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Adsorption and desorption of a gold–iodide complex onto cellulose acetate membrane coated with polyaniline or polypyrrole: a comparative study

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Abstract Cellulose acetate membranes (M1) with controlled thickness were coated with an electroconductive polymer, and the resulting composites were characterized by SEM, XPS, electrical conductivity, and mechanical measurements. A comparative study of M1 coated with polyaniline (PANI) or with polypyrrole (PPy) for adsorption and subsequent desorption of a gold–iodide complex was performed. The PANI-coated M1 (M2) and that coated with PPy (M3) are effective adsorbents for recovery of the AuI_2^- complex. The adsorption of gold on the membranes was attributed to the exchange between the dopant ions and the AuI_2^- complex ions. The adsorption equilibrium data fitted the Langmuir isotherm model for both membranes M2 and M3. The desorption of the AuI_2^- complex with a NH_4OH solution 3 M reached 97% for M3 membrane. This study shows a convenient method for the recovery of gold through the use of a complex with iodine without cyanide solutions.

Introduction

A large number of publications about the use of different polymeric materials to prepare electroconductive membranes for a variety of applications have been reported, including chitosan-grafted-polyaniline (PANI) with the ability to separate water–isopropanol mixtures [1], polypyrrole (PPy)-coated carbon nanotubes that can be directly used as supercapacitor electrodes without any backing metal films or binders [2], PANI-grafted-polyacrylonitrile used for the reversible immobilization of GOD [3], PANI asymmetric hollow fiber membranes for gas separation [4], PANI–polypropylene membrane with nanofiltration properties [5], PPy doped with sulfonated calix[6]arene in the cation exchange membrane for transferring metal ions [6], PPy-based composite membranes for transport of anions and cations across membranes [7], and composite conducting membrane for the development of new dry cells [8]. In a previous study, cellulose acetate–PANI membranes were tested as ion-exchange materials of a gold–iodide complex [9].

In this context, films containing electroconductive polymers with ionic exchange properties and electrooxidation have been reported; specifically solvation effects on ion exchange were observed in PPy films [10] and an anion exchange was shown to occur in the electropolymerized PANI films [11] and PANI/multi-walled carbon nanotube composite films for electrooxidation of methanol [12].

Also, the recovery of precious metals using different techniques and materials has been reported. For example, ZnO nanopowder for noble metal recovery [13]; the recovery of gold, silver, palladium, platinum, etc. through biosorption [14]; the recovery of copper using activated carbon and ion-exchange resins [15]; the use of mesoporous silica matrix for the adsorptive recovery of Au^{3+} [16]; the recovery of gold by a combined method of biosorption

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and incineration [17, 18]; the recovery of gold using a combination of biosorption, biocrystallization, and pyrocrystallization techniques [19]; the adsorption of different heavy metal ions using anion exchange polymer [20]; adsorption of Au(III) using various resins [21]; sorption of gold onto activated carbon [22]; selective recovery of gold by cementation or adsorption onto activated carbon or ion-exchange resins [23]; reduction of gold ions from an aqueous acidic $HAuCl_4$ solution using gold–PPy film composite [24]; etc. In a previous study, we reported the kinetic experiments of adsorption of a gold–iodide complex onto acetate cellulose–PANI membranes [25].

This study is focused on two main objectives, the first is a modification to the previous method of the membrane preparation, introducing the use of an applicator to control the thickness of the membranes before coating them with electroconductive polymers, and the second objective is to perform a comparative study for the adsorption of gold from iodine–iodide aqueous solutions, using cellulose acetate membranes alternatively coated with PANI and PPy as adsorbent material, and subsequent desorption with a simple treatment with NH_4OH.

Experimental

Materials

The materials used in this study included cellulose acetate (CA) powder, 39.7 wt% acetyl content, average Mn = 50,000 (Aldrich); poly(acrylic acid, sodium salt) (PAA) 35 wt %, Mw 15,000 (Aldrich); acetic acid, glacial (Sigma); hydrochloric acid (Merck); ammonium persulfate (Fermont); triphenyl phosphate 99% (TPP), (Aldrich); potassium iodide, (Fermont); iodine 99.99%, (Fermont); gold powder 99.99%, (Aldrich); ferric chloride ACS, (Fermont); ammonium hydroxide, (Monterrey). Aniline 99%, (Aldrich), and pyrrole 98% (Aldrich) were distilled under vacuum in nitrogen atmosphere before use. All other reagents were used as received.

