

Preparation, Characterization, and Adsorption Properties of Cellulose Acetate-Polyaniline Membranes

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ABSTRACT: Four lots of cellulose acetate (CA) membranes, modified with polyacrylic acid, using various plasticizers, and coated with polyaniline (PANI) were prepared. The morphology of the membranes was evaluated by using scanning electron microscopy, and the membranes showed larger pore size when the plasticizers were used. The electrical conductivity of the modified membranes and coated with PANI increased by two orders of magnitude when the plasticizer triphenyl phosphate was

used. The strain at break improved by an order of magnitude and the glass transition temperature (T_g) showed an average decrease of 36°C when the membranes were plasticized. Finally, these membranes were tested as ion-exchange materials of a gold-iodide complex. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1216–1224, 2009

Key words: membranes; conducting polymers; mechanical properties; ion exchangers

INTRODUCTION

Polyaniline (PANI) is an intensively studied polymer due to its electrical, electrochemical, and optical properties and due to its high environmental stability, which confers it potential use in many applications including sensors, rechargeable batteries, anticorrosion coatings, electrochromic displays, selective membranes, etc.^{1–6} Nowadays, a number of compound materials based on mixtures of PANI with insulating materials such as cellulose acetate (CA)^{7–9} and poly(methyl methacrylate)¹⁰ have been synthesized, resulting in good electrical conductivity. The polymeric membranes used for the processes of separation and filtration is a field of attractive study for the scientific community, which is attributed to its application in day-to-day life, a clear example of which is, water purification and desalination via reverse osmosis.^{11–13}

Membranes formed with conjugated polymers have been studied because of their transport properties, because they can function as potential membranes for separating molecules from fluids. This property can be improved with a support matrix that provides mechanical strength and facilitates the transport of the molecules throughout the mem-

brane. This concept has been applied to different kinds of support matrices such as polycarbonate, cellulose, and CA.¹⁴ With the objective of conferring flexibility to CA matrices, the mixture of plasticizers of phthalic and phosphoric acid esters has been used.¹⁵ CA is commonly used to prepare membranes for different uses and various methods have been developed to control its pore diameter using polyelectrolytes.¹⁶ The presence of residual polyelectrolytes in the inner wall of the pore could function as a template to fasten electroconductive polymers to the membrane and to improve the electroconductive properties. The purpose of creating electrically conductive membrane (called electromembrane) is its potential application in processes of electrodialysis in ion separation.¹⁷ Togwen Xu and coworkers^{18,19} carried out some works related to electrodialysis using bipolar membrane reporting applications in organic acid production and regenerating flue-gas desulfurizing agents.^{20,21} Also a new route for preparing an anion exchange membrane using linear engineering plastics has been reported.²² Mirmohseni and Saeedi (1998)²³ carried out the first report on the separation by electrodialysis of a mixture of H₂SO₄/H₃PO₄ and HNO₃/H₂SO₃ using PANI membranes. Sata and Ishii (1999)²⁴ reported that the transport properties in electrodialysis of composite membranes prepared from cation exchange membranes and PANI, and these composite membranes showed sodium ion permselectivity in electrodialysis when compared with divalent cations at an

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optimum polymerization time. Nagarale et al. (2004)²⁵ developed composite membranes by polymerization of a thin layer of PANI in the presence of a high oxidant concentration on a single face of a sulfonated cation-exchange membrane and quaternary aminated anion-exchange membranes. Relative dialytic rates of Na₂SO₄, CaCl₂, and CuCl₂ were estimated with reference to NaCl on the basis of electro-dialysis experiments, and it was concluded that it is possible to separate different electrolytes using PANI composite ion-exchange membranes. Tan and Belanger (2005)²⁶ modified Nafion membranes by polymerization of aniline using ammonium peroxodisulfate as the oxidant. It is demonstrated that the ionic transport of both H⁺ and Zn²⁺ will be dependent on the amount of PANI disrupting the ionic paths and not necessarily the total amount of PANI. Sivaraman et al. (2007)²⁷ reported the electrochemical modification of cation exchange membrane with PANI for improvement in permselectivity. Acrylic acid grafted fluorinated ethylene propylene copolymer after sulphonation (FEP-g-AA-SO₃H) was used as the cation exchange membrane for modification. PANI is deposited electrochemically on the membrane. The electro-dialysis experiment shows improved permselectivity for the divalent cations. On the other hand, Montes Rojas (2007)²⁸ reported an easy method to modify the exchange membranes of electro-dialysis with electrosynthesized PANI. The polarization curves used in electro-dialysis of a nitrate solution showed some differences when using a modified membrane, possibly due to concurrent proton migration. Amado et al. (2004)^{29,30} developed composite membrane of high-impact polystyrene/PANI membranes for acid solution treatment by electro-dialysis; in this study, it was found that a synthesized membrane can be used to recover zinc in acid media. They have been reported also the development of polyurethane/PANI membranes for zinc recovery through electro-dialysis, being that these membranes can represent an alternative to commercial membrane for the metal finishing industry.³¹

In addition, these electromembranes differs from the conventional ion-exchange membranes due to the nature of the separation mechanism. The separation in an electromembrane is based on the electrical potential and/or magnetic field "barrier" generated by passing current through the membrane, whereas the separation in a conventional ion-exchange membrane relies on the relative ionic affinity of the compounds being separated.¹⁷

Heap leaching (HL) is a geotechnological method for processing of low-grade gold-containing ores and rejects of concentration plants. Alkaline solutions of cyanides are used in enormous amounts as a lixiviant for gold, which gives rise to quite a number of ecological problems; therefore, the use of al-

ternative lixiviant has been developed. The system iodine iodide has been suggested to extract gold of several sources.³² The main advantages of this process are high stability of the solution, low oxidation potential, and low possibility of reaction between iodine and sulfurous minerals.

In our study, we considered two main objectives: The first was to prepare a novel porous material with better mechanical and electroconductive properties, and our second objective was to evaluate the ion-exchange property of PANI, which has been studied only to a little extent.³³ To obtain an electroconductive membrane with ionic exchange capacity for anions is important because of its potential application in recovery processes in extractive metallurgy.

In the present article, we report the effect of plasticizers on the mechanical properties, T_g value, morphology, and electrical conductivity of CA membranes modified with polyacrylic acid (PAA) and coated with PANI. A preliminary evaluation of the properties of ionic interchange was made using gold iodine iodide solutions.

EXPERIMENTAL

Materials

Materials used were: CA powder, Aldrich. Poly (acrylic acid, sodium salt) (PAA) 35 wt %, w 15,000, Aldrich. Acetic Acid, Glacial, Sigma; Hydrochloric Acid, Merck; Ammonium persulfate, Fermont; Dimethyl phthalate 99% (DMP), Aldrich; Diethyl phthalate 99% (DEP), Aldrich; Triphenyl phosphate 99% (TPP), Aldrich; Potassium iodide, Fermont; Iodine 99.99%, Fermont; Gold, powder 99.99%, Aldrich; Anilina 99%, Merck, was distilled under vacuum in nitrogen atmosphere before use. All other reagents were used as received.

Preparation of CA membrane

CA membranes without and with PAA (CA and CA/PAA, respectively) and four lots of CA/PAA membranes using different plasticizers was prepared. For the preparation of the lot CA, 4 g of CA was weighed and dissolved in 50 mL of acetic acid, with constant stirring for 4 h. For the preparation of the lot CA/PAA, 4 g of CA 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 1 h. Four lots of plasticized membranes were prepared using the solution CA/PAA as the base. The first lot contains DMP plasticizer (lot A), the second lot contains DEP (lot B), and the third lot contains TPP (lot C). For these three lots, the CA : PAA : plasticizer weight ratio was 100 : 50 : 25. The membranes of lot D were prepared with a

TABLE I
Composition of Membranes

Components		Composition in weight parts
CA	Cellulose acetate	100
CA/PAA	Cellulose acetate : poly(acrylic acid)	100 : 50
Lot A	CA : PAA : DMF	100 : 50 : 25
Lot B	CA : PAA : DEF	100 : 50 : 25
Lot C	CA : PAA : TFF	100 : 50 : 25
Lot D	CA : PAA : DMF : DEF : TFF	100 : 50 : 25 : 25 : 2

mixture of the three plasticizers, using a DMP : DEP : TPP weight ratio of 25 : 25 : 2. This ratio is commonly used to plasticize CA.¹⁵ The composition of membranes is shown in Table I.

Membranes were prepared by phase inversion in a wet process. An aliquot of the solution corresponding to each lot of membrane was poured onto a flat glass plate of ~ 10 cm diameter. The excess of the solution was removed, leaving the plate covered by a fine layer. It was then placed in a coagulation bath (ice water mixture) for 30 s. The plate with the solution was then immersed in the same cold water for 15 min. Finally, the membrane was peeled off from the glass plate, washed in the same water, and dried at 25°C for 24 h on filter paper.

Coating of membranes with PANI

A solution 0.5M of aniline was prepared. Aniline was dissolved in 0.02M aqueous solution of HCl. Membranes were cut into strips to facilitate their coating and were placed in a glass vessel containing the aniline solution. The strip was immersed in the solution for 5 min. The strip was retired, drained, and placed in a glass vessel containing a solution of ammonium persulfate 0.5M, for 5 min. Subsequently, membranes were dried at 25°C for 24 h.

Characterization

The morphology of the membranes was evaluated by using a JEOL 5410LV scanning electron microscopy (SEM), operated at 15 kV. The electrical conductivity of the membranes 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 Proam multimeter. The evaluation of the mechanical properties of membranes was made following norm ASTM D 1708-93 for microtensile specimens. The samples were conditioned for 1 week to 23°C and 50% of humidity. Tests of stress and strain at break were performed with a speed of 0.1 mm min⁻¹, using a universal machine Tinius Olsen 1000. Differential thermal

analysis (DTA) was carried out on an equipment SDT 2960 simultaneous DSC-TGA TA instruments. Samples were taken approximately from 4 mg and it was warmed up until 600°C at a heating and cooling rate of 10°C min⁻¹ under a flow of 23 mL min⁻¹ of air. To test potential application as ion-exchange membrane, a leaching solution of 12 g iodine total (I₂ + KI) was used, with a KI to I₂ ratio of 2 : 1. The gold-iodide complex was prepared using the leaching solution, to which a predetermined amount of gold was added so that the Au concentration was 20 ppm. The concentration was verified by atomic absorption spectroscopy. Pieces of membranes were submerged in the gold-iodide solution under constant magnetic agitation for 12 h, after which the pieces of membranes were immediately removed from the gold-iodide solution. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy. The gold concentration in the gold-iodide solutions was determined with a Perkin Elmer 3110 atomic absorption spectrometer.

