more rigid behavior than TDI membranes. This is related to the nature of isocyanate due to the number of aromatic rings. This polyurethane transition has been reported before by other authors [7, 35, 36].

In addition, $\text{Tan}\delta$ values show that MPH and MPKAl have the maximum values at around 80°C, whereas MPKAc and MPKN do not show this maximum (Figure 6(a)). This behavior, at elevated temperatures, implies that a high $\text{Tan}\delta$ value has a significant nonelastic strain component, while a low value means a more elastic material. Thus, these results in concordance with storage modulus give evidence that keratin produces more rigid membranes when MDI is used.

On the other hand, $\text{Tan}\delta$ for TDI membranes (Figure 6(b)) shows the maximum around 0.33 at 90°C to TPH. For TPKN and TPKAc, a maximum appears at around 112°C, indicating that keratin provides to TDI membranes high thermal stability, in spite of their flexibility.

This maximum signal in $\text{Tan}\delta$, observed in both MDI and TDI membranes, is related to the thermal transition exposed before and detected at around 100°C. The analyzed viscoelastic behavior in these membranes strongly depends

on the isocyanate and the pH of keratin solutions used in the polymerization reaction. So, it is important to consider that when the membrane is synthesized, the water of the keratin solution is involved in two competitive phenomena. One is the production of gaseous CO_2 that expands creating softer foam; the other phenomenon is when urea domains are generated by water and amino groups reacting with isocyanate; this produces hard segments and crosslinking, and therefore a rigid cell. Having in mind these considerations, when the pH of keratin solution is reduced to 2.5, keratin tends to separate from water and this is available to react freely with MDI producing a rigid MPKAc membrane. In the case of TDI, pure water reacts easily yielding the more rigid membrane: TPH; whereas pH of keratin solution loses its effect over hard segments production. At the same time, CO_2 production is facilitated with TDI producing a softer material in agreement E' results and SEM images, where TPH shows a higher number of opened cells compared to MPKAc with the highest quantity of closed cells.

3.3. Cr(VI) Removal Results. The highest Cr(VI) removal percentages for each PU-keratin membrane as a function of pH in chromium aqueous solution are summarized in Table 2. It is observed that with pH of 5.7, none of the seven membranes reached high removal percentages; only TPKAc achieved around 8% at 90 min of process; the rest of the membranes have lower values. In general, for this pH, TDI membranes have better performance than MDI, since only a 3% in removal percentage was reached by MPKAl at 30 min; the other MDI membranes adsorb below this value.

It is remarkable that when pH of Cr(VI) solution is diminished, better removal results are obtained. If pH is decreased at 2.5, both kinds of membranes show more affinity toward Cr(VI) ions. MPKAc achieves the most high removal percentage of these series: 22% at 30 min. TDI membranes removal is also controlled by pH, since with TPH membrane