Preparation of CA membrane coated with PANI or PPy

CA membranes modified with PAA and plasticized with TPP (M1) were prepared using a modification of the procedure described in a previous article [9]. CA (4 g) was weighed and dissolved in 50 mL of acetic acid, with constant stirring for 4 h, and subsequently, 5 mL of PAA was added under stirring for 2 h. Finally, 1 g of TPP was added to the solution, under continuous agitation for 2 h.

The membranes were prepared using the phase inversion method. The solution was dispersed using an applicator (Elcometer 3600) on a glass plate of approximately 15 × 25 cm. The use of this applicator is a modification to the reported method [9], to improve the uniformity of the membranes. The plate was then placed in a coagulation bath (ice water mixture) for 5 min. The plate with the solution was then immersed in the ice–water mixture for additional 30 min. Finally, the membrane was peeled off from the glass plate, washed in water, and dried at 25 °C for 24 h on filter paper. PAA is water-soluble, and it was added to CA to induce the formation of pores and increase the contact area of the membrane with the solution containing the gold complex. For the coating of membranes with PANI (M2), a solution 0.5 M of aniline in HCl 0.02 M was prepared. The membranes were cut into strips to facilitate their coating. The strip was immersed in 100 mL of aniline solution for 5 min. Next, the strip was removed, drained, and placed in a glass vessel containing a solution of ammonium persulfate 0.5 M for 5 min. Subsequently, the membranes were dried at 25 °C for 24 h. For the coating of the membranes with PPy, (M3), a similar procedure described for the coating with PANI was used, instead 0.5 M ferric chloride and 0.5 M pyrrole solutions, with equal contact times as in case of PANI. Washing of M2 and M3 with 0.2 M HCl removes residual monomer, oxidant, and its decomposition products. A final washing with acetone removes low-molecular-weight organic intermediates and oligomers.

SEM imaging

The morphology of the membranes was examined using a JEOL 5410LV Scanning Electron Microscopy (SEM), operated at 15 kV. The samples were gold-sputtered before the SEM examination.

XPS

XPS spectra were measured on a Perkin-Elmer vacuum Products model PHI 5100 photoelectron spectrometer with Mg Kα exciting radiation used at 15 kV and 10 mA; the base pressure was approximately 10^{-9} Torr. Survey scans in the range 0–1100 eV. To compensate the surface charging effects, all binding energies were referenced to the C (1s) carbon peak at 284.6 eV. A Gaussian deconvolution curve-fitting was performed to evaluate the different contributions associated at the various types of nitrogen bonds present on the material. The full width at half maximum (FWHM), the position, and intensity of the contribution were optimized by a computer program giving the best fit to the experimental data.

Electrical conductivity

The electrical conductivity was measured by the standard two-point probe method. The measurements were done at

25 °C with tungsten electrodes of 6 mm diameter and a Steren Mul-040 multimeter.

Mechanical analysis

The tensile properties of the membranes were determined using a Universal testing machine (MINIMAT) equipped with a 200 N load cell using a constant crosshead speed of 1 mm min^{-1}. The evaluation was performed as described in the ASTM D882 "Test methods for tensile properties of thin plastic sheeting" standard. Before testing, the samples were conditioned at a 60% relative humidity and room temperature, 25 °C.

Test of application as ion-exchange membranes

Using the procedure described in a previous article [25], the leaching solution was prepared as follows: 12 g iodine total (I_2 + KI) were used, with a KI to I_2 ratio of 2:1. The solution of gold–iodide complex ($\mathrm{AuI_2}^-$) was prepared using the leaching solution, to which a predetermined amount of gold was added to achieve the concentration of 10 ppm. The total Au concentration was verified by atomic absorption spectroscopy using a Perkin-Elmer 3110 atomic absorption spectrometer.

The experiments of the adsorption kinetics of $\mathrm{AuI_2}^-$ on coated membranes were performed as follows: the membranes were cut into pieces of 1 × 1 cm. The pieces of membranes were introduced in an Erlenmeyer flask, and submerged in the solution of $\mathrm{AuI_2}^-$ complex, under constant magnetic agitation (155 rpm), after which the pieces of membranes were immediately removed from solution of the $\mathrm{AuI_2}^-$ complex. The contact time of the membrane with the solution of $\mathrm{AuI_2}^-$ complex was changed in a range of 0–720 min. The initial concentration of Au was 10 ppm. The experiment was carried out at 25 °C. The membrane concentration was 10 g L^{-1} (solid/liquid ratio; grams of membrane/liter of solution). The concentration of Au in the solution was determined by atomic absorption spectroscopy.