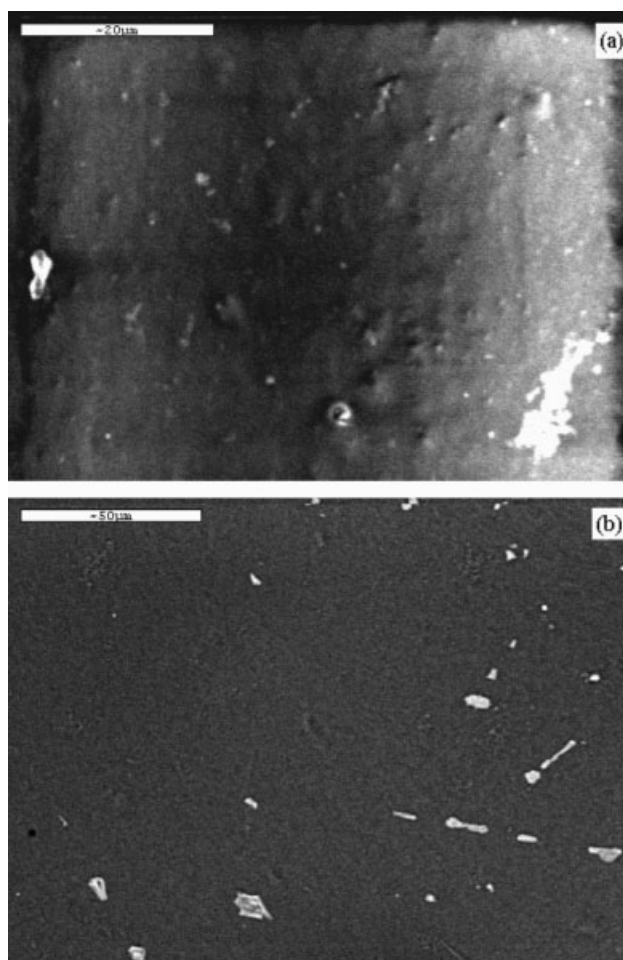


Figure 1 SEM micrographs of the surface of cellulose acetate membranes without poly(acrylic acid), CA, with magnification of $\times 750$ (a) uncoated (b) coated with PANI.

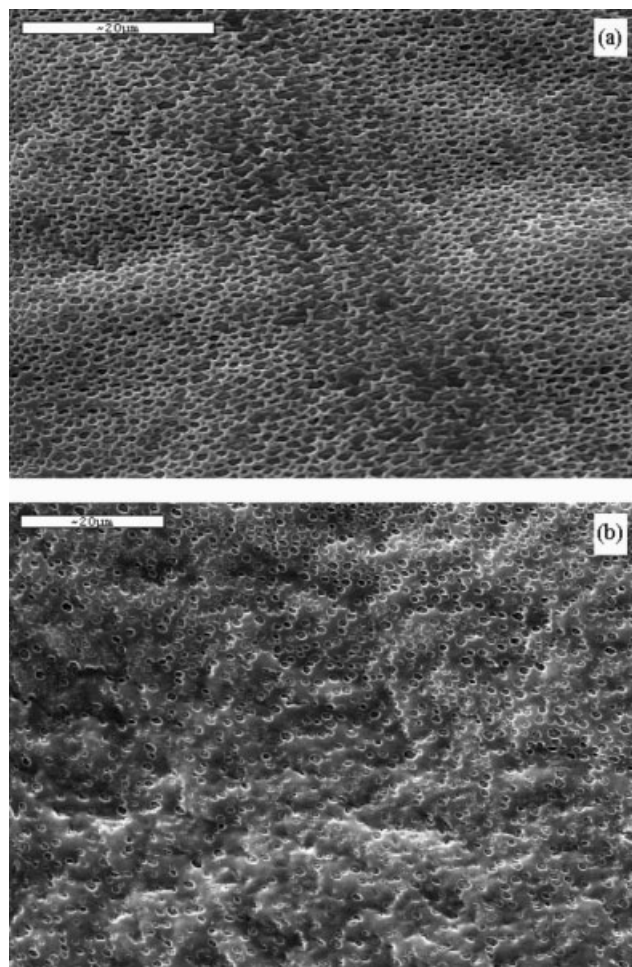


Figure 2 SEM micrographs of the surface of cellulose acetate membranes modified with poly(acrylic acid) (CA/PAA) with magnification of $\times 750$ (a) uncoated (b) coated with PANI.

RESULTS AND DISCUSSION

When PAA was added to CA membranes, a material with porosity needed for its potential application in ion-exchange processes was obtained. Figures 1 and 2 show the SEM micrographs of the surface of lots of membranes before and after coating with PANI, respectively. Figure 1 shows CA membranes without PAA, (CA), and the membranes does not shown appreciable porosity. The membrane without coating presented a clear color [Fig. 1(a)] and that with one coating presented a thin, dark layer corresponding to the PANI [Fig. 1(b)]. Figure 2 corresponds to CA membranes with PAA, and it was observed that the initial porosity of membranes is due to the modification with the PAA, showing pores with diameter between 0.5 and 2 μm [Fig. 2(a)], and with PANI the pore size was unaffected appreciably [Fig. 2(b)].

To improve the mechanical properties of CA membranes, three plasticizers were added. Figures 3–6 show the SEM micrographs of the surface of lots

of plasticized membranes before and after coating with PANI. The pore size in all lots using any plasticizer was greater than that in unplasticized membranes. This increase is attributed to the partial dissolution of plasticizer in water during the membrane formation in the coagulation bath. Figure 3(a,b) shows the SEM micrograph of a membrane lot A before and after coating with PANI, respectively. The pore size before coating ranges from 2 to 6 μm [Fig. 3(a)]. Two types of pores can be observed in the membrane coated with PANI [Fig. 3(b)], well-defined pore with diameter between 3 and 11 μm and larger pores formed by the union of two or more pores. This union of pore surface is attributed to a small degradation of the membrane, due to contact with the solution of aniline dissolved in aqueous HCl. In the case of lot B, membranes without coating have a pore size ranging from 3 to 14 μm [Fig. 4(a)] and after coating with PANI there occurs union of pores, creating larger pores and irregular diameter,

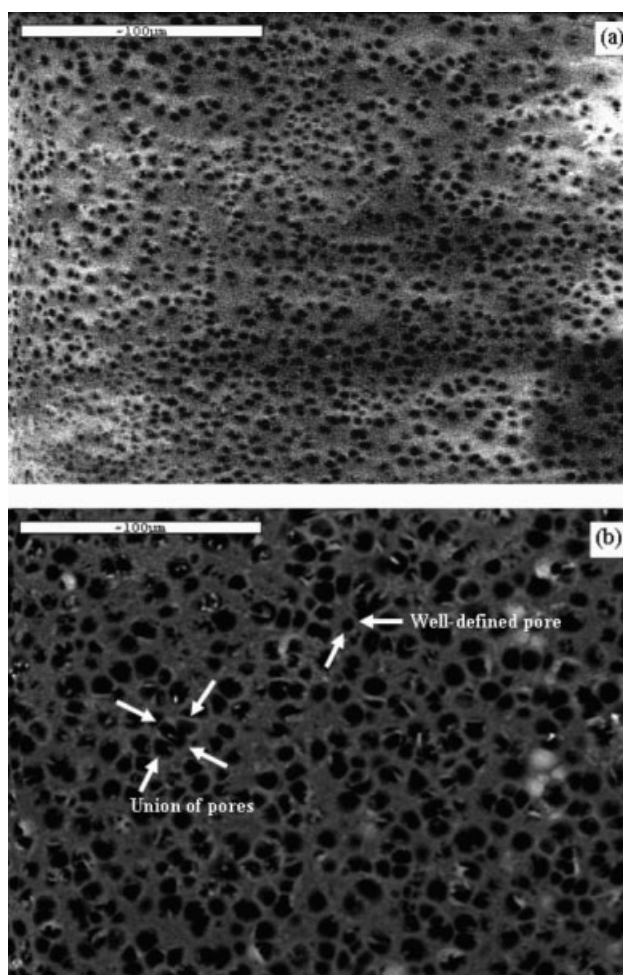


Figure 3 SEM micrographs of the surface of membranes of lot A with magnification of $\times 500$ (a) uncoated (b) coated with PANI.

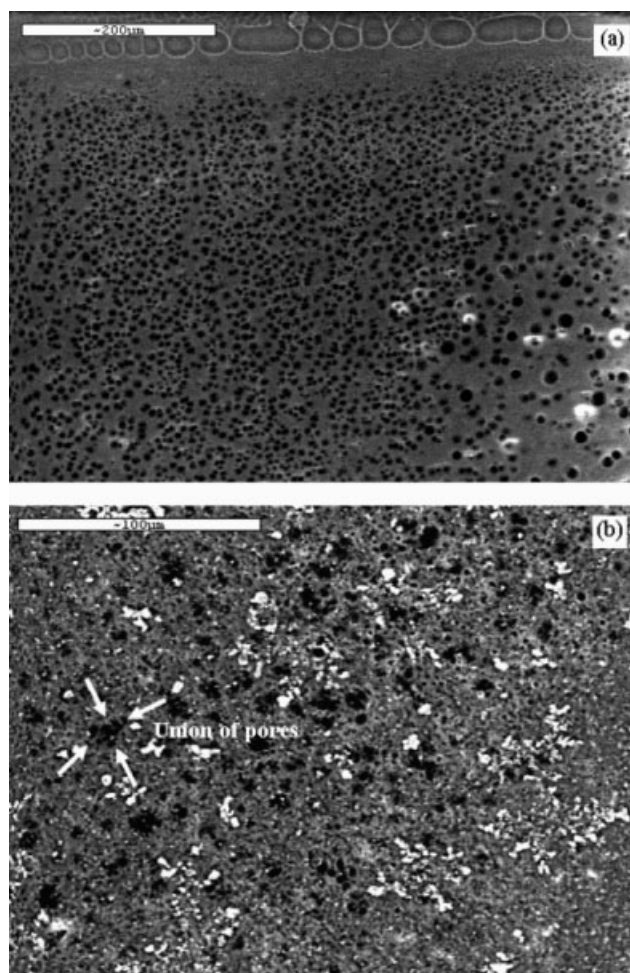


Figure 4 SEM micrographs of the surface of membranes of lot B with magnification of $\times 500$ (a) uncoated (b) coated with PANI.

which varies from 6 to 15 μm [Fig. 4(b)]. In the case of lot C, no significant difference was observed in the pore size before and after coating with PANI. The pore size of this lot without coating was 3–9 μm [Fig. 5(a)] and after coating the pore size was 3–10 μm [Fig. 5(b)]. Membranes lot D without coating shows a very large pore size of up to 154 μm [Fig. 6(a)]. We can clearly observe smaller pores within the larger pores, making it obvious that the membrane presents an asymmetric structure. The superficial pore size is unaffected appreciably by coating with PANI [Fig. 6(b)].

The increased pore size in membranes of lots A and B containing plasticizers DMF and DEF, Figure 3(b) and 4(b) respectively, coated with PANI is attributed possibly to an acid hydrolysis of the plasticizers on the surface of membrane, and this hydrolysis could be generated by the aqueous HCl, which functions as a solvent for aniline during the coating of the membrane. To confirm this hypothesis, the simulation of these reactions was realized using the

software HiperChem. The values for Gibbs free energy change (ΔG) of reaction of membrane lots A and B were $-2618 \text{ Kcal mol}^{-1}$ and $-3358 \text{ Kcal mol}^{-1}$, respectively. Whereas the value in membranes of lot C was $115,987 \text{ Kcal mol}^{-1}$; these results show that in lots A and B a hydrolysis reaction of plasticizer can take place, whereas for the lot C this reaction is impossible because of the high value for ΔG of reaction. The hydrolysis reactions proposed are shown in Figure 7.

Figure 8 shows the SEM images of the cross-section of a membrane of lot A. With an increase of magnification to $200\times$, the pores of the surface and cross-section can be observed [Fig. 8(a)], which clearly shows that the pores of the surface are larger than the pores on the cross-section, and with an increase of magnification to $750\times$ [Fig. 8(b)], it can be observed that the pore on surface can follow several paths to cross to the other side of the membrane, and this is a proof that exist asymmetric structure on the membrane.

