

Removal of Copper Ions from Simulated Wastewaters Using Different Bicomponent Polymer Membranes

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Abstract The main goal of this study was to explore the suitability and performance of bicomponent polymer membranes based on acrylonitrile copolymers-polyvinyl alcohol (PVA) mixtures and small quantities of anion (Purolite A100) or cation exchange resin (Purolite C150), prepared by phase inversion. Membranes were used for copper removal from synthetic wastewater solutions. A three detachable cylindrical

compartment electro dialysis cell without recirculation of the electrolytes and synthetic solutions of various concentrations, similar to a copper electrowinning electrolyte, were used. The electro dialysis unit operates under galvanostatic control. The effect of pH on electro dialysis separation of Cu^{2+} and on the solution conductivity has been also investigated. The laboratory electro dialysis cell performance was evaluated in terms of *percent of extraction (pe)* and *current efficiency (ce)*. Experimental results showed that the ionic transfer in electro dialysis cell was especially affected by concentration. The highest values for the *pe* (>81 %) and the *ce* (>25 %) of copper ions were obtained at maximum concentration in copper ions (3 g/L), indicating a better performance of the ion extraction. The transport of copper ions was also correlated with flux data. The ion exchange membranes were characterized using FT-IR spectroscopy, ESEM, and electrochemical impedance spectroscopy.

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1 Introduction

Removal of various toxic heavy metal ions such as copper, nickel, lead, cadmium, zinc, chromium, and mercury from anthropogenic sources such as metallurgical, galvanizing, metal finishing, electroplating, mining, power regeneration, electronic device manufacturing, and tannery industries is highly important for

environmental remediation. These heavy metals are persistent, bioaccumulative and toxic (Mosa et al. 2011; Lito et al. 2012).

The use of copper baths in the electroplating industry generates a strong concern related to environmental impacts due to the copper toxicity. Although some minute amounts of copper are necessary, (copper being an oligoelement that is essential for human health), the excessive ingestion of copper brings about serious toxicological concerns, such as stomach-aches, dizziness, vomiting, and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death (Mohammadi et al. 2004; Caprarescu et al. 2012a, b).

Removal of heavy metal ions is currently carried out using various technologies, including reverse osmosis, electrodialysis, precipitation, solvent extraction, filtration, adsorption, and ion exchange.

Reverse osmosis and ion-exchange can be effectively used to reduce the metal ions, but are limited due to a number of disadvantages such as the requirement of high amount of water, wastage of water a bit high, and high initial and operational costs, in addition to the limited pH range for the ion-exchange resin (Strathmann 2010; Dalla Costa et al. 2002; Shi et al. 2010; Lee et al. 2008).

Electrodialysis with ion-exchange membranes represents one of the most important membrane separation technologies in which ionized species in solution are transported, through anion and cation-exchange membranes, under the influence of an electric field. Depending on their charge, ions pass through one membrane and are restricted by the other, resulting in formation of diluted and concentrated compartments. The transport for ion depends, especially, on its charge, mobility, solution conductivity, relative concentrations, and applied voltage.

Electrodialysis exhibits several advantages, such as the possibility to repair and disassembly the stack, easiness to manually clean the membranes or replace them, low chemical usage, long life of membranes, selective removal of target species, flexibility in removal rate (through voltage control), good water recovery rate, multiple contaminant removal, and low energy consumption.

Electrodialysis can be used in the wastewater treatment of industries with galvanic production because it allows the reuse of the diluted solution as rinse-water

and of the concentrated solution in the electroplating bath (Mohammadi et al. 2004; Caprarescu et al. 2012a, b; Strathmann 2010; Dalla Costa et al. 2002; Shi et al. 2010; Lee et al. 2008; Park et al. 2006).

The aim of the present study was to investigate the copper removal from synthetic wastewater solutions by electrodialysis process using bicomponent acrylic-PVA ion-exchange membranes. PVA was used to increase the hydrophilicity and so to enhance the ion transport. The effects of solution conductivity and solution pH, under the constant applied cell current, were investigated.