Equilibrium experiments

In the equilibrium experiments, membranes coated with PANI or PPy were used as follows: the membranes were cut first into pieces of 1 × 1 cm. Different amounts of mass membranes, ranging from 2 to 30 g L^{-1}, were introduced in Erlenmeyer flasks and submerged in the solution of $\mathrm{AuI_2}^-$ complex, under constant magnetic agitation (155 rpm) for 12 h, after which the pieces of membranes were immediately removed from the solution of the $\mathrm{AuI_2}^-$ complex. The experiment was carried out at 25 °C. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

To obtain the adsorption isotherms, solutions of different concentrations of Au were used (range 1–10 ppm). The solid/liquid ratio (grams of membrane/liter of solution) used varied from 2 to 30 g L^{-1}. The membranes were cut into pieces of 1 × 1 cm and were introduced in Erlenmeyer flasks and submerged in the $\mathrm{AuI_2}^-$ complex solution, under constant magnetic agitation (155 rpm) for 12 h, after which the pieces of membranes were immediately removed from the $\mathrm{AuI_2}^-$ complex solution. The experiment was carried out at 25 °C. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

Desorption test of the complex ($\mathrm{AuI_2}^-$)

The desorption experiment was performed using a NH_4OH solution 3 M, the membrane with ($\mathrm{AuI_2}^-$) was placed in the solution, varying the contact time in a time interval from 0 to 720 min. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

Results and discussion

Figure 1a shows the SEM micrographs of the surface of the M1 membrane, showing a fairly homogeneous pores sizes with diameter between 3 and 5 μm. Figure 1b shows the SEM images of the cross section of the M1 membrane, where the pores of the surface and cross section can be observed. It can also be appreciated that the pores on one surface can follow several paths to cross to the other side of the membrane, and this is a proof that there exists an asymmetric structure in the membrane. With the use of the applicator, the reported method [9] was improved, having control of the thickness of the membranes obtained. In the case of the M2 and M3 membranes, it was observed that the electroconductive polymer is deposited into the holes of the membrane M1 as shown in Fig. 1c and d, respectively.

The surface chemical composition of M1, M2, and M3 membranes were determined utilizing XPS analysis. The relative concentrations of the main elements: C, N, O, and Cl were calculated from the corresponding photoelectron peak area after the sensitivity factor corrections (SF = 0.25, 0.42, 0.66, and 0.73 for C1s, N1s, O1s, and Cl2p, respectively), (Table 1). The results are consistent with the ideal structures proposed for (a) PANI and (b) PPy at the maximum level of doping, 0.5 and 0.3 respectively, Fig. 2. The XPS analysis of the M2 membranes indicates the existence of sulfur; this can be explained if more counterions, like sulfate or hydrogensulfate anions, participate in the protonation of PANI along with the chloride anions. This result agrees with previous report [26]. The presence of iron in the M3 membranes is shown by XPS analysis. This result can be due to the fact that the PPy was