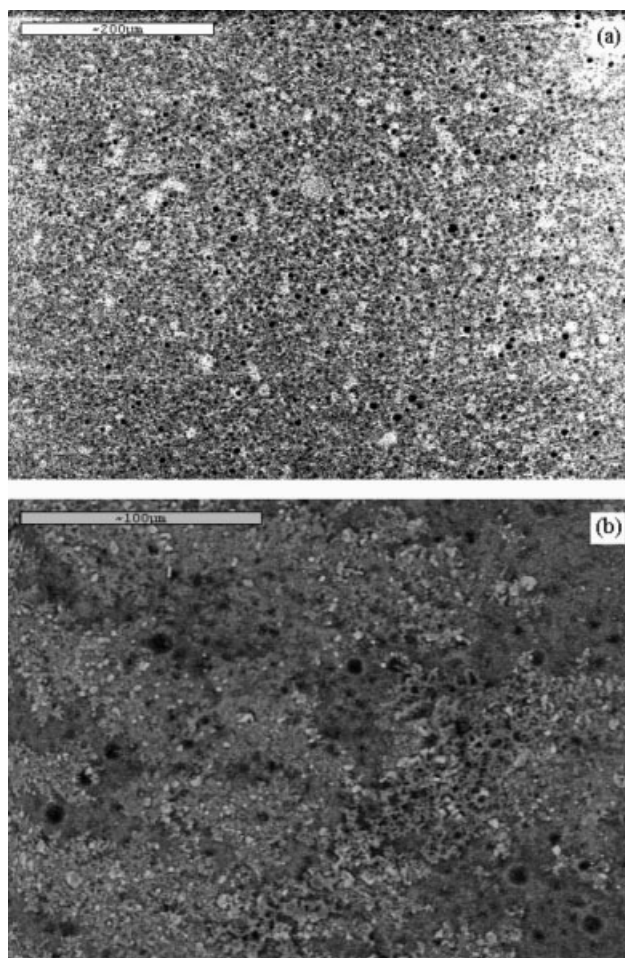


Figure 5 SEM micrographs of the surface of membranes of lot C with magnification of $\times 500$ (a) uncoated (b) coated with PANI.

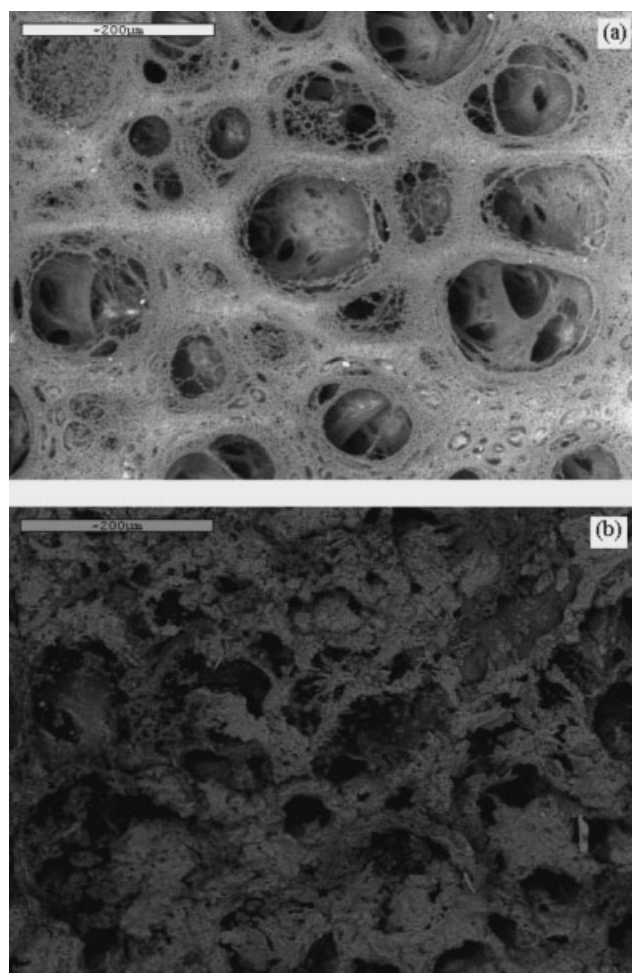


Figure 6 SEM micrographs of the surface of membranes of lot D with magnification of $\times 500$ (a) uncoated (b) coated with PANI.

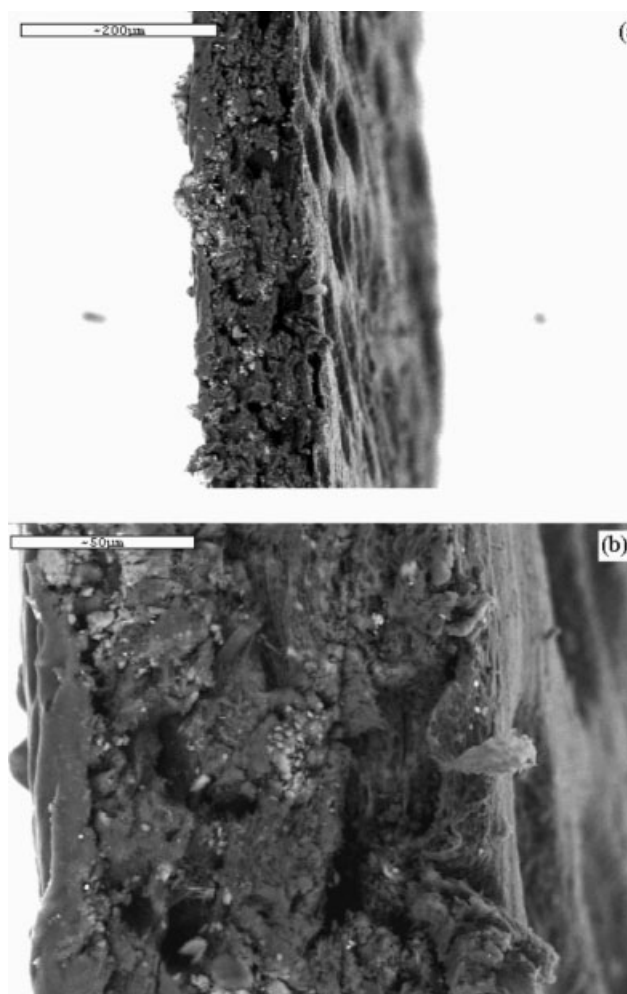


Figure 8 SEM micrographs of the cross-section of a membrane of lot A coated with PANI (a) with magnification of $\times 200$ (b) with magnification of $\times 750$.

When CA/PAA/plasticizer membranes were coated with PANI, an electroconductive material with potential application in electro dialysis processes and ion exchange were obtained. Table II summarizes the electrical conductivity determined for each lot of membrane coated with PANI.

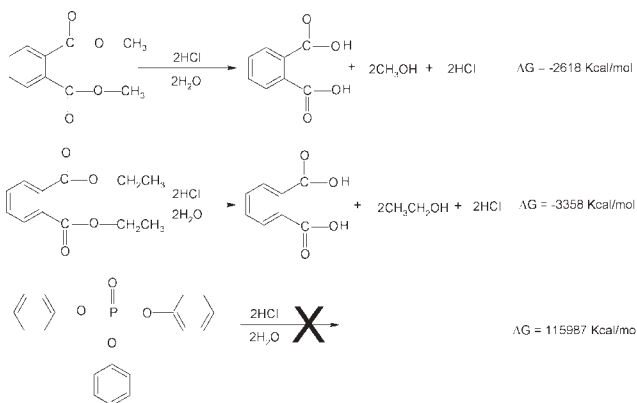


Figure 7 Proposed acid-hydrolysis reaction for plasticizers.

The electrical conductivities of the membranes ranged from 10^{-8} to $10^{-3} \text{ S cm}^{-1}$ depending on the conditions of preparation. The electrical conductivity of the membranes prepared with polyelectrolyte PAA is three orders of magnitude greater than that of the

TABLE II
Electrical Conductivity Values for Each Lot of Membrane Coated with Polyaniline

	Electrical conductivity (S cm^{-1})
AC-PANI	1.03×10^{-8}
AC/PAA/PANI	1.51×10^{-5}
Lot A-PANI	3.68×10^{-4}
Lot B-PANI	2.21×10^{-4}
Lot C-PANI	1.37×10^{-3}
Lot D-PANI	5.57×10^{-4}

TABLE III
Mechanical Properties of Unplasticized and Plasticized Membranes

Membrane	Stress at break (MPa)	Strain at break (%)
AC	25.23 ± 4.81	3.8 ± 0.2
AC/PAA	9.38 ± 1.29	0.2 ± 0
Lot A	1.81 ± 0.11	2.6 ± 0.5
Lot B	2.02 ± 0.18	3.8 ± 0.4
Lot C	1.86 ± 0.04	3.5 ± 0.3
Lot D	1.74 ± 0.13	3.2 ± 0.4
^a Lot C	0.75 ± 0.11	4.4 ± 1.6

^a Coated with PANI.

membranes without PAA. This result could be correlated to the pore formation. The nonporous membranes without PAA (AC-PANI) have no electrical path percolation, whereas membranes with pores provide the path percolation through PANI on the cross-section of the membrane, and in this way, an electrically conductive membrane is obtained. In addition, the PAA serves as a template for the polymerization of aniline, PANI, thus aniline is polymerized in a more orderly manner, resulting in longer chains of PANI with fewer ramifications, and therefore a better electrical conductivity value is obtained.³⁴ The incorporation of plasticizers enhances the electrical conduction of the membranes because the plasticizers bring greater order to chains of PAA. We can establish that the plasticizer indirectly helps to have a more ordered structure of PANI facilitating the transport charge carrier, increasing the electrical conductivity. The lot C has the maximal value in electrical conductivity because the plasticizer in this lot, TPP, is a molecule with greater volume than the other plasticizers used, providing higher order to PAA chains and consequently to PANI. These same observations have been reported also by Doufor and supported by WAXD studies.^{35,36}

The mechanical properties of the unplasticized and plasticized membranes were studied using stress-strain measurements (Table III), and by means

TABLE IV
 T_g Values Determined by DTA of Unplasticized and Plasticized Membranes

Membrane	T_g (°C)
AC	135.92
AC/PAA	155.97
Lot A	118.99
Lot B	110.71
Lot C	122.80
Lot D	127.88
^a Lot C	113.86

^a Coated with PANI.

of DTA, the value of the T_g for each membrane was determined (Table IV).

When PAA was added to CA membranes, the % strain at break is reduced remarkably from 3.8% to 0.2%, accompanied with an increase in the T_g value of CA, which indicates that a crossover could exist between the chains of CA and PAA, reducing mobility of polymeric chains and causing a rigidity in the material. In membranes CA/PAA with plasticizers, an increase in % of strain accompanied by a diminution of stress at break and T_g value was observed. This phenomenon is attributed to the fact that the plasticizers can locate between the chains of polymers, decreasing intermolecular bonding forces where the free sliding of polymeric chains is permitted.³⁷ We can observe that the membranes to which the mixture of the three plasticizers was added to plasticize CA; according to the concentration recommended in literature,¹⁵ presented values of stress and strain at break are very similar to the values for membranes that involve a single plasticizer. We can observe that the improvement of the mechanical properties obtained with the use of the plasticizer is not significantly affected by the coating with PANI.

A potential application of membranes obtained is as ion-exchange material, due to PANI chains are doped with chloride ions, which could be interchanged with other anions, for example, the gold-iodide complex. Taking advantage of this property, tests of ionic interchange for the gold recovery using as lixiviant solution complex iodine-iodide was realized.