Electrodialysis experiments were evaluated in terms of *percent of extraction* (pe) and *current efficiency* (ce).

2 Experimental

2.1 Reagents

Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sulphuric acid (98 %), purchased from Chimopar Bucharest and Merck Millipore, respectively, were used without further purification.

Acrylonitrile, vinyl acetate, and dimethyl sulfoxide (DMSO) were purchased from Fluka. All chemicals were of analytical grade. Polyvinyl alcohol 90–98 was prepared in the laboratory by solution polymerization of vinyl acetate (azoisobutyronitrile initiation) in methanol, followed by methanolysis conducted using NaOH as catalyst.

2.2 Membrane Sample Preparation

There were used two different types of bicomponent acrylic-PVA ion-exchange membranes. These membranes were obtained by phase inversion using a mixture composed of 80 % acrylic copolymer (90 % acrylonitrile: 10 % vinyl acetate) and 20 % polyvinyl alcohol with the global concentration of 8 % in dimethyl sulfoxide (DMSO) by dissolving both components at 90 °C for 2 h, in the presence of 5 % ion exchange resin (Purolite A100 or Purolite C150) (Purolite Company), calculated to the polymer mixture.

The acrylic copolymer had a relative viscosity (0.3 % in dimethylformamide at 30 °C) of 1.58 and PVA presented an acetalization degree of 99.12 % and an average numerical polymerization degree of 900.

The polymer solution was cast at room temperature onto a glass plate (70, 110, and 4 mm). The draw-down

technique was used in order to obtain wet films with thickness in range of 180 to 200 μm . Afterwards, the plate was immersed in a coagulation bath containing 80 % isopropanol: 20 % water and kept for 30 min. Then these membranes were intensively washed with distilled water at room temperature.

Purolite A100 is a macroporous polystyrenic weak base anion exchange resin having tertiary amine functionality and Purolite C150 is a macroporous poly(styrene sulfonate) strong acid cation exchange resin having sulfonic acid functionality (Badawy et al. 2009; Caprarescu et al. 2012a, b).

2.3 Experimental Apparatus

The original electro dialysis cell, consisting of three PVC detachable cylindrical compartments, between which the two acrylic ion-exchange membranes were introduced, is presented in Fig. 1. Each compartment has a volume of 29.85 mL and the effective area of the membranes was 23.32 cm^2 . The working electrodes, both of pure lead and with effective area of 23.32 cm^2 , were arranged in the electro dialysis cell at the extremities.

The distance between anode and cathode electrodes was 3.6 cm. The thickness of each compartment was 0.92 cm. The distance between the membranes was 1.2 cm.

All the experiment studies were carried out at room temperature (25 ± 3 $^{\circ}\text{C}$) and without recirculation, in

batch-mode operation. The time of the experiments was of 1.5 h.

A synthetic solution containing copper ions was prepared by dissolving copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sulphuric acid (98 %) (molar ratio 1:1) in distilled water to obtain two copper ions concentration: 1.5 or 3 g/L. Electro dialysis cell compartments were filled with the same solution, in order to reduce the effect of diffusive transport between compartments.

A constant anode–cathode current of 0.2 A (current density 8.58 mA/cm^2) was applied between two lead electrodes by a power supply (Protek, Germany). The experimental current density was based on the actual surface area of the membranes. During the experimental studies, the imposed current promotes the motion of different ions due to the electric field created within the electro dialytic cell. The SO_4^{2-} ions, with electronegative sign, move from the central compartment toward the anodic compartment crossing the anion exchange membrane. At the same time, the anion exchange membrane impedes the passage of the protons generated in the anode as a consequence of water oxidation. SO_4^{2-} ions take part at the composition of the plating baths as catalyst. On the other hand, copper is present in the cationic Cu^{2+} form at the acidic pH of the solutions. The released H^+ ions are also transported through the cation exchange membrane. Therefore, H^+ and Cu^{2+} ions, with positive charge, compete for the transport toward the cathodic compartment, where the deposition of metallic copper on the cathode surface occurs.