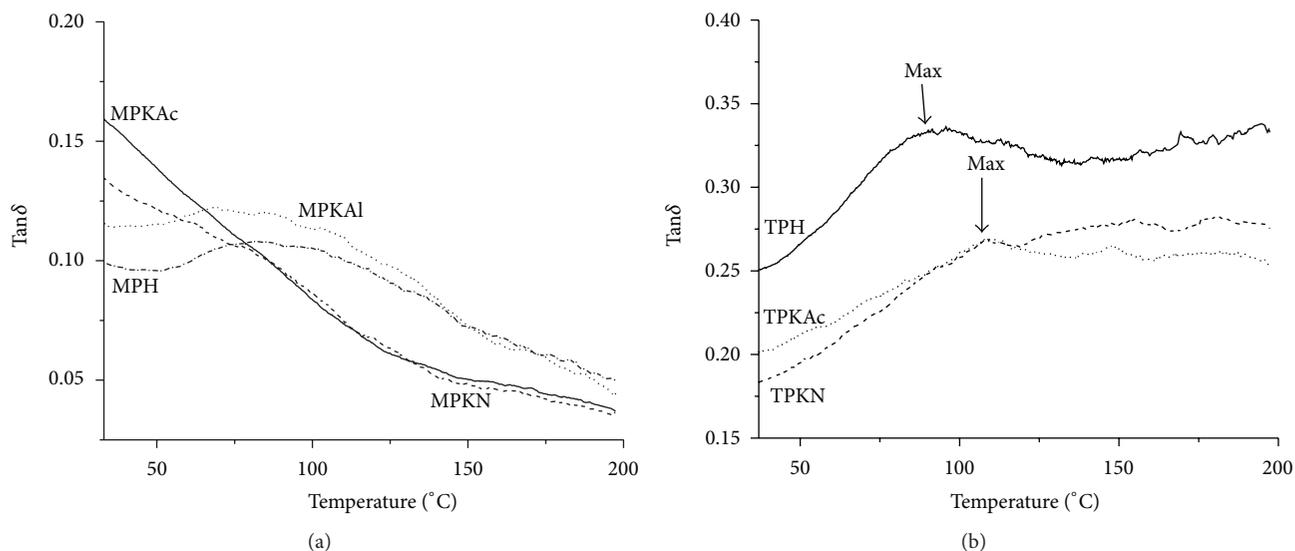


FIGURE 6: Tangent δ of PU-keratin membranes; (a) for MDI and (b) for TDI.

TABLE 2: Maximum values of Cr(VI) removal percentages through filtration process with PU-keratin membranes as function of pH.

Type of membrane	pH 5.7		pH 2.5		pH 1.5	
	Maximum value of Cr(VI) removal percentage	Time of removal (min)	Maximum value of Cr(VI) removal percentage	Time of removal (min)	Maximum value of Cr(VI) removal percentage	Time of removal (min)
MPH	0.81	90	6.44	240	25.24	90
MPKN	1.96	270	11.54	270	29.22	240
MPKAc	2.79	60	22.21	30	41.06	270
MPKAl	3.75	30	8.07	270	57.91	240
TPH	1.53	90	14.28	270	37.14	120
TPKN	4.19	30	13.06	30	38.16	180
TPKAc	8.14	90	5.77	270	26.47	60

a maximum removal percentage of 14% at 270 min was reached. TPKN reaches 13% of removal and TPKAc shows a minimum range for Cr(VI) removal: around 1 and 5%.

On the other hand, the highest removal percentages were achieved using Cr(VI) solution with pH of 1.5. MPKAl has the capacity to remove 57% of Cr(VI) with a regular tendency, which is observed also for the other membranes but with less removal ability. MPKAc reaches removal efficiency of 41%; for MPKN, the removal percentage was 29% and MPH shows 25%. The results with TDI membranes at pH of 1.5 are also higher than with the other pH values. The maximum removal percentage was achieved by TPKN (38%); TPH removal capacity was very similar, and its higher value was 37%. TPKAc shows a maximum removal value of 26%.

These results show that pH is the variable that most influences the removal of Cr(VI) in PU-keratin membranes. This can be explained because when pH is reduced, the membrane is charged positively due to protons presence, as was exposed by several authors [37–39]. In addition, pH below 4.0 (keratin isoelectric point) [19] produces that amino acids behave as cations increasing the electrostatic affinity. At

the same time, the chemical species of chromium in water are negative ions for all pH values (HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$). Therefore, when the pH is gradually reduced the PU-keratin membrane surface is more positively charged and the attraction between ions is stronger resulting in a more efficient Cr(VI) removal. In the other hand, when the pH of the Cr(VI) solution is increased, the negative charges on the polymer composite surface start appearing and the negative Cr ions are repelled [17, 38]. Figure 8 provides the chemical species of Cr(VI) as a function of pH and the variation of keratin charge according to its isoelectric point.

Figure 9 shows the behavior of removal process for MPKAl and TPKAc membranes using three different pH values (5.7, 2.5, and 1.5). The adequate morphology of these membranes (observed in Figures 3(c) and 3(h)), with their well integrated and uniform cells, is reflected in the regular tendency of the adsorption curves, which in addition to the pH influence (better adsorption at pH of 1.5) provide a good performance for these membranes. Specifically, the Cr(VI) removal percentage for the best membrane is from 30 to 57%. At the same time, it is worthy of mention that this