To test the potential application as ion-exchange material, membranes of lot C were used. The result obtained in this experiment is presented in Table V. We can observe that the amount of gold adsorbed by unit of adsorbent mass diminishes with the increase of the solid/liquid ratio. This observation apparently indicates that a low proportion of membrane promotes the most efficient use of the same, possibly due to smaller amount of adsorbent material; the active sites of membranes present a lower

TABLE V
Values Obtained in the Tests of Potential Application as Ion-Exchange Membrane for Gold Recovery from Gold-Iodide Solutions

Solid/liquid ratio (mg mL ⁻¹)	Gold loading on membrane (mg g ⁻¹)		Fraction of extracted gold	
	Value	± Error	Value	± Error
1	1.2666	±0.1154	0.0629	±0.0051
2.5	0.9466	±0.1222	0.1153	±0.0141
5	0.9466	±0.1006	0.2366	±0.0251
7.5	0.9422	±0.0630	0.3462	±0.0201
10	0.9366	±0.0862	0.4635	±0.0397

competition among them for the process of interchange of chloride ions by the Au-Iodide complex, (AuI_2^-). Nevertheless, to obtain a suitable gold recovery, it is necessary to obtain good results in terms of the fraction of extracted gold. Figure 9 shows the fraction of extracted gold vs. the solid/liquid ratio (mg of membrane/mL solution), it is possible to observe a linear increase of the fraction of extracted gold as the amount of adsorbent material is also increased; this can be explained in terms of a greater capacity of adsorption available in the case of a high value of the solid/liquid ratio. A blank experiment (membrane uncoated with PANI) was realized for each solid/liquid ratio to know ion exchange properties of membrane coated with PANI, (Table VI), for all solid/liquid ratio the fraction of extracted gold is increased with the PANI coating. Finally, we can say that the best gold recovery is obtained for the prepared samples at a solid/liquid ratio of 10.

CONCLUSIONS

SEM analysis shows that the porosity of CA membranes is due to the modification with the PAA. This porosity is accompanied by an increase in electrical conductivity of $10^{-8} \text{ S cm}^{-1}$ (nonporous membranes) to $10^{-5} \text{ S cm}^{-1}$ for membranes with PAA. The use of plasticizers indirectly gives a more ordered PANI, with highest conductivity values, $10^{-3} \text{ S cm}^{-1}$, membrane lot C. With the increase in % strain at break and the diminution in $T_{g'}$, it can be concluded that the plasticizers improve the mechanical properties of membranes. Finally, good results were obtained

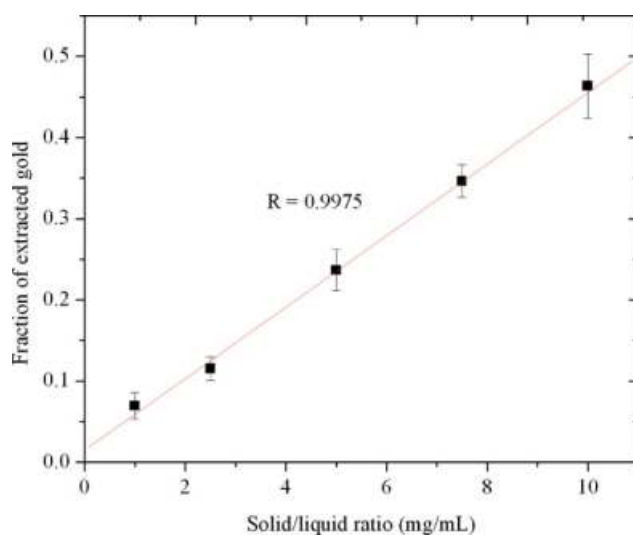


Figure 9 Effect of the solid/liquid ratio on the fraction of extracted gold by membranes of lot C, using a gold-iodide solution, with an initial gold concentration of 20 ppm.

TABLE VI
Fraction of Extracted Gold of Membranes without PANI (Blank) and Coated with PANI

Solid/liquid ratio (mg mL ⁻¹)	Fraction of extracted gold (blank)	Fraction of extracted gold (with PANI)
1	0.0253	0.0629
2.5	0.0456	0.1153
5	0.0837	0.2366
7.5	0.1294	0.3462
10	0.1852	0.4635

with the use of these membranes in the gold recovery from gold-iodide solutions.

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Adsorption of a Gold-Iodide Complex (AuI_2^-) onto Cellulose Acetate-Polyaniline Membranes: Equilibrium Experiments

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ABSTRACT: The adsorption of AuI_2^- complex onto acetate cellulose-polyaniline membranes was investigated. Kinetic experiments showed a rapid adsorption of this complex, which was attributed to an ion-exchange mechanism. Equilibrium adsorption results were represented by the Langmuir model, showing a correlation coefficient of 0.9852. Langmuir parameters K and Q_m were found to be 0.2937 L mg^{-1} and

1.2394 mg g^{-1} , respectively. Approximately 94% of AuI_2^- was adsorbed when a solid/liquid ratio of 40 g L^{-1} (grams of membrane/ liter of solution) was used. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2670–2674, 2009

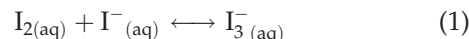
Key words: conducting polymers; separation techniques; membranes; ion exchangers

INTRODUCTION

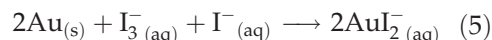
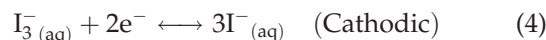
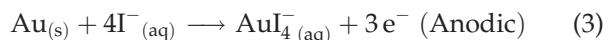
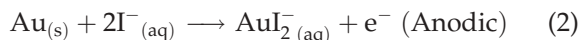
Precious metals, such as silver, gold, and platinum, are recovered from a wide variety of sources. In addition to traditional precipitation processes, solvent extraction and ion-exchange processes are also used.¹ Chlorine was used to dissolve gold from ores and concentrates, during the second half of the 19th century in Australia and North America.² At the beginning of the 20th century, this process was gradually replaced by the more economical alkaline cyanide leaching.³ Alkaline solutions of cyanides are used in large amounts as solvents for gold, which gives rise to a number of potential ecological problems.⁴ Main concerns in the mining industry at the present time are the increase in environmental awareness and more restrictive environmental legislations. Thus, alternative methods become necessary to replace old technologies to comply with new regulations. Although potassium cyanide is the most economical lixiviant at the moment, it raises certain concerns regarding the operators' health. These include the adsorption through the skin and accidental ingestion of cyanide salts by the operators, and the formation of deadly hydrogen cyanide gas. Dangerous situations may occur when cyanide ions form organic and inor-

ganic complexes, which are difficult to destroy by conventional methods contaminate effluent streams.⁵

Based on the above considerations, several researchers have been investigating alternative lixivants, which include the halogen group.^{6–8} From this group, iodine forms the most stable gold complex in aqueous solutions, even up to a pH of 14.⁹ The dissolution of gold in an iodine/iodide solution is an oxide-reduction process (redox), which can be shown in terms of an electrochemical cell, which includes separate anodic and cathodic chemical reactions. This process begins with the formation of the triiodide ion as follows^{10,11}:



This ion serves as an oxidant in the following electrochemical reactions.



The standard potentials of reactions (5) and (6) of gold in iodide solutions are: $E^0\text{AuI}_2^-/\text{Au} = 0.578\text{V}$

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and $E^0\text{AuI}_4^-/\text{Au} = 0.550\text{V}$. Therefore, the reaction (5) is the most acceptable mechanism for the dissolution of gold with triiodide ions as an oxidizing agent.¹²

The use of activated carbon for the recovery of gold from leach liquors has gained wide acceptance in the mining industry. The most common method of extraction is the carbon-in-pulp process. The gold adsorption occurs from a slurry containing fine ground rock particles and possibly a number of other metals in solution and organics, which may poison the carbon.¹³ Recently, there has been interest in using ion-exchange resins instead of activated carbon. Lukey et al.¹⁴ investigated the properties of five weak-base type resins that contain a small amount of strong base groups and different aliphatic amino functional groups. The experimental data showed that gold cyanide adsorbed onto each resin in both nonsaline and highly saline solution as $[\text{Au}(\text{CN})_2]^-$ complex. In either of these processes, the adsorbent was in granular form and was contacted with a leached slurry in a series of agitated tanks. From both kinetics and equilibrium points of view, a better way of contacting the adsorbent and the solution is the use of a packed column. In the case of granular adsorbents, the flow of mine slurry through a packed bed is not practical because the slurry blocks the bed. If ion-exchange membranes could be used for treating gold slurries, it would be possible to simulate a packed bed by passing the slurry through a column in which a number of parallel sheets of membrane are placed.¹³ Diniz et al.¹⁵ reported matrices containing polyaniline displaying ion-exchange properties, the matrices being selective to anions based upon their radii, with a cut-off value around 240 pm.

The present authors reported the synthesis of cellulose acetate (CA) membranes coated with polyaniline (PANI)¹⁶ porous membranes with good electrical and mechanical properties were obtained. These membranes showed a potential use in a process to recover gold.

PANI is an intensively studied polymer due to its electrical, electrochemical, and optical properties and its high environmental stability, which confers it potential use in many applications including sensors, rechargeable batteries, anticorrosion coatings, electrochromic displays and selective membranes among others.¹⁷⁻²² CA is commonly used to prepare membranes for different uses and various methods have been developed to control its pore diameter using polyelectrolytes.²³

The property of ion exchange of polyaniline is reported since 1972 by Muller and Jozefowicz.²⁴ By September 2008, 17,073 references containing "polyaniline" as keyword were found, of which only 1.2% of references were found containing "ion exchange" as associated keyword (SciFinder). Thus, there

exists interest to take advantage of this property of PANI. In this article, the ion-exchange properties of CA-PANI membranes synthesized are reported. The goal of this work was to test the membranes as potential ion-exchange adsorbents for the recovery of gold from iodine-iodide aqueous solutions.

EXPERIMENTAL

Materials used in this study included CA powder (Aldrich), poly(acrylic acid, sodium salt) (PAA) 35 wt %, w 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). Anilina 99% (Merck) was distilled under vacuum in nitrogen atmosphere before use. All other reagents were used as received.

Preparation of CA membranes coated with PANI

CA membranes modified with PAA and plasticized with TPP were prepared. The membrane preparation was performed according to the procedure described in a previous article.¹⁶ 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 one hour. Finally, 1 g of TPP was added to the solution, while keeping stirring for 1 h.

The membranes were prepared by phase inversion in a wet process. An aliquot of the solution corresponding to each batch of membrane was poured onto a flat glass plate of approximately 10 cm diameter. The excess of the solution was removed, leaving the plate covered by a fine layer of solution. The plate was then placed in a coagulation bath (ice water mixture) for 30 s. The plate with the solution was then immersed in the cold water for 15 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.

For the coating of membranes with PANI, a solution of 0.5M of aniline was prepared. Aniline was dissolved in 0.02M aqueous solution of HCl. The membranes were cut into strips to facilitate their coating and were placed in a glass vessel containing the aniline solution. The strip was immersed in the solution for 5 min. The strip was removed, drained, and placed in a glass vessel containing a solution of ammonium persulfate 0.5M, for 5 min. Subsequently, the membranes were dried at 25°C for 24 h.

Test of application as ion-exchange membranes

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 (AuI_2^-) was prepared using the leaching solution, to which a predetermined amount of gold was added to achieve the range of concentration 2.5–20 ppm. Total Au concentration was verified by atomic absorption spectroscopy using a Perkin Elmer 3110 atomic absorption spectrometer.