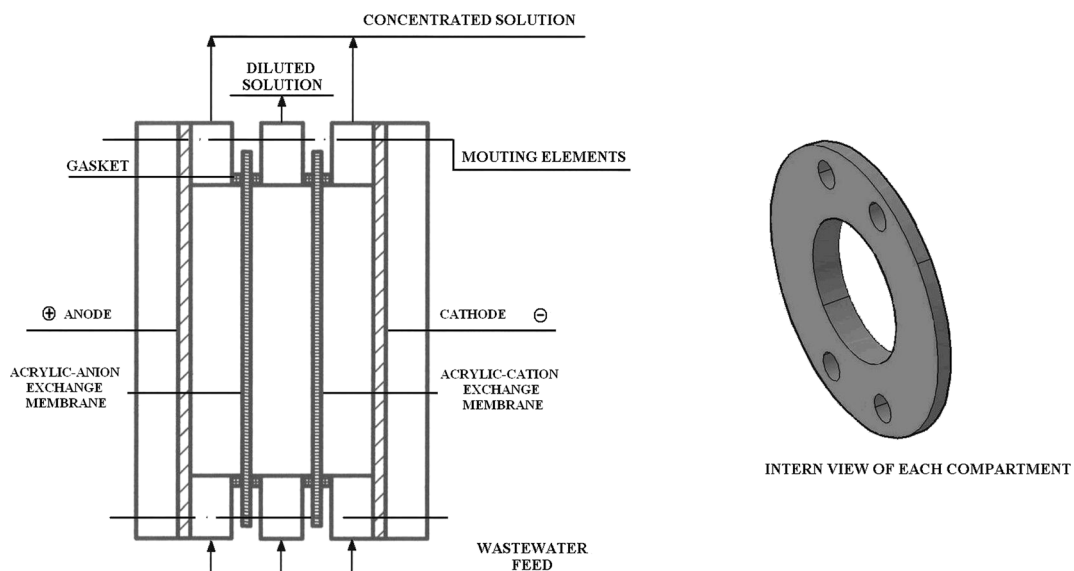


Fig. 1 Schematic diagram of the three-compartment laboratory electro dialysis cell

The conductivity of solutions was measured using a conductivity meter type PIERRON (France) equipped with a bell type conductivity electrode system. It contains two plan-parallel platinum disk electrodes.

The pH of the solutions was measured by a pH meter type HI 8915 (HANNA Instruments, Germany) that contains a temperature sensor. Copper concentration was determined by titration method (Caprarescu et al. 2012a, b).

2.4 Membrane Characterization

2.4.1 Fourier Transform Infrared Spectroscopy

Morphology structure of the membranes was measured in attenuated total reflectance (ATR) mode on a Tensor 37, Bruker instrument using the Golden Gate unites in the spectral range of 400–4,000 cm^{-1} .

2.4.2 Environmental Scanning Electron Microscopy

Morphology and structure surface of the membranes were observed with a FEI-Quanta 200 microscope. The environmental scanning electron microscopy (ESEM) images were obtained in low vacuum mode.

2.4.3 Electrochemical Impedance Spectroscopy

The impedance measurements were carried out using a VoltaLab 40 Dynamic Electrochemical System in the frequency range from 100 kHz to 1 Hz and a potential amplitude perturbation of 10 mV.

Electrochemical experiments were performed at ambient temperatures using a dedicated electrochemical cell consisting of two plan-parallel platinum disk electrodes. The obtained membranes were clamped between these electrodes. This cell, the associated system and the evaluation procedure, was presented elsewhere (Vaireanu et al. 2008).

3 Results and Discussion

3.1 Effect of pH and Solution Conductivity on Cu^{2+} Separation

Table 1 presents the pH and the conductivity values for the untreated and treated waters, from all three cell compartments, measured after 1.5 h, at room temperature for two copper ions concentration.

The low pH values are due to the acidic electrolyte solutions. At low pH, the high H^+ concentrations compete with Cu^{2+} at the cathode plate surface. Moreover, the electrodeposition process was influenced by H_2 evolution, leading to dendrite formation.