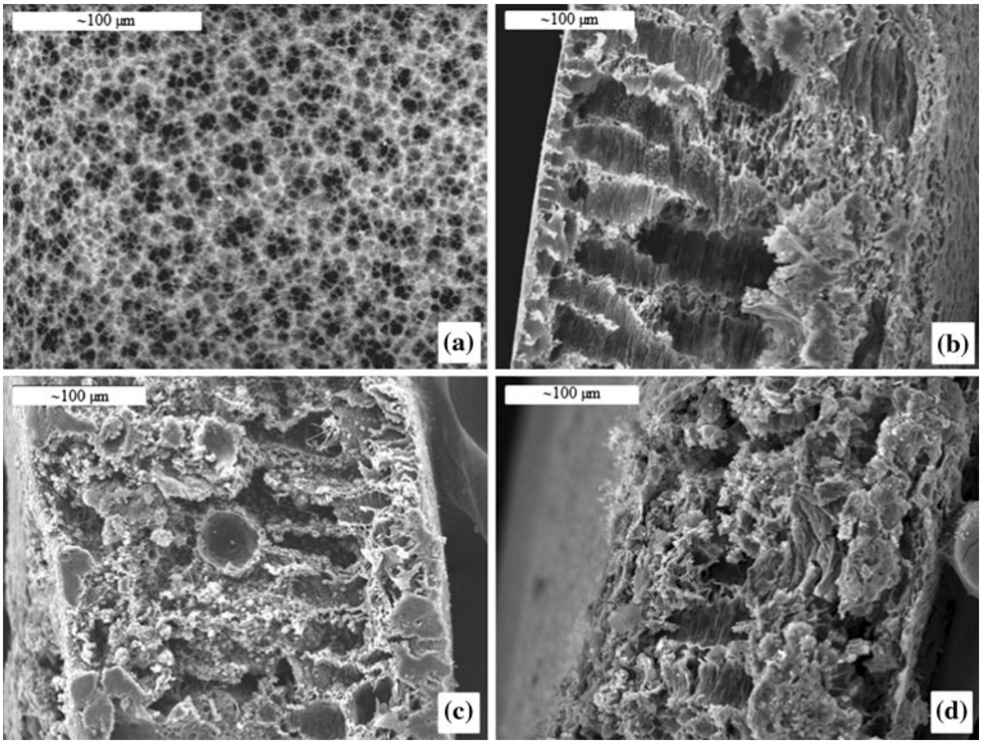

Fig. 1 SEM micrographs of **a** M1 membrane surface, **b** M1 membrane cross section, **c** M2 membrane cross section, and **d** M3 membrane cross section

Table 1 Composition of samples resulting from XPS quantitative analysis

	C/%	N/%	O/%	Cl/%	S/%	Fe/%	*N*/*C* ratio
M1	54.02	–	45.2	–	–	–	–
M2	67.14	3.96	24.07	0.72	2.75	–	0.059
M3	69.33	9.28	11.01	5.88	–	0.95	0.133

prepared using $FeC1_3$ as oxidant; after washing, iron content remains [27].

The *N*/*C* weight ratio in the membrane M2 and M3 are found to be 0.059 and 0.133, respectively. These results can be utilized to calculate an approximate weight fraction of PANI (X) or PPy (Y) using the following relations [28]:

$$\frac{N}{C} = \frac{X(28/182)}{X(144/182) + (1 - X)(192/406)} \qquad (1)$$

$$\frac{N}{C} = \frac{Y(28/130)}{X(96/130) + (1 - Y)(192/406)}. \qquad (2)$$

The formula of PANI in the membrane can be represented by $[(C_6H_4NH)(C_6H_4NH)]_n$ and CA $[(C_8O_6H_{11})(C_8O_6H_{11})]_n$. *X*, the surface weight fraction excluding the incorporated TPP is calculated to be 0.21. The formula of PPy in the membrane can be represented by $[(C_4H_2NH)(C_4H_2NH)]_n$ and CA $[(C_8O_6H_{11})(C_8O_6H_{11})]_n$. *Y*, the surface weight fraction excluding the incorporated TPP is calculated to be 0.35. These results are consistent with those reported for the % maximum polymerization of aniline and pyrrole, 80 and 100%, respectively [29, 30].

The N1s core-level spectra of the M2 and M3 membranes have been deconvoluted by assigning binding energies, shown in Table 2, and as illustrated by the spectrum in Fig. 3. The N1s peaks of both M2 and M3 were fitted with four components, two of the four peaks of each membrane are assigned to two types of positively charged nitrogen, $–N^+–$ and $=N^+–$ [31–34]. M2 membranes showed a protonation degree of 48%, and M3 membranes showed a protonation degree of 29%. The formation of N^+ is due to the polaron species. The level of doping, defined as $[N^+]/[N]$, was found to be 0.48 and 0.29 for M2 and M3 membranes, respectively. This result agrees well with the typical maximum doping levels for PANI and PPy reported in the literature [35].

When the M1 membranes were coated with PANI or PPy, an electroconductive material with potential application in