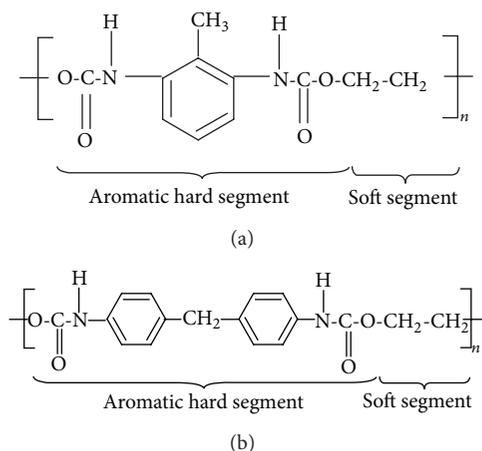


FIGURE 7: Chemical polyurethane zones, soft and hard segments: (a) TDI, (b) MDI.

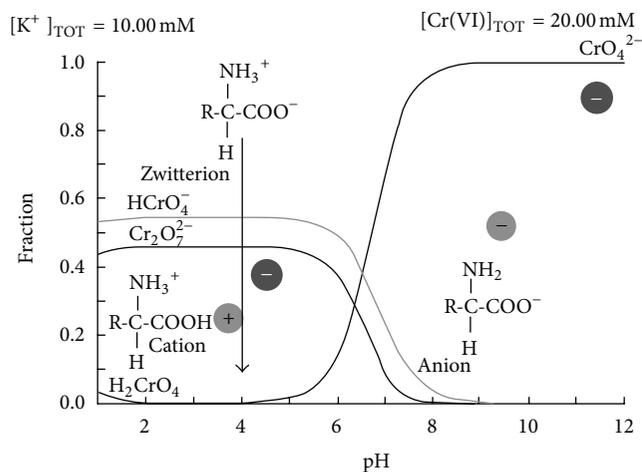


FIGURE 8: Distribution of Cr(VI) species as a function of pH.

is a continuous process, suitable of flux drops by fouling mechanisms, which are strongly influenced by the surface charge of the membrane [40]. Therefore, the membranes with the lowest adsorption values are also those with uneven process behavior as is observed in Figure 9.

Keratin is an important biopolymer that has begun a specific application in materials related to environmental remediation, based on its interesting characteristics to remove metal pollution. Table 3 shows the highest result obtained in this paper and some of the most relevant results obtained by other authors. It is clear that keratin removal efficiency varies amply, not only in processed and complex materials [6, 9, 27, 29] but also if it is used as a simple biosorbent [4, 8, 28, 30, 31]. Our results show the variations as a function of uptake time, pH of keratin solutions according to isoelectric point of this protein, pH of chromium solutions and structural characteristics of membrane. The performance of this membrane (57% of Cr(VI) removal) was superior compared with our previous results [6], the adsorption is significantly high due to presence of keratin, thus is demonstrated that a minimum quantity of

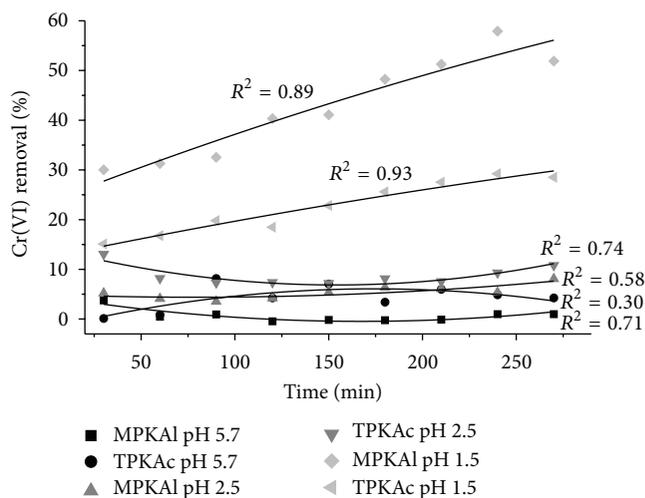


FIGURE 9: Cr(VI) removal percentages of MPKAL and TPKAc membranes as function of pH and time in the filtration system by continuous flow.

keratin (1.75%) with the adequate support could be as useful as feather fiber biosorbent (100% of keratin) [4, 8, 28, 30]. Some additional factors that affect the performance of keratin to remove metals are initial metal concentration, chemical treatment, and ionic charge of metal pollutants.