In the central cell compartment, the value of pH decreases which could be associated to the OH^- consumption. The electrical resistance of the solution decreases (Caprarescu et al. 2012a, b; Abou-Shady et al. 2012; Peng et al. 2011; Ergun et al. 2008; Rodrigues et al. 2008; Vallois et al. 2003; Raissouni et al. 2007; Amado et al. 2004).

The values of solution conductivities measured in the anodic, central, and cathodic compartment were also determined in comparison to untreated wastewater.

In the central compartment for both values of concentration of copper ions, the conductivity decreases in comparison to untreated wastewater. This indicates that the Cu^{2+} and SO_4^{2-} ions were removed. The values of conductivity increase in the anodic compartment in comparison to untreated wastewater and can be due to the H^+ ion produced in this compartment.

In the cathodic compartment, the values of conductivity decrease in comparison to untreated wastewater. This may be attributed to Cu^{2+} transport from the central compartment to cathodic compartment that conducted to copper electrodeposition reaction on the cathode lead (Caprarescu et al. 2012a, b).

The cell voltage increase can be attributed to the decrease in the conductivity of the central cell compartment solution as a consequence of the ionic species removal, increasing the solution electrical resistance (Caprarescu et al. 2012a, b; Peng et al. 2011; Rodrigues et al. 2008; Vallois et al. 2003; Raissouni et al. 2007).

3.2 Transport Numbers of Cu^{2+} and SO_4^{2-}

Transport numbers for Cu^{2+} and SO_4^{2-} were determined by Eqs. (1) and (3) (Rodrigues et al. 2008; Vallois et al. 2003) as follows:

$$t_i = \frac{z_i \cdot J_i \cdot F}{i} \quad (1)$$

$$\sum_1^n t_i = 1 \quad (2)$$

where t_i is the transport number of the i species, z is the valence of the i species, J_i is the flux of the i species

Table 1 Monitoring of the electro dialysis treatment process for each sample

Samples	Parameters	Initial	
		1.5 g/L	3 g/L
Untreated wastewater	pH	1.34	1.15
	Conductivity (mS cm ⁻¹)	22.3	36.4
		1.5 h	
		1.5 g/L	3 g/L
Treated water from anodic compartment	pH	1.11	1.02
	Conductivity (mS cm ⁻¹)	35.1	46.5
Treated water from central compartment	pH	1.31	1.10
	Conductivity (mS cm ⁻¹)	21.0	33.6
Treated water from cathodic compartment	pH	1.36	1.08
	Conductivity (mS cm ⁻¹)	18.3	28.5

(mol/cm² s), F is the Faraday constant, and i is the current density (mA/cm²).

Table 2 presents the values of transport numbers determined for Cu²⁺ ($t_{Cu^{2+}}$) and SO₄²⁻ ($t_{SO_4^{2-}}$), for different solutions, after 1.5 h of experiment.

The transport number of a counter-ion in the ion-exchange membrane is generally close to 1 and that of the co-ion close to 0 while in the solution the transport numbers of anions and cations are not very different. The transport number of the cations is lower in the solution in comparison with the transport number of the cations in the membrane because at the surface of a cation-exchange membrane facing the dilute solution, the concentration of ions in the dilute solution is reduced. The number of anions is reduced in the boundary layer due to the electroneutrality by migration in the opposite direction (Strathmann 2010).

From Table 2, one may notice the decrease of the SO₄²⁻ transport number as the initial concentration increased, which involves an increase of the H⁺ transport number through the anion exchange membranes.

Table 2 Transport numbers of Cu²⁺ ($t_{Cu^{2+}}$) and SO₄²⁻ ($t_{SO_4^{2-}}$)

Concentration of copper ions, g/L	$t_{Cu^{2+}}$	$t_{SO_4^{2-}}$
1.5	0.06	0.94
3.0	0.20	0.80

In literature, the phenomena of H⁺ leakage were explained by studying the kinetics of transport of anions and protons through anion exchange membranes placed in an acid medium. It was suggested that the apparent rate constant of H⁺ transport remains practically constant whatever the acid concentration of the solution. Because the over-voltage interfacial transfers protons, the current efficiency becomes independent of the acid concentration (Rodrigues et al. 2008; Vallois et al. 2003; Raissouni et al. 2007; Amado et al. 2004).