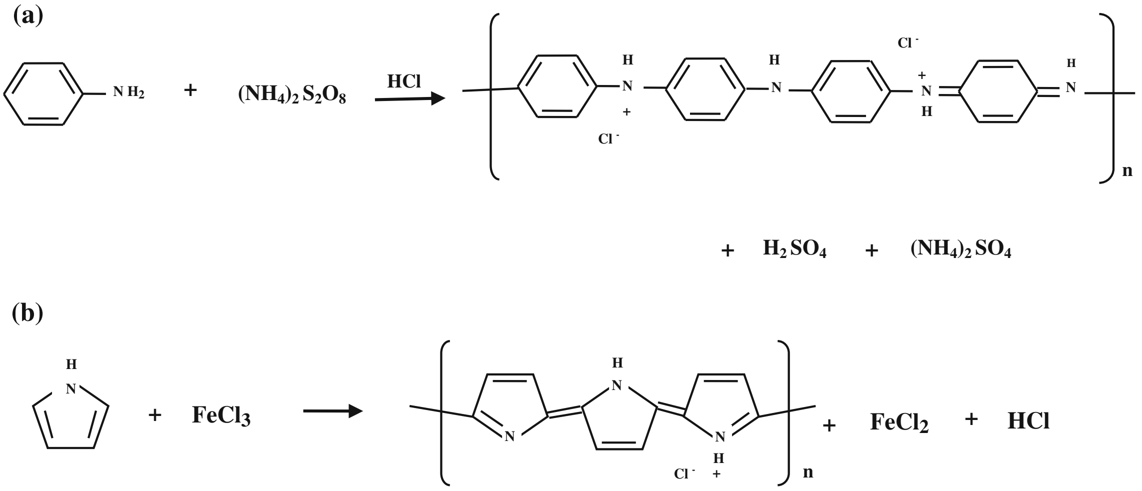

Fig. 2 Ideal structures proposed for **a** polyaniline and **b** polypyrrole at the maximum level of doping, 0.5 and 0.3, respectively

Table 2 Distribution (%) of N species on the surface of M2 and M3

	–N=	–NH–	N^+		Doping level N^+/N
			$–N^+–$	$=N^+–$	
Binding energy (eV)	399.09	399.88	401.99	400.94	
M2	9.59	42.21	18.59	29.61	0.48
Binding energy (eV)	398.22	399. 77	400.7	401.62	
M3	17.14	53.31	16.15	13.40	0.29

ion exchange was obtained. Table 3 summarizes the electrical conductivity determined for each membrane coated with PANI or PPy. The electrical conductivities of the membranes ranged from $<10^{-10}$ to 10^{-3} depending on the electroconductive polymer used. The electrical conductivity of the membranes prepared with PPy is one order of magnitude greater than that for the PANI-coated membrane. The electric conductivity of M2 and M3 remains constant for at least 6 months, which is the period when this study was carried out.

Values of tensile strength, Young′s modulus, and strain at break are shown in the Table 3. The M2 membranes show higher values of the three properties as compared to membranes M3. These results suggest that the membrane coated with PANI is a membrane with better mechanical properties than that coated with PPy.

The membranes coated with PANI or PPy were used in the absorption kinetic studies. The results are presented in Fig. 4, where the percentage adsorption of Au was calculated according to the following expression:

$$\text{Percentage adsorption of Au} = \frac{(C_0 - C) \times 100}{C_0} \qquad (3)$$

where C_0 is the initial concentration of total Au (ppm), and C is the concentration of Au (ppm) in the solution at time t. Figure 4 shows that the percentage adsorption of Au increases with time and achieves equilibrium at about 360 min for both membranes, coated with PANI or PPy, and for an initial Au concentration of 10 ppm. In the metallurgy industry, gold mines report Au concentrations between 0.5 and 10 ppm [36–38]; therefore, our study was conducted using solutions of different concentrations of Au (range 1–10 ppm). It can be seen that the adsorption of Au remained almost constant, implying that equilibrium has been reached. The membranes coated with the PANI showed a higher gold recovery than those coated with PPy. These results are consistent with the ideal structures proposed for PPy and PANI at the maximum level of doping, which in PANI is greater (0.5) than for PPy (0.3). The adsorption capacity of the membranes can be attributed to the interchange reaction between the counterions used to give electrostatic stability in the electroconductive polymer and the AuI_2^- complex anion of the solution. The complete polymerization reaction of aniline and pyrrole is shown in Fig. 2.

Figure 5a shows a schematic drawing of our model of the ion exchange for PPy, similar for that reported for PANI [25]. The AuI_2^- complex displaces the dopant anions, Cl^- and HSO_4^- for PANI, and Cl^- for PPy, thus remaining adsorbed on the membrane. This fact was confirmed by the almost complete absence of the chloride and sulfur peaks in the XPS spectrum of the M2 and M3 membranes after being in contact with the AuI_2^- solution.