All tests as ion-exchange membranes were made at 25°C. Kinetic experiments were done to determine the time of contact necessary to achieve equilibrium conditions of the membrane-solution system. The membranes were cut into square pieces of 1×1 cm. The pieces were introduced in an Erlenmeyer flask, and submerged in to the solution of AuI_2^- complex, under constant magnetic agitation (155 rpm), after which the pieces of membranes were immediately removed from the solution. The contact time of the membrane with the solution of AuI_2^- complex varied in the range of 0–720 min. One experiment was done per contact time tested. In all the experiments, the initial concentration of total Au was kept at 10 ppm. The solid/liquid ratio used was 10 g L^{-1} (grams of membrane/liter of solution). The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

Equilibrium experiments

In the equilibrium experiments, membranes coated with PANI were used. The effect of the solid/liquid ratio versus percentage of Au adsorption was tested. For these experiments, the membranes were cut into pieces of 1×1 cm. Different amounts of mass membranes, ranges from 1 to 40 g L^{-1} , were introduced in to Erlenmeyer flasks and submerged in the solution of 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 AuI_2^- complex. 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 2.5–20 ppm). The solid/liquid ratio (grams of membrane/liter of solution) used varied from 1 to 40 g L^{-1} . The membranes were cut into pieces of 1×1 cm and were introduced into Erlenmeyer flasks and submerged into the solution of AuI_2^- complex, under constant magnetic agitation (155 rpm) for 12 h, after which the pieces of membranes were immediately removed from the solution. The concentration of Au in the solution was analyzed by atomic absorption spectroscopy.

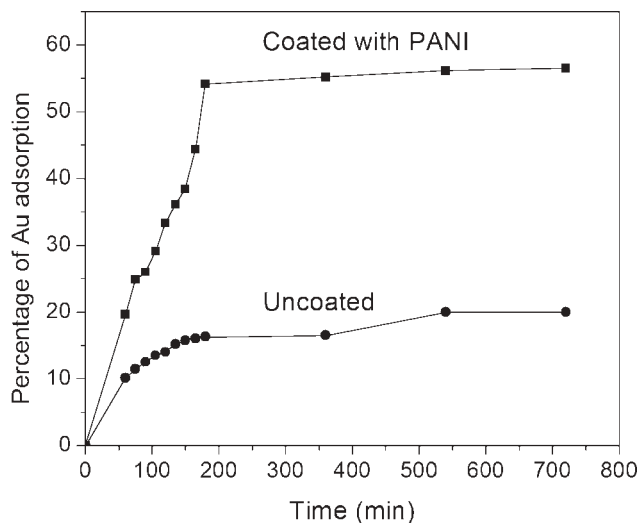


Figure 1 Adsorption kinetics of AuI_2^- complex onto CA membranes without and with coated of PANI, solid/liquid ratio = 10, $[Au_i] = 10$ ppm, $T = 25^\circ\text{C}$.

RESULTS AND DISCUSSION

A detailed description of the porous membranes obtained in this study is presented elsewhere.¹⁶ A summary of their characteristics follows. The pore size varied from 3 to $10 \mu\text{m}$. Uncoated membranes showed a thickness of 0.042 cm, whereas coated membranes of 0.127 cm. The membranes coated with PANI showed electrical conductivity in the order of $10^{-3} \text{ S cm}^{-1}$ and its mechanical properties were acceptable.

CA membranes uncoated and coated with PANI were used in testing kinetic. The results are presented in Figure 1, where the percentage adsorption of Au was calculated according to the following expression

$$\text{Percentage adsorption of Au} = \frac{(C_0 - C) \times 100}{C_0} \quad (7)$$

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 1 shows that the percentage adsorption of Au increases with time and achieves equilibrium at about 180 min for membranes coated with PANI, and 540 min for membranes uncoated for an initial Au concentration of 10 ppm. It shows that the adsorption of Au remained constant, implying equilibrium has been reached. To verify the equilibrium conditions has been obtained, a sample of one of the experiments was left sealed over a week, upon which the chemical analysis of this solution was repeated. The results verified that the solution concentration remained constant.

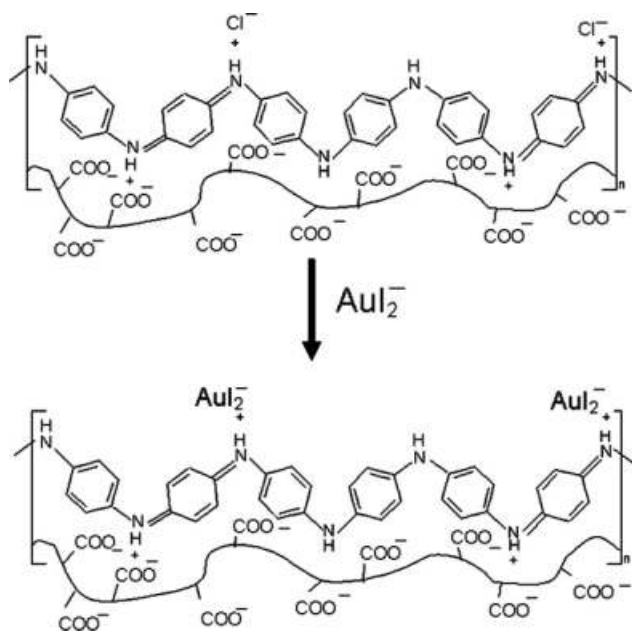


Figure 2 Schematic representation of the ion-exchange process of AuI_2^- onto CA-PANI membranes.

The results in Figure 1 indicate that the adsorption kinetics is faster than those reported for commercial resins and membranes of anion exchange, and activated carbon using cyanide as leaching solution for Au, which attained conditions equilibrium in the range of 1200–2500 min.¹³ Membranes coated with PANI presented adsorption kinetics faster and with higher gold recovery than those obtained with uncoated membranes. These results are attributed to the presence of PANI. CA membrane contains PAA, which serves as a template for PANI chains. These chains get doped with chloride ions, which are used to give electrostatic stability, these chloride ions may be interchanged with other anions, such as the AuI_2^- complex. We proposed this mechanism to explain these results. Figure 2 shows a schematic drawing of our model of ion exchange. Wang²⁵ reported that the relative anion-exchange selectivity decreased in the following order: $I^- > SCN^- > NO_3^- > Br^- > Cl^- > F^-$. This sequence agrees with that for quaternary ammonium anion exchangers. To verify that Cl^- was indeed exchanged during the process by AuI_2^- complex, the concentration of Cl^- was determined before and after the contact by ion chromatography. The concentration of Cl^- in solution before and after the process was less than 1 ppm and 15 ppm, respectively. Hence, an ion exchange between Cl^- and AuI_2^- complex is likely to have occurred.

In the equilibrium experiments, only membranes coated with PANI were tested. This was based on the fact that the percentage of Au adsorption was higher than for uncoated membranes. Figure 3 shows the effect of the solid/liquid ratio; grams of mem-

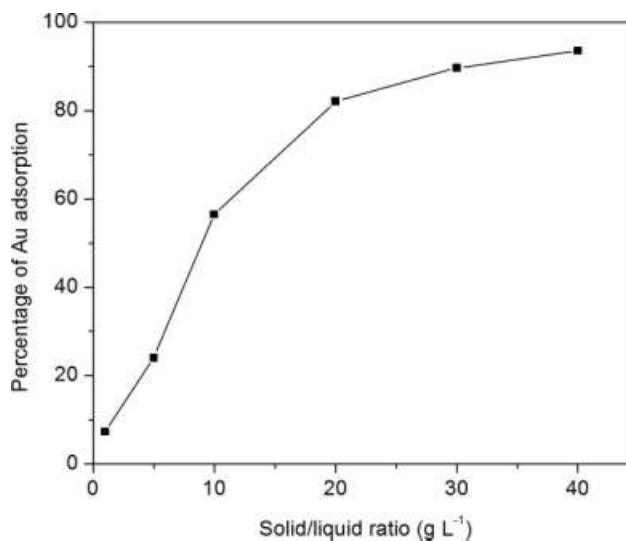


Figure 3 Effect of the solid/liquid ratio; grams of membrane/liter of solution, on the percentage adsorption of AuI_2^- complex of membranes coated with PANI.

brane/liter of solution on the percentage adsorption of AuI_2^- complex of membranes coated with PANI. It is noted that the percentage of extracted gold increases as the amount of adsorbent material increases. This is an expected result because the larger the amount of membrane, the greater capacity of adsorption is available. The percentage adsorption of Au, using a solid/liquid ratio of membrane of 40 g L⁻¹ was about 94%. Value is acceptable, and over 90% of published by Wang and Liang²⁶ in the adsorption of gold ions onto chitosan and *N*-carboxyl methyl chitosan.

The equilibrium experimental data were adjusted in the linear forms of isotherms of Langmuir and

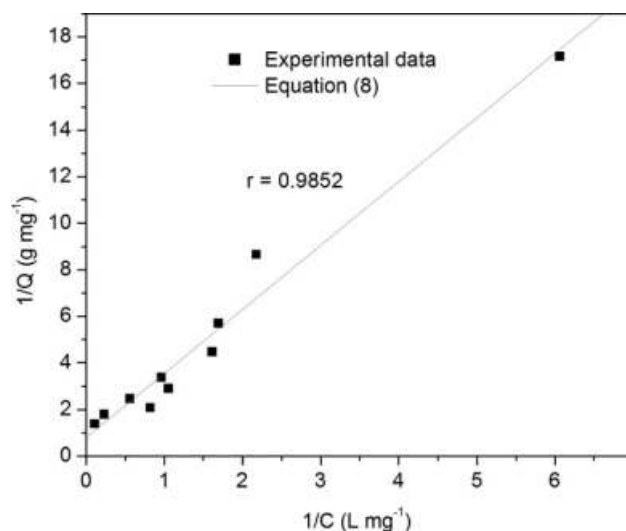


Figure 4 Adsorption isotherm of Langmuir for AuI_2^- complex on CA-PANI membranes.

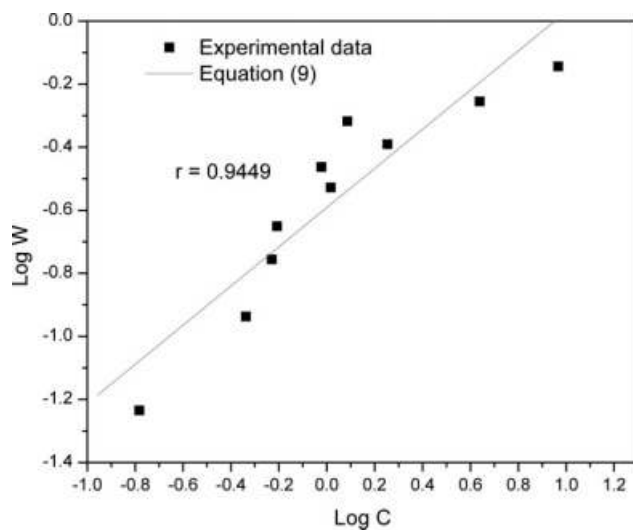


Figure 5 Adsorption isotherm of Freundlich for AuI_2^- complex on CA-PANI membranes.