The Cu²⁺ transport number increases with an increase in the initial concentration and may be due to the cation exchange membranes that have a higher specific permselective property and to the fact that the intrinsic mobility of H⁺ in the presence of water is larger than that of OH⁻.

The low values for transport number of Cu²⁺ ions demonstrated an excellent selectivity and good separation properties of the studied membranes.

A decrease in SO₄²⁻ ions transfer with the increasing in concentration is essentially due to the decrease in the membrane selectivity (Rodrigues et al. 2008; Vallois et al. 2003; Raissouni et al. 2007; Amado et al. 2004; Boucher et al. 1997; Yamauchi et al. 1991; Hirata et al. 1992).

3.3 The Flux of Cu²⁺, Percent Extraction, and Current Efficiency

The flux values were evaluated for all experimental conditions. The flux of Cu²⁺ (J) was determined by using the following Eq. (3) (Ergun et al. 2008; Rodrigues et al. 2008):

$$J = \frac{V \cdot (C_i - C_f)}{A \cdot t} \quad (3)$$

where J is flux of copper ion, (g/cm² s), V is the cathodic compartment volume (L), C_f is the final concentration of the copper ion (g/L), C_i is the initial concentration of the copper ions (g/L), A is the effective working area of the membrane (cm²), and t is the working time (s).

The laboratory electro dialysis cell efficiency was evaluated in terms of *percent of extraction* (pe) and *current efficiency* (ce), defined by Eqs. (4) and (5), respectively (Caprarescu et al. 2012a, b; Hirata et al. 1992; Marder et al. 2004; Abou-Shady et al. 2012):

Table 3 The values of Cu²⁺ flux, percent of extraction (pe), and current efficiency (ce) during 1.5 h of electro dialysis for different values of concentration

Concentration of Cu ²⁺ , g/L	J, g/m ² s × 10 ⁻⁷	pe, %	ce, %
1.5	1.84	51.7	12.6
3.0	5.78	81.2	25.2

$$pe = \frac{C_i - C_f}{C_i} * 100(\%) \tag{4}$$

where C_i is the initial concentration of the copper ion and C_f is the final concentration of the copper ion.

$$ce = \frac{z \cdot V \cdot C \cdot F}{I \cdot t} * 100(\%) \tag{5}$$

where z is the valence of the ion, V is the total volume of the aqueous solution in all compartments (dm³), C is the concentration of copper ions in the feed solution (mol/dm³), F is the Faraday's constant (96485 A s/mol), I is the electric current applied (A), and t the time (s).

From Table 3, one may notice that for an electro dialysis process, duration of 1.5 h, the flux of copper ions increased with increasing the copper ion concentration. This is probably due to the transported amount of copper which increased with increasing the concentration of copper ions (Ergun et al. 2008; Rodrigues et al. 2008).