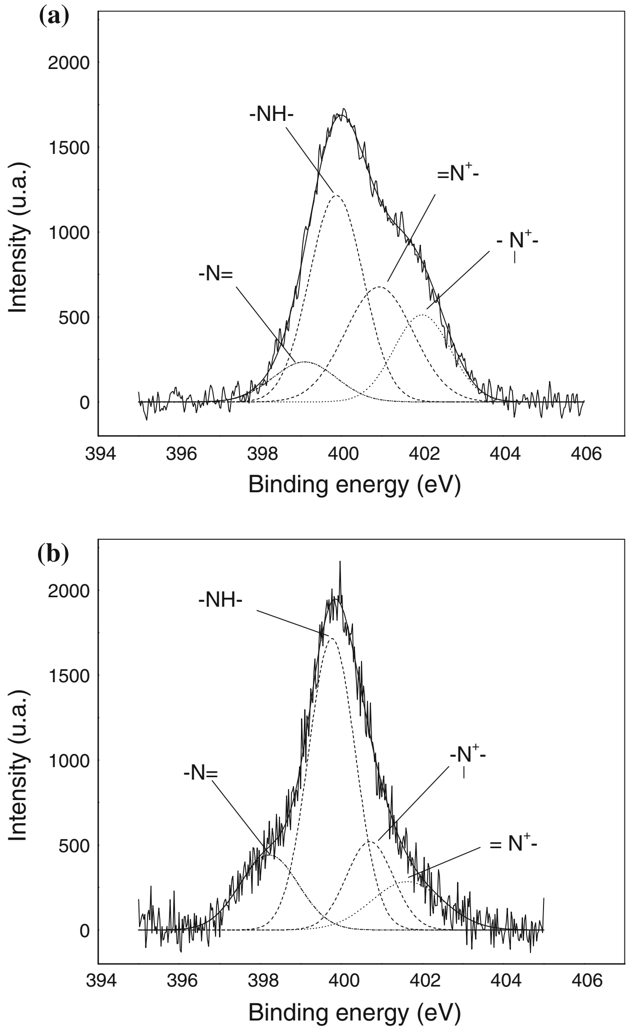

Fig. 3 N1s XPS core-level spectra of the **a** M2 membrane and **b** M3 membrane

Figure 6 shows the effect of the solid/liquid ratio; grams of membrane/liter of solution on the percentage adsorption of AuI_2^- complex for the membranes coated with PANI or PPy. In both cases, the percentage of the extracted amount of gold increased as the amount of adsorbent material increases. This is an expected result because the larger the amount of membrane surface, the greater capacity of adsorption is available. However, the percentage of gold adsorption is higher for the membranes coated with PANI, which is an expected result because of the level of doping of PANI and PPy, as mentioned above.

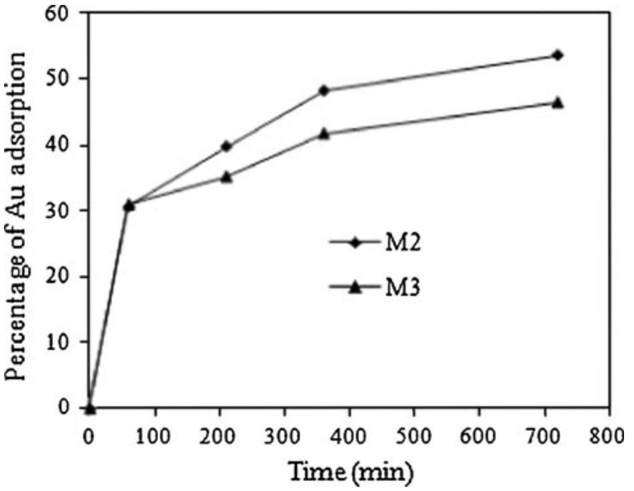

Fig. 4 Adsorption kinetics of AuI_2^- complex onto M2 and M3, solid/liquid ratio = 10, $[Au_i] = 10$ ppm, $T = 25$ °C

To this date, studies about gold recovery through the AuI_2^- complex using ionic-exchange resins have not been reported. However, it is known that for gold recovery using the $AuCN^-$ complex, recoveries of 30% at pH above 10 is obtained, using MN100 resin [39].

The equilibrium experimental data were adjusted to the linear isotherms of Langmuir, Freundlich, and Temkin. The best agreement was found for the Langmuir model for both the PANI-coated and the PPy-coated membranes. The equation of this model is shown in (4).

$$\frac{1}{Q}=\frac{1}{Q_\mathrm{m}KC}+\frac{1}{Q_\mathrm{m}} \tag{4}$$

where Q is the amount of Au adsorbed per unit weight of membrane at equilibrium concentration (mg g^{-1}), C is the equilibrium concentration of Au (ppm) in the aqueous solution, Q_m is the maximum capacity of adsorption, and K is the constant of the isotherm of Langmuir. The best linear fit of the experimental data for both membranes M2 and M3 was obtained for the Langmuir isotherm, as shown in Fig. 7. These results suggest a monolayer adsorption process, without lateral interactions between the adsorbed molecules. Table 4 shows the parameters of the equations of Freundlich and Langmuir. Figure 8 shows desorption of (AuI_2^-) complex with NH_4OH solution 3 M at 720 min, reached 97% for M3 membrane and 74% for M2 membrane. At equivalent conditions of treatment with NH_4OH and considering a lower maximum level of doping of PPy

Table 3 Electrical conductivity and mechanical properties values of M1, M2, and M3