Freundlich. The equations are shown in (8) and (9), respectively.

$$\frac{1}{Q} = \frac{1}{Q_m K C} + \frac{1}{Q_m} \quad (8)$$

$$\text{Log} Q = \text{Log} c_1 + \frac{1}{c_2} \text{log} C \quad (9)$$

where Q is the amount of Au adsorbed per unit weight of membrane at equilibrium concentration (mg/g), C is the equilibrium concentration of Au (ppm) in the aqueous solution, Q_m is the maximum capacity of adsorption, K is the constant of the isotherm of Langmuir; c_1 and c_2 are empirical constants of Freundlich. Figures 4 and 5 show the equilibrium isotherms of Langmuir and Freundlich, respectively. The best linear fit of experimental data was obtained by the Langmuir isotherm. The values for K and Q_m were found to be 0.2937 L mg^{-1} and 1.2394 mg g^{-1} , respectively. The linear fitting showed a correlation coefficient (r) of 0.9852. Therefore, these results suggest a monolayer adsorption process, without lateral interactions between the adsorbed molecules.²⁷

CONCLUSIONS

CA-polyaniline membranes are effective adsorbents for recovery of AuI_2^- complex. The adsorption of Au

on CA-polyaniline membranes was attributed to the exchange of Cl^- and AuI_2^- complex ions. The adsorption equilibrium data were found to obey the Langmuir isotherm model. Kinetics and equilibrium experiments showed that CA-PANI membranes represent a promising alternative for a gold recovery process without the use of cyanide solutions. Through this analysis we show the application of the polymeric material prepared.

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Fibrous membranes of cellulose acetate and poly(vinyl pyrrolidone) by electrospinning method: preparation and characterization

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Review

Fibrous membranes of cellulose acetate and poly(vinyl pyrrolidone) by electrospinning method: preparation and characterization

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Abstract

Fibrous membranes of cellulose acetate (CA) and poly(vinyl pyrrolidone) (PVP) were obtained by using the electrospinning method. Systematically varying the experimental conditions, the optimal conditions for preparation of fibrous membranes were found: both CA and PVP a concentration of 8% weight. The CA was dissolved in a acetone: water solution, ratio volume 80:20 and the PVP is dissolved in ethanol:water solution, ratio volume 85:15. The flow rate for both polymers was 1.5 mL h^{-1} . The same applied voltage value and the distance between the needle and collection plate was for both polymers, 15 kV and 15 cm respectively. The morphology of fibrous membranes was evaluated by microscopy electronic scanning (SEM). The CA fibers showed ribbon morphology, while the PVP fibres were cylindrical, in both cases with diameters in the micrometer range. Thermogravimetric Analysis (TGA) showed that the CA show a complete degradation to 445°C , while the fibrous membranes PVP required a value of temperature for degradation of up to 571°C . Fibrous membranes PVP/CA/PVP shows a higher value of strain at break (%), and a lower value of tensile strength (MPa) compared to CA/PVP/CA.

Keywords: *Membranes, composite, morphology, thermogravimetric analysis (TGA), mechanical properties*

1. Introduction

Electrospinning technique is a method widely used in recent years, to produce polymeric fibers with diameters from nanometer to micrometer scale. According to a review in SciFinderScholar in 1994 only 2 publications were made, but the number of publications has increased so rapidly over time, up to the year of 2008 there were 1278 research papers published. Figure 1 presents the data obtained in SciFinderScholar of this growth of publications with respect to time.

In these publications, a large number of applications and different materials have been reported. Including Nylon, obtaining uniform ultrafine fibers [1], poly(ethylene) used in tissue engineering and biomedical materials [2,3], seda for use in biomedicine and tissue engineering [4,5], poly(methyl methacrylate) used in Nanofibers electroconductive [6-8], poly(acrylonitrile) obtaining micro-nanotubes with potential use for the storage of hydrogen, platelet adhesion, lithium batteries [9-12], cellulose with applications in biomaterials and membranes for the purification of antibodies [13-17], poly(vinyl alcohol) used in tissue engineering, biomedical materials, bactericides, study the effect of polarity, electronic devices and gas sensors [18-24] and other materials.

When there is an electrospinning process, a continuous strand of a polymer liquid (i.e., solution or melt) is ejected through a nozzle by a high electrostatic force to deposit randomly on a grounded collector as a non-woven fiber mat [25]. A candidate material to produce nano and micrometric fibers with application in tissue engineering, controlled release of drugs and bactericide is cellulose acetate (CA) [26-37]. Besides, the poly(vinyl pyrrolidone) (PVP) is another material widely used, for developing nanofiber with application in microencapsulation, controlled release of drugs and chemical and biological sensors [38-43]. The goal of this report is to investigate the optimal conditions for preparation of fibrous membranes of cellulose acetate and poly(vinyl pyrrolidone) via electrospinning.

2. Experimental

2.1 Materials

Materials used were: Cellulose acetate (CA, white powder; $M_n = 50,000$), Aldrich. Poly(vinyl-pyrrolidone) (PVP, white powder; $M_w = 360,000$), Aldrich. Acetic acid glacial, Sigma. Acetone, Aldrich. Ethanol, Aldrich. All the reagents were used as received.

2.2 Fibrous membrane preparation

To prepare fibrous membranes, five variables were studied. The concentration of polymer solution, solvent used, the applied voltage, the flow of the solution and the distance between the needle and plate collector. In the case of fibrous membranes of CA, an acetone-water mixture was used as a solvent, varying the polymer concentration in the range of 5 to 10%W. For fibrous membranes PVP, an ethanol-water mixture was used, varying the polymer concentration in the same range as for CA.

The polymer solution was transferred into a plastic syringe of 10 mL capacity and a needle of 0.8 mm in diameter. Using a syringe pump kdsScientific, the flow of velocity was varied in the range of 0.1-5 mL h⁻¹. A strong voltage was applied to the polymer solution in a range of 10-30 kV, using a power supply high voltage, Spellman, model CZE 1000R. Finally the distance between the needle and the collector plate varied in the range from 5 to 20 cm. A collector plate of aluminum with a square (10 cm x 10 cm) was used.

2.3 Characterization

The morphology of the fibrous membranes was evaluated by using a JEOL 5410LV scanning electron microscopy (SEM), operated at 15 kV. Thermogravimetric analysis (TGA) was carried out on an equipment SDT 2960 simultaneous DSC-TGA TA instruments. Samples were taken approximately from 5 mg and it was warmed up until 600°C at a heating and cooling rate of 10°C min⁻¹ under a flow of 20 mL min⁻¹ of nitrogen as purge gas. Tensile tests were performed on fibrous membranes. Testing was performed using a Universal testing machine (MINIMAT) equipped with a 200 N load

cell, and a constant crosshead speed of 1 mm/min. Rectangular samples, 31.75 x 4.76 mm were cut to allow an initial gage length equal to 12.5 mm. Before testing the samples were conditioned at a 55 % relative humidity and room temperature, 28 °C

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3. Results and discussion

3.1 Electrospinning process: Optimum preparation conditions

Systematically varying the experimental conditions, the optimal conditions for preparation of fibrous membranes were found, which are described below. Both CA and PVP a concentration of 8% weight was found. The CA was dissolved in a acetone:water solution, ratio volume 80:20. The PVP is dissolved in ethanol:water solution, ratio volume 85:15. The flow rate for both polymers was 1.5 mL h⁻¹. The same applied voltage value and the distance between the needle and collection plate was found for both polymers, 15 kV and 15 cm respectively. Using these experimental conditions, fibrous membranes from CA and PVP were obtained, which presented a white color.

3.2 Morphology of fibrous membranes

Figures 2 and 3 show the SEM micrographs from fibrous membranes CA and PVP, respectively. The membrane CA is composed of fibers with ribbon morphology. As well as have holes and some porosity. While the fibrous membranes PVP have fibers with morphology cylindrical, with diameters varying from 1 to 3 μm . In both polymers, diameters in micrometer range were obtained. The holes observed in fibrous membranes CA suggests its application in separation processes.

In order to obtain cellulose acetate microtubes and take advantage of the high solubility in water from PVP, fibrous membranes composite of CA y PVP were made. Fibers were trying to be formed in the central part of PVP and coated with CA, then wash them and try to disseminate the PVP in water and thus obtain microtubes of CA (METHOD I, CA/PVP/CA). Also fibers containing PVP at the surface and CA in the center were made (METHOD II, PVP/CA/PVP), with the aim of comparing their morphology with fibers prepared above.

For both experiments two syringes with needles of different lengths were used. The longer needle is connected to the syringe containing the polymer is expected at the center of the fiber and the shorter needle is connected to the syringe containing the polymer which must be on the fiber surface.

The fibers were washed for 4 h, then left to dry at room temperature for 12 h. The SEM micrographs, of these fibrous membranes composite, before and after washing with water are shown in Figure 4 and 5.

In figure 4(a) shows the existence of cylindrical fibers with values of diameters ranging from 0.6 to 2 μm . After washing, Figure 4(b), clearly shows a decrease in the diameter of the fiber, possibly due to diffusion of PVP to water. In the case of fibrous membrane composite PVP/CA/PVP (Figure 5), similar results were found.

3.3 Thermogravimetric Analysis (TGA)

Analysis of weight loss due to temperature was performed for each type of fibrous membrane, in order to deduce whether the PVP diffuses into the water when the washing is made. In Figures 6(a) and 6(b) show the thermograms of fibrous membranes from CA and PVP respectively. In both cases, the first weight loss was significant at 100 $^{\circ}\text{C}$ attributed to the loss of moisture and solvent adsorbed in the fibers. Fibrous membrane CA showed a weight loss of 15%, while the fibrous membranes PVP by 20%, higher value due to the high hygroscopicity from PVP. In the case of CA show a complete degradation to 445 $^{\circ}\text{C}$, while the fibrous membranes PVP required a value of temperature for degradation of up to 571 $^{\circ}\text{C}$.

Figure 7 and 8 shows a comparison of the thermal stability of fibrous membranes composite of CA and PVP, (a) before and (b) after washing with water. A thermogram of fibrous membrane composite CA/PVP/CA is shown figure 7, (a) shows a weight loss of 2% at 100 $^{\circ}\text{C}$ attributed to the loss of moisture and residual solvent, this is an intermediate value of present by CA and PVP (Figure 6). Finally, the total degradation is presented to the 590 $^{\circ}\text{C}$, attributed to the PVP. The thermogram of fibrous membrane composite after washing with water (Figure 7(b)), presented temperature of total degradation to 450 $^{\circ}\text{C}$, indicating the absence of PVP in the membrane. This analysis indicates the diffusion of PVP to water when the membrane is washed. A thermogram of fibrous membrane composite PVP/CA/PVP, (a) before washing, (b) after washing is shown in Figure 8, for unwashed membranes (Figure 8(a)), observations similar to fibrous membrane composite CA/PVP/CA were found. Due it remains a mixture of these two materials, CA and PVP, without importance the accommodation of both. After washing the fibrous membranes, a decrease in the

temperature of total degradation is observed, attributed to the diffusion from PVP to water. In the case of fibrous membrane composite CA/PVP/CA, after washing, the temperature of total degradation, tends to make the same that CA (Figure 7), indicating that the PVP diffuses into water in the wash. In the case fibrous membrane composite PVP/CA/PVP, after washing with water (Figure 8(b)) presents greater thermal stability, with a difference of 30°C. Also shows that the temperature for total degradation is closer to the temperature of PVP pure, this indicates that the material may contain PVP even after washing, suggesting a better interaction between both components.

3.4 Tensile tests

Values of tensile strength, Young's Modulus and strain at break are shown in the table 1. Fibrous membranes PVP/CA/PVP shows a higher value of strain at break (%), and a lower value of tensile strength (MPa) compared to CA/PVP/CA. These results suggest that the membrane obtained by METHOD II (PVP/CA/PVP) is a composite membrane with better mechanical properties due to better interaction between both components. These results are consistent with those obtained in thermogravimetric analysis.