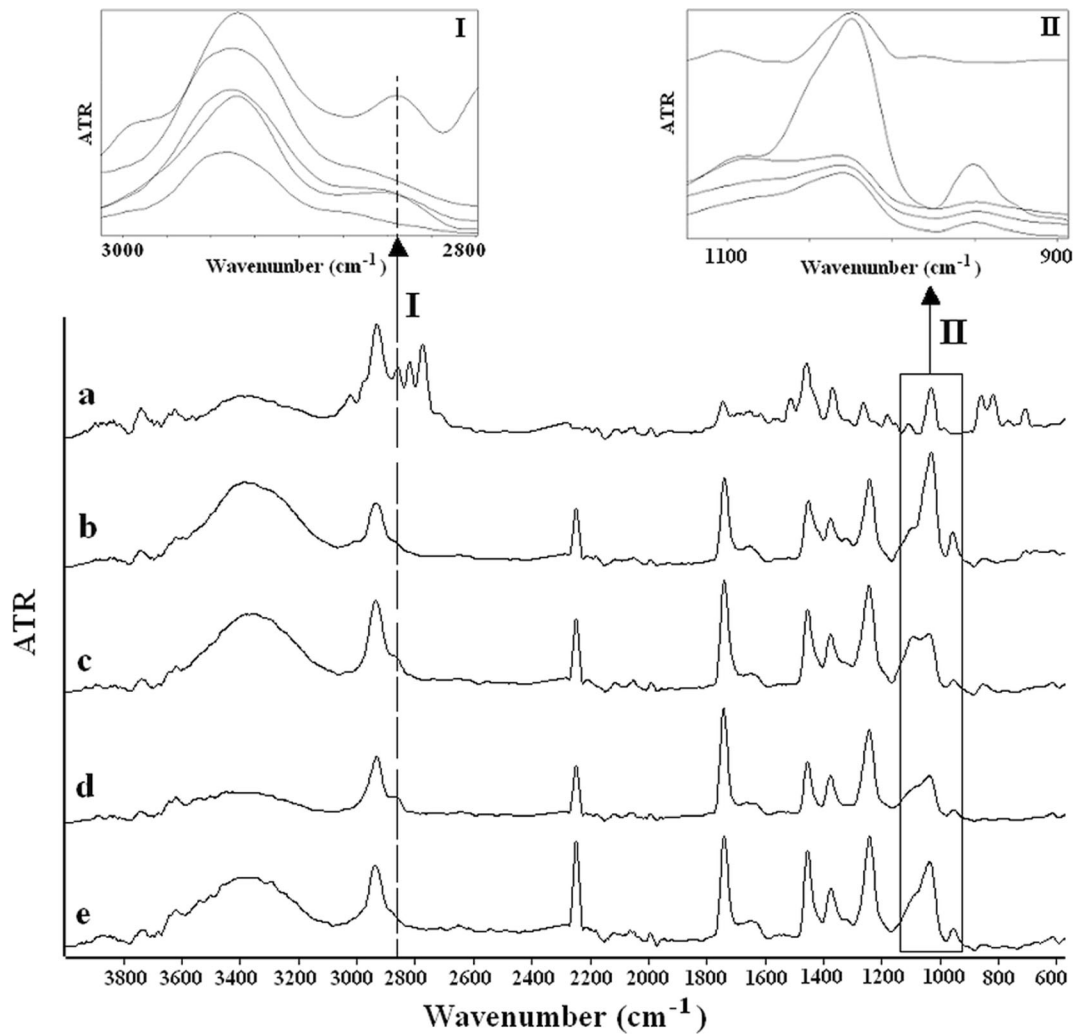


Fig. 2 FT-IR spectra of acryl-PVA anion exchange membranes (Purolite A100) for different values of Cu²⁺ concentration: *a* Purolite A100 powder, *b* membrane without Purolite A100, *c*

membrane with Purolite A100 blank, *d* membrane with Purolite A100, concentration 1.5 g/L, *e* membrane with Purolite A100, concentration 3 g/L

The flux of copper ions was maximum at concentration of 3 g/L.

It was observed that the extraction percent of copper ions increases with an increase in solution concentration and the highest value of extraction percentage of copper ions was obtained at a maximum current of 0.20 A. The formation of copper ions increases at higher value of concentration.

It was observed that the extraction percent of copper increased when the initial concentration of copper in the feed solution increased due to the enhanced flux of copper. The lower Cu^{2+} recovery at lower pH is due to a decrease of conductivity values (Caprarescu et al. 2012a, b; Dalla Costa et al. 2002).