Membrane	Electrical conductivity (S cm^{-1})	Tensile strength (MPa)	Young′s modulus (MPa)	Strain at break (%)
M1	$<10^{-10}$	1.015 ± 0.166	20.654 ± 3.117	13.4 ± 3.5
M2	$2.02 \times 10^{-4} \pm 3.56 \times 10^{-5}$	1.574 ± 0.485	26.645 ± 6.165	9.5 ± 2.5
M3	$2.68 \times 10^{-3} \pm 1.82 \times 10^{-3}$	0.614 ± 0.218	12.054 ± 0.735	4.0 ± 1.6

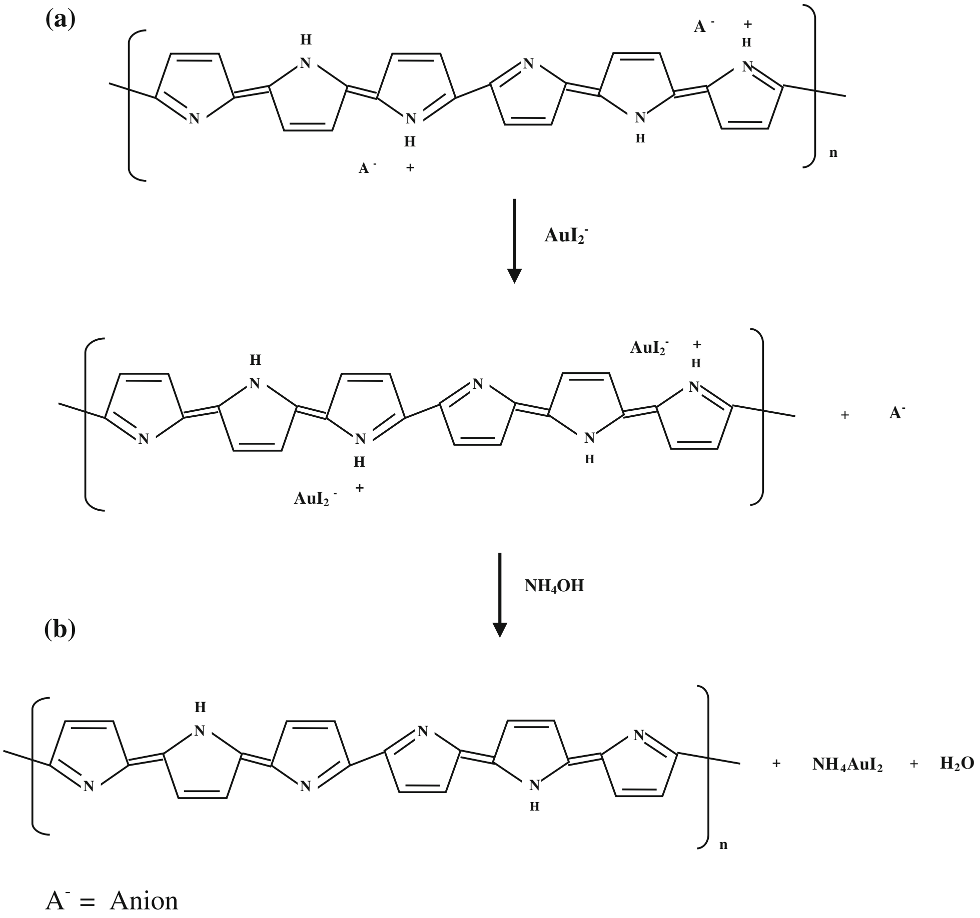

Fig. 5 Schematic representation **a** of the ion-exchange process and **b** of the desorption process of AuI_2^- onto M3 membranes

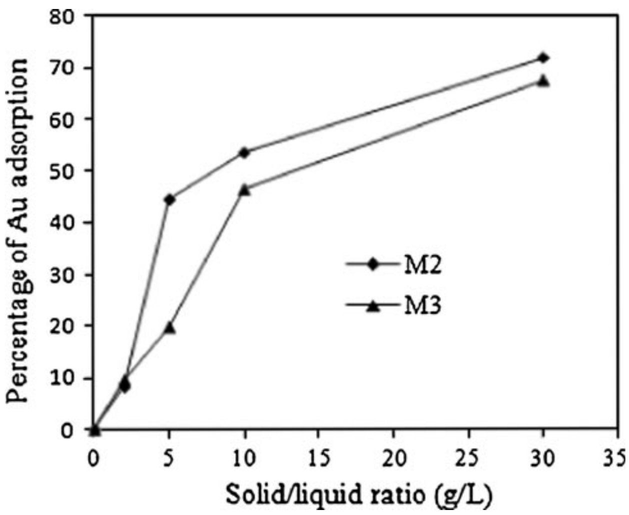

Fig. 6 Effect of solid/liquid ratio; grams of membrane/liter of solution, on the percentage adsorption of AuI_2^- complex on membranes with coated of PANI (M2) or PPy (M3)

compared to PANI, almost complete desorption of the complex AuI_2^- of M3 membrane is achieved. These results are consistent with those obtained in the adsorption of gold complex revised above. The gold complex desorption mechanism proposed for the membranes coated with PANI and PPy is ionic-exchange, and Fig. 5b shows the mechanism of desorption proposed for PPy.