4. Conclusions

Fibrous membranes of CA and PVP, and respective membranes composite were fabricated via electrospinning. The fibrous membranes of PVP showed a morphology of cylindrical fibers, whereas, in the fibrous membrane CA showed ribbon morphology with holes and porosity. The membranes composite showed morphology of cylindrical fibers with diameter in the range of 0.6 to 2 μm . It follows by TGA that occurs diffusion of PVP to water at the time from washed of the fibrous membrane composite of CA and PVP. By METHOD I, fibers with PVP in the centre are obtained, with the diffusion of PVP to water, suggesting the formation of fibers only CA. Thermograms of fibrous membranes composite obtained by METHOD II, PVP/CA/PVP, suggest remnants of PVP even after washing. Tensile tests of membranes composite PVP/CA/PVP shown better mechanical properties that membranes composite CA/PVP/CA, due to better interaction between its components, in agreement with the results obtained by thermogravimetric analysis. The materials obtained show characteristics suitability for potential applications in tissue engineering

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Figure captions

Figure 1. Number of publications of electrospinning over time.

Figure 2. Microphotography by SEM of a fibrous membrane CA, 1500x.

Figure 3. Microphotography by SEM of a fibrous membrane PVP, 1500x.

Figure 4. Microphotography by SEM of fibrous membrane composite CA/PVP/CA, (a) before washing, (b) after washing, 1000x.

Figure 5. Microphotography by SEM of fibrous membrane composite PVP/CA/PVP, (a) before washing, (b) after washing, 1000x.

Figure 6. Thermograms of fibrous membranes from (a) CA and (b) PVP.

Figure 7. Thermograms of fibrous membranes composite CA/PVP/CA, (a) before and (b) after washing with water.

Figure 8. Thermograms of fibrous membranes composite PVP/CA/PVP, (a) before and (b) after washing with water

List tables

Table 1. Values of tensile strength, Young's modulus and strain at break of fibrous membranes composite.

For Peer Review

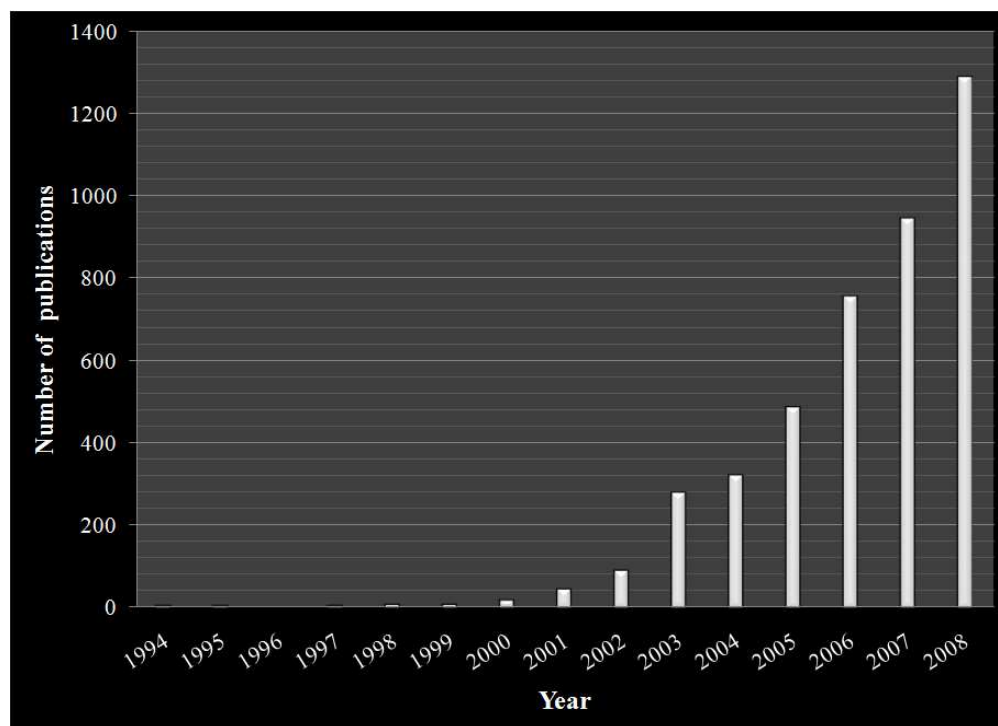


Figure 1. Number of publications of electrospinning over time.
241x174mm (96 x 96 DPI)

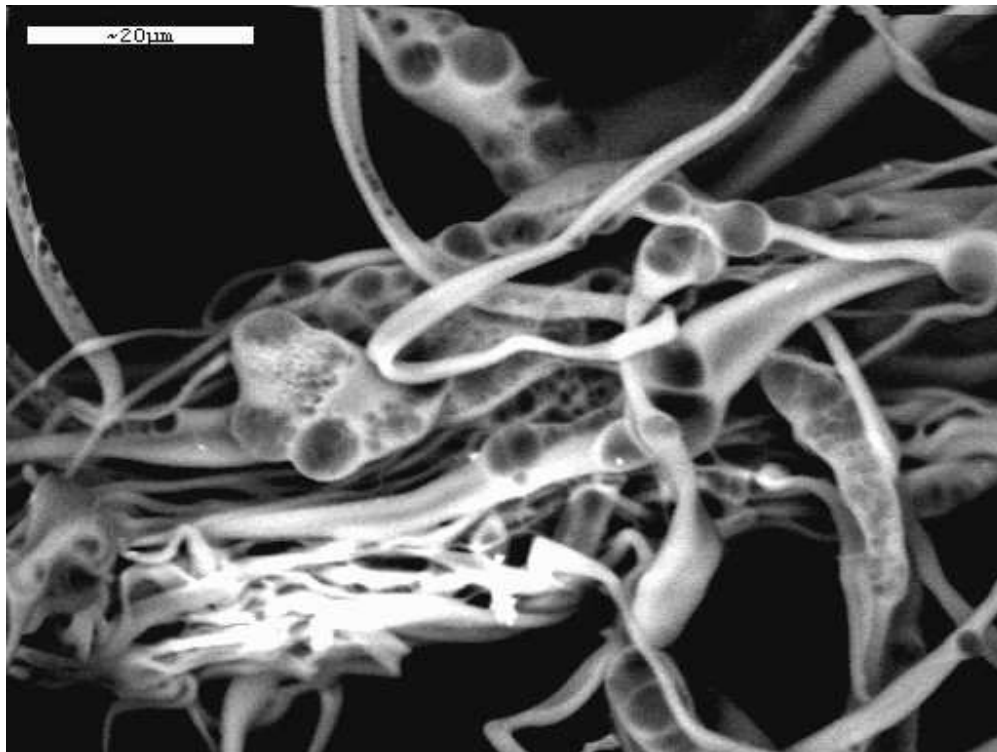


Figure 2. Microphotography by SEM of a fibrous membrane CA, 1500x.
135x101mm (96 x 96 DPI)

review

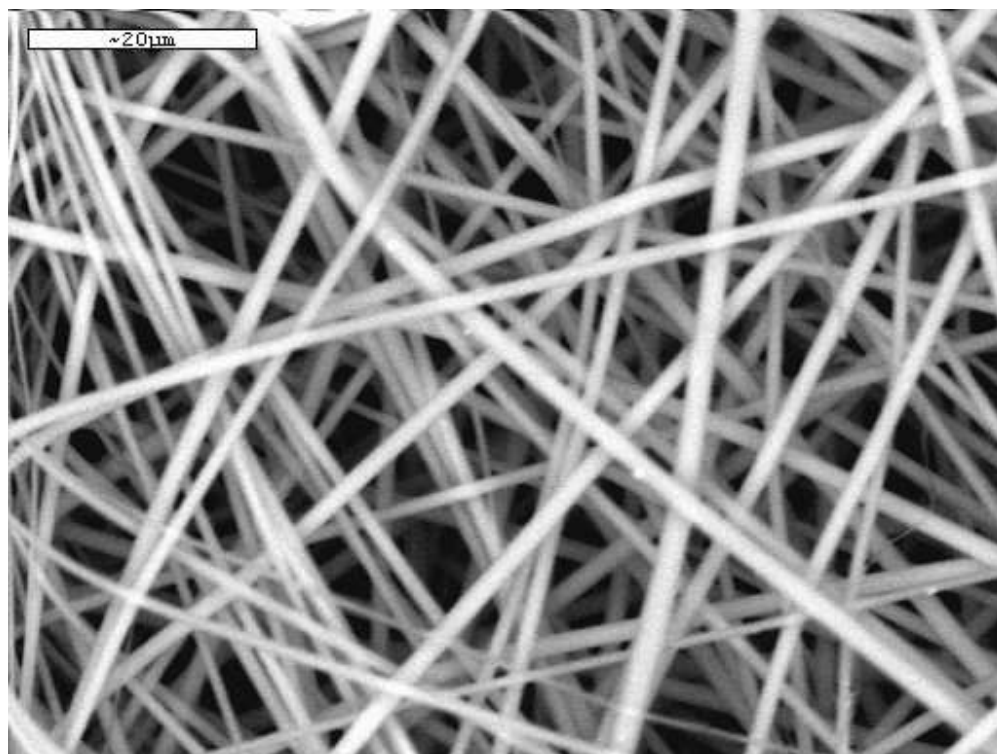


Figure 3. Microphotography by SEM of a fibrous membrane PVP, 1500x.
135x101mm (96 x 96 DPI)

Review

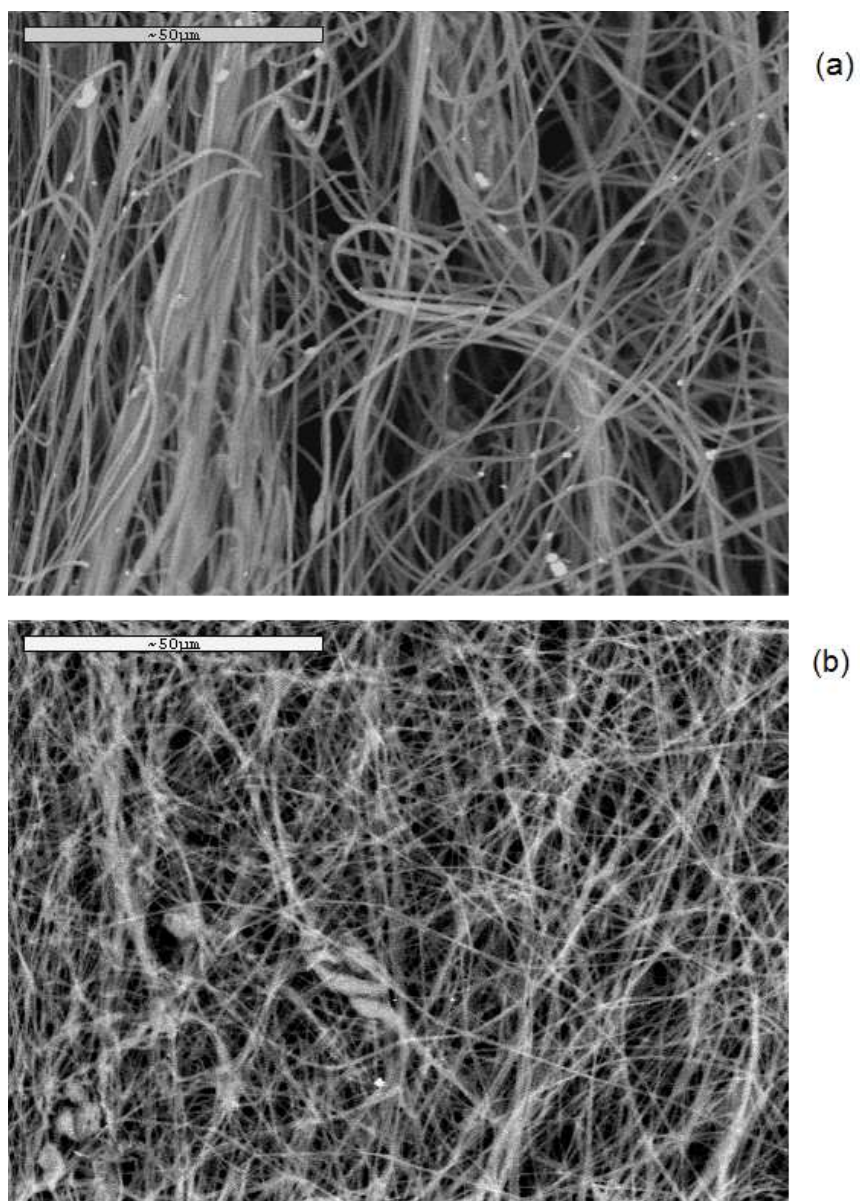


Figure 4. Microphotography by SEM of fibrous membrane composite CA/PVP/CA, (a) before washing, (b) after washing, 1000x. 148x208mm (96 x 96 DPI)