3.4. Infrared Spectroscopy. Figure 10 shows the normalized infrared spectra for MDI (10I) and TDI (10II) membranes, all before the removal process. The spectra have the same characteristic absorption bands identified for PU. The most important signals are $\nu(\text{N-H})$ band around 3313 cm^{-1} for secondary and primary amines [7, 41]; vibrations between 2980 and 2867 cm^{-1} characteristic of $\nu(\text{C-H})$ [7, 42]; the remaining isocyanate group appears nearby 2276 cm^{-1} for MDI and its absence in TDI evidences a complete reaction [7, 43]. Another characteristic band that can be observed in Figure 10 is the $\nu(\text{C=O})$ at different wavenumbers: the urethane carbonyl group at 1724 cm^{-1} and 1727 cm^{-1} for MDI and TDI spectra, respectively [7, 42, 43]; urea carbonyl group displays this band at 1712 cm^{-1} for MDI and by 1714 cm^{-1} for TDI [7, 41, 42]. It can be seen that the intensity of the urethane carbonyl band is higher for MDI, whereas for TDI urea, carbonyl signal is more intense than urethane carbonyl; this can be explained taking into account that water is highly responsible for urea domains and TDI membranes were formed with more water than MDI membranes. At the same time, MPH membrane was formed using more water compared to the rest of MDI membranes. At 1649 cm^{-1} , it is observed the $\nu(\text{C=O})$ for MDI, whereas for TDI it is found at 1662 cm^{-1} ; this absorption corresponds to the amide carbonyl group and urea carbonyl [13, 42]. The band at 1594 cm^{-1} can be assigned as a vibration out of plane combination of in plane $\delta(\text{N-H})$ and $\nu(\text{C-N})$ of amide II [44]. In the same region of amide II, the signals at 1538 cm^{-1} for MDI and at 1534 cm^{-1} for TDI, respectively, correspond to $\nu(\text{C-N})$ [41]. Aliphatic contributions are observed at 1457 cm^{-1} , 1415 cm^{-1} , 1373 cm^{-1}

TABLE 3: Keratin as biosorbent or functional component in materials applied in removal of metal pollution from water.

Material Description	Metallic species removed	Maximum removal	Keratin included	Reference
Polyurethane-feather keratin solution membrane	Cr(VI)	57%	0.2 g (1.75%)	This paper
Polyurethane-feather keratin biofiber membrane	Cr(VI)	38%	15%	[6]
Feather fibers	Pb(II)	81.6%	100%	[4]
Wool keratin/polyamide 6 nanofibres	Cu(II)	97%	90%	[27]
Feather fibers	Cu(II)	0.77 mmol/g	100%	[28]
	Zn(II)	0.95 mmol/g		
Membrane of wool keratose/silk fibroin blend	Cu(II)	2.88 $\mu\text{g}/\text{cm}^3$	50%	[29]
Algerian sheep hoof powder	Hg(II)	68 mg/g	100%	[30]
	Ca	93.88%		
Chicken feather aminoacid solution immobilized on silica surfaces	Mg	72.55%	1 g	[9]
	Fe	97.13%		
	Mn	95.66%		
	Pb	100%		
Feather fibers	Cu	48.8%		
	Zn	3.8%	100%	[8]
	Cd	17.0%		
	Ni	10.9%		
Chicken feather alkaline solution	Cu	0.14 mmol/g	5 mg/cm^3	[31]
	Zn	0.17 mmol/g		