Conclusions

Cellulose acetate membranes, M1, with a well-controlled thickness were prepared and characterized by SEM, XPS, electrical, and mechanical measurements. M1 membranes coated with PANI, M2 membranes show higher effective mechanical properties that the M1 membranes coated with PPy, M3 membranes. M2 and M3 membranes are effective adsorbents for the recovery of AuI_2^- complex. The adsorption of Au on these membranes was attributed to the exchange between the dopant ions and the AuI_2^- complex anion. The adsorption equilibrium data were found to obey the Langmuir isotherm model for M2 and for M3. Desorption of AuI_2^- complex with NH_4OH solution 3 M reached 97% for M3 membranes. This study shows a convenient method for the recovery of gold through a complex with iodine without the use of cyanide solutions.

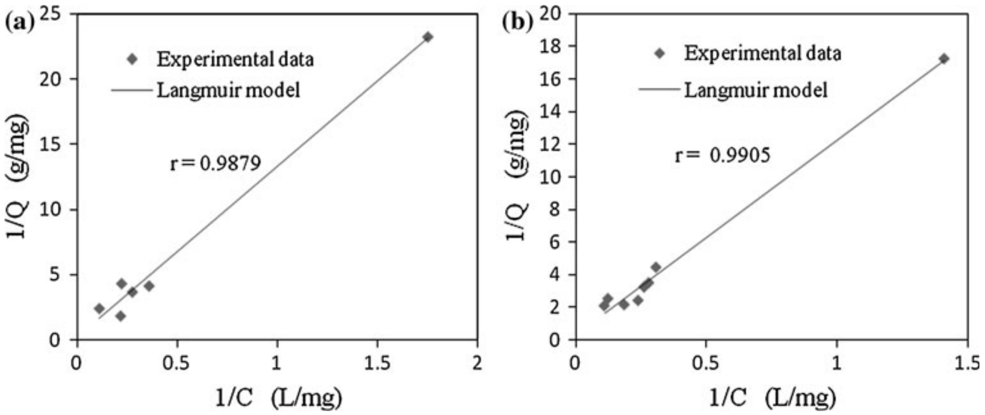

Fig. 7 Adsorption isotherm of Langmuir for AuI_2^- complex **a** on M2 membranes and **b** on M3 membranes

Table 4 Model parameters of Langmuir, Freundlich and their corresponding correlation coefficients for the M1, M2, and M3

Membrane	Langmuir model			Freundlich model		
	K, mg^{-1}	Q_{max}, mg g^{-1}	r	c_1, mg g^{-1}	$1/c_2$	r
M2	0.0198	3.858	0.987	0.0822	0.868	0.857
M3	0.0278	3.003	0.990	0.0905	0.844	0.907

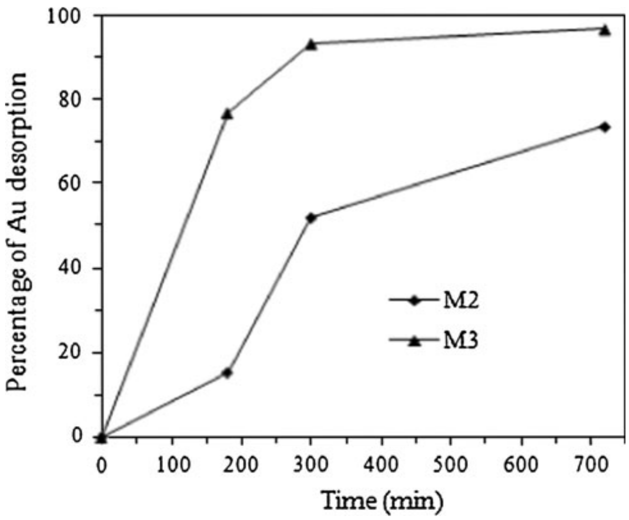

Fig. 8 Percentage of Au desorption against time of M2 and M3 membranes

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