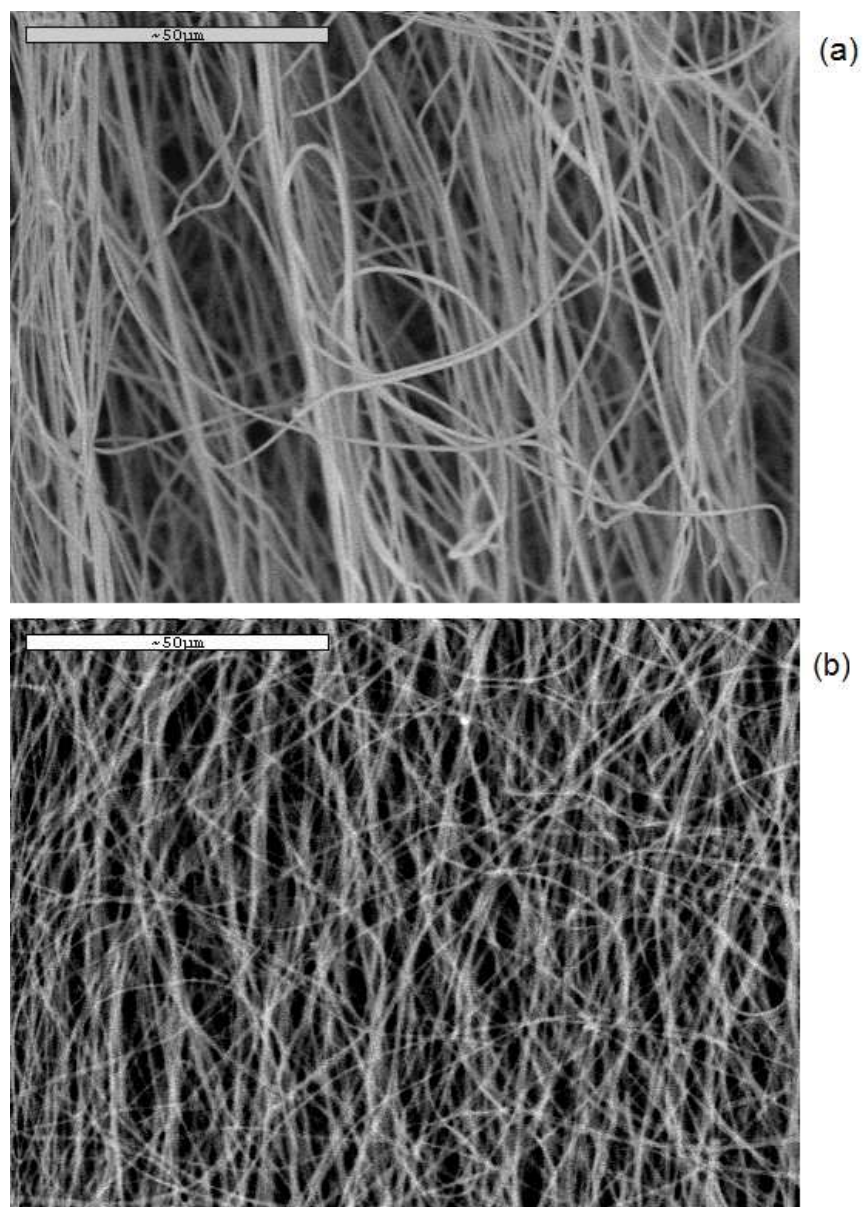


Figure 5. Microphotography by SEM of fibrous membrane composite PVP/CA/PVP, (a) before washing, (b) after washing, 1000x.
148x206mm (96 x 96 DPI)

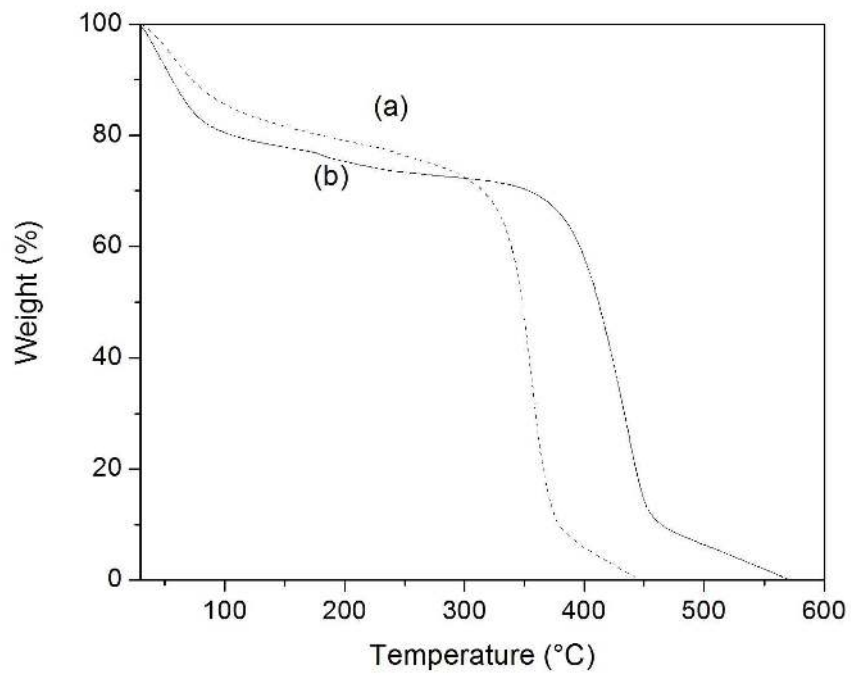


Figure 6. Thermograms of fibrous membranes from (a) CA and (b) PVP.
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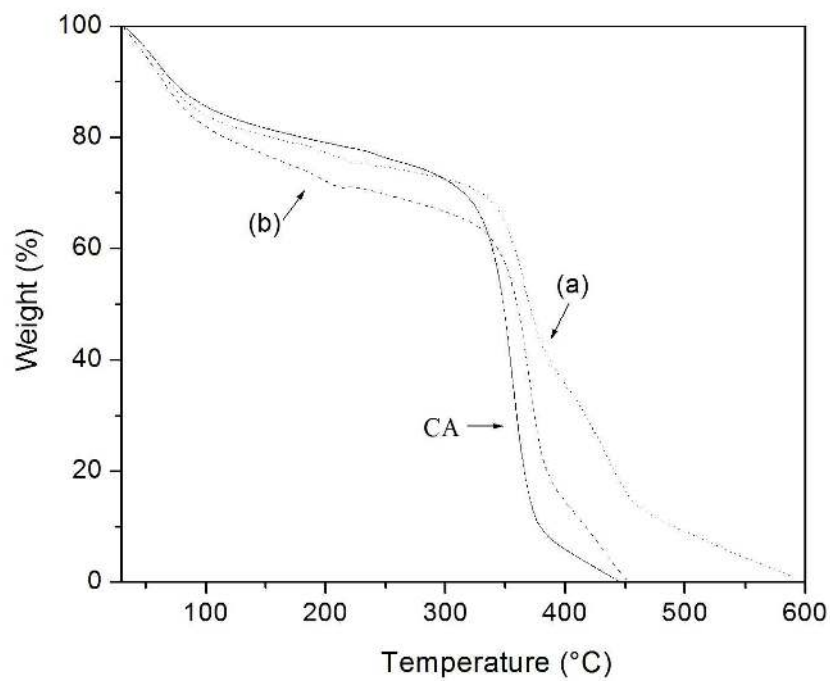


Figure 7. Thermograms of fibrous membranes composite CA/PVP/CA, (a) before and (b) after washing with water.
279x215mm (150 x 150 DPI)

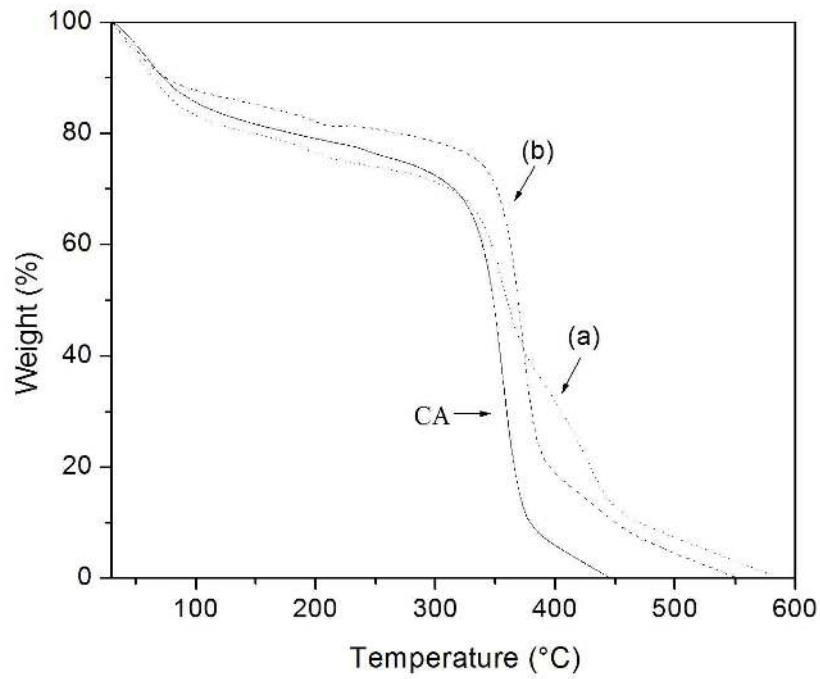


Figure 8. Thermograms of fibrous membranes composite PVP/CA/PVP, (a) before and (b) after washing with water.
279x215mm (150 x 150 DPI)

Table 1. Values of tensile strength, Young's modulus and strain at break of fibrous membranes composite.

Fibrous membrane	Tensile strength (MPa)	Young's Modulus (MPa)	Strain at break (%)
PVP/CA/PVP	17.907 ± 3.36	588.504 ± 92.89	6.25 ± 0.57
CA/PVP/CA	37.084 ± 5.988	1556.845 ± 279.225	3.01 ± 0.39

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