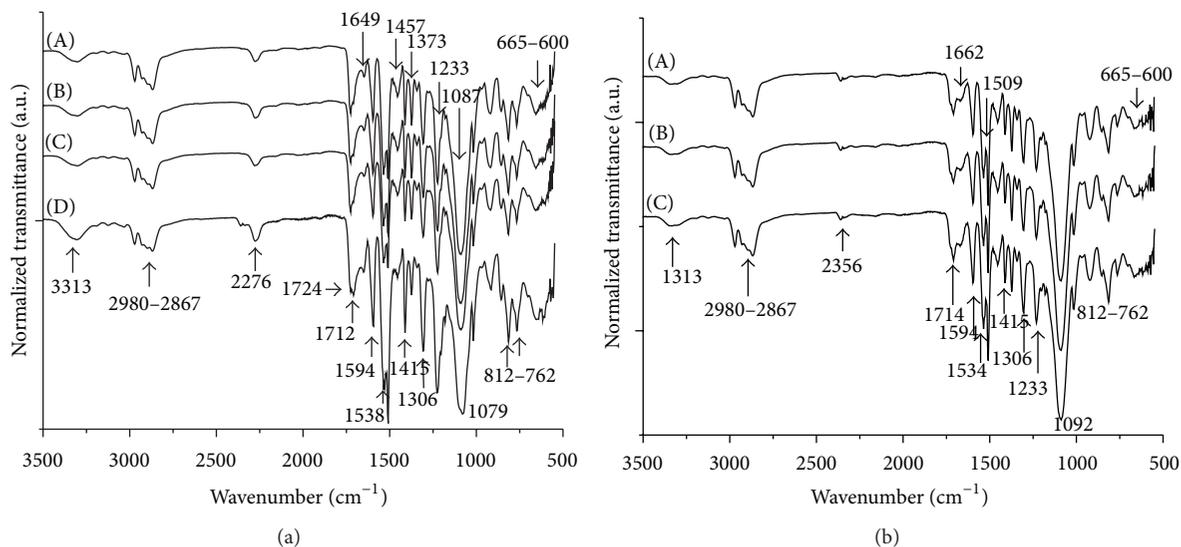


FIGURE 10: IR normalized spectra of PU-keratin membranes before removal process: (a) with MDI, (A) MPKAl, (B) MPKAc, (C) MPKN, and (D) MPH. (b) with TDI, (A) TPKAc, (B) TPKN, and (C) TPH.

and 1306 cm^{-1} [7]. The signal at 1233 cm^{-1} has been related to $\delta(\text{N-H})$ and $\nu(\text{C-N})$ of amide III, both functional groups are present in PU and keratin [45]. The band for $\nu(\text{C-O-C})$ also provides evidence of keratin presence in Figure 10(a), since this signal undergoes a shift toward 1079 cm^{-1} in the case of the MPH membrane. This shift was induced in the absence

of keratin for MPH synthesis. This effect is not significant in the case of TDI membranes (Figure 10(b)), where the peak at 1092 cm^{-1} remained constant for all spectra. The bands at $812-762 \text{ cm}^{-1}$ correspond to the $\delta(\text{C-H})$. The 762 cm^{-1} band is stronger for MDI than for TDI; this suggests a major contribution by MDI and this could be due to the double

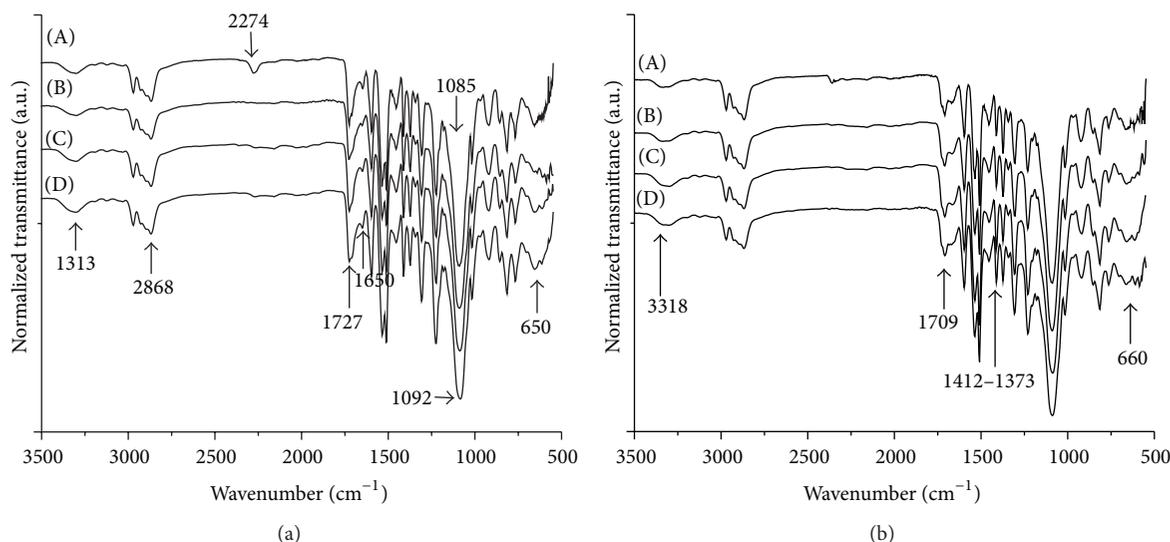


FIGURE 11: IR normalized spectra of membranes after the removal process; (a) for MPKAl membranes: (A) before removal process, (B) pH 5.7, (C) pH 2.5, and (D) pH 1.5. (b) for TPKAc membranes: (A) before removal process, (B) at pH 5.7, (C) at pH 2.5, and (D) at pH 1.5.

aromatic ring present in this type of polymer in comparison with TDI membranes. The bands between 665 and 600 cm^{-1} are attributed to the NH wagging and $\nu(\text{C-S})$ [6, 7, 45].

Figure 11 shows the infrared normalized spectra for membranes MPKAl and TPKAc after the removal process at different pH values in the removal medium. In the MPKAl spectra (Figure 11(a)), several changes in the intensity of the bands are observed under chromium solution, but these changes are more representative when the pH is lower (spectrum d). This phenomenon is more perceptible on the $\nu(\text{N-H})$ at 3313 cm^{-1} , $\nu(\text{C=O})$ at 1724 cm^{-1} , and $\nu(\text{C-S})$ bands at 665–600 cm^{-1} . At 2276 cm^{-1} , the vibration corresponding to the remaining isocyanate disappears in all cases under chromium contact, which indicates the dissociation of the isocyanate molecule and its interaction with metal ions. This statement is supported by the increase of the $\nu(\text{N-H})$ band at 3313 cm^{-1} . Besides, when the pH is decreased to 1.5, the $\nu(\text{C-O-C})$ signal at 1087 cm^{-1} shows a shift to 1092 cm^{-1} ; this functional group is formed by the isocyanate and alcohol group or could be formed by an isocyanate and the acid side of the amino acid keratin chain. It is suggested that the electrostatic attractions between the membrane and the metallic species are strong enough to modify the vibrational mode in this moiety.

In addition, TPKAc membranes (Figure 11(b)) also have some changes in their spectra when Cr(VI) solutions pass through. The described signals at 3313 cm^{-1} and 1714 cm^{-1} for $\nu(\text{C=O})$ and between 665 and 600 cm^{-1} were modified in their intensities. Besides, the intensities in the range from 1415 to 1272 cm^{-1} change; while the 1415 cm^{-1} peak increases, the 1373 cm^{-1} decreases, so the chromium membrane interactions affect directly the $\delta(\text{C-H})$ vibration [14, 17].

4. Conclusions

Polyurethane-keratin membranes, using two types of isocyanates, were successfully synthesized and applied as

separation membranes to remove Cr(VI) in aqueous solution. The polyurethane-keratin foam microstructure was directly affected by the type of isocyanate (MDI or TDI) and the pH on keratin solution (acid keratin 2.5, neutral keratin 6.0, or alkaline keratin 9.5). The microstructural study by SEM allows establishing a correlation between the keratin pH and the cell opening, which is also reflected in the adsorption behavior. Additionally, morphologic changes in the membranes were not detected after the removal process, which indicates an adequate structural resistance useful for several cycles of water treatment processing. DMA results show that the storage modulus is higher for MDI membranes and the highest value corresponds to MPKAc due to less formation of gaseous CO_2 and therefore the formation of more rigid foam. In the case of TDI membranes, the absence of keratin in urea microdomains plays an important role that overtakes the CO_2 production, since contrary to expectations, TPH (with more CO_2 formation) is the most rigid membrane in this set. The Cr(VI) removal results show that pH in the removal system directs the efficiency of the process. When pH is reduced, the surface is more positively charged and attracts the negative Cr(VI) ions. The functional groups affected by the removal process according to the IR analysis were C=O, C-O-C, and C-S; these were mainly observed when the pH was lower. Finally, the most efficient system was MPKAl with a Cr(VI) solution of pH 1.5, removing up to 57% of the initial chromium concentration.

Conflict of Interests

The authors do not have potential conflict of interests.

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