The results suggest that the *pe* of the ionic species is higher (>81 %) when higher concentrations are applied (3 g/L). The formation and evolution of the H_2 and O_2 reduce the current efficiency. The Faradic process at the anode (oxygen evolution) results in the regeneration of free protons in the feed compartment. This leads to a reduction in current efficiency for electro dialysis due to the competing transport of hydrogen ions across the membrane, especially as the free protons are more mobile than the metal ions (Caprarescu et al. 2012a, b; Amado et al. 2004; Boucher et al. 1997; Yamauchi et al. 1991; Hirata et al. 1992).

The *current efficiency* was low at low concentration, possible due to the high concentration of active H^+ , which retarded permeation of Cu^{2+} through the cation

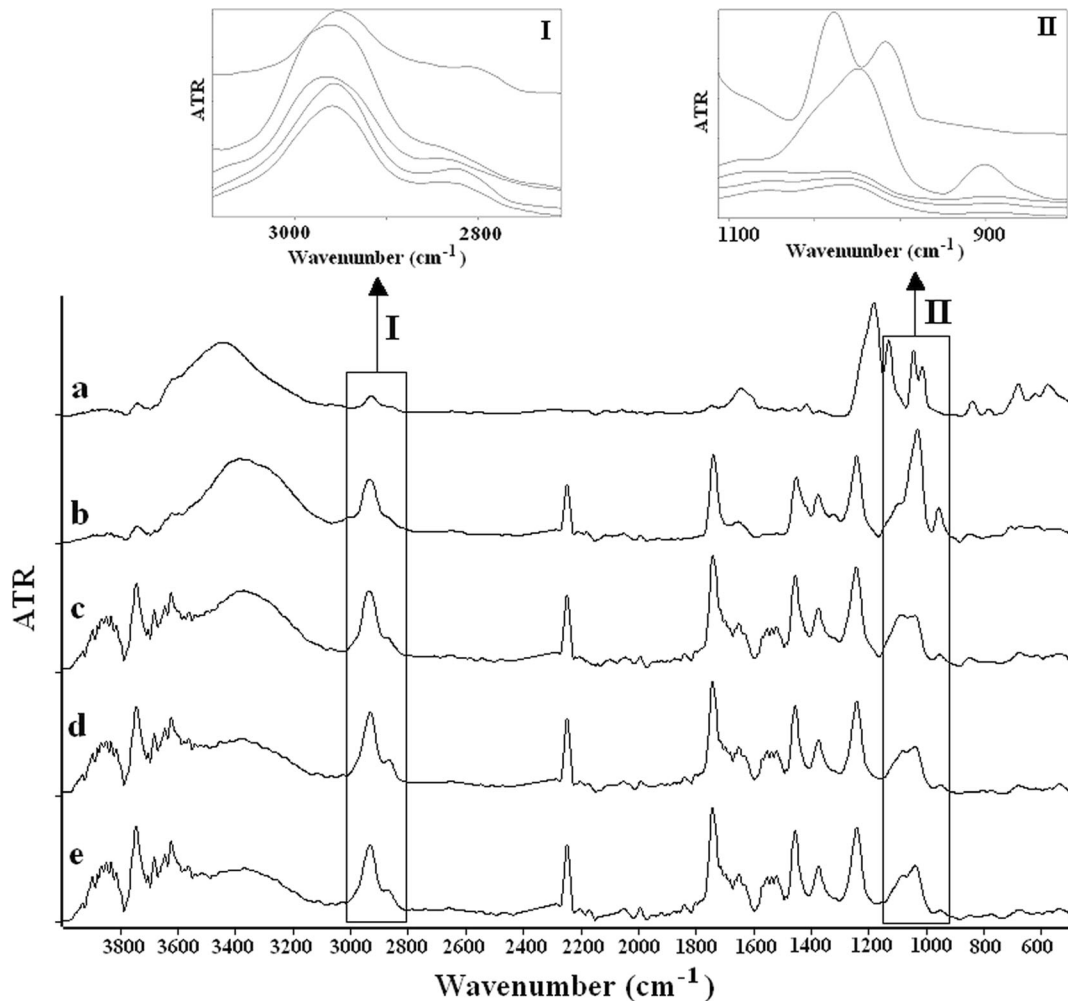


Fig. 3 FT-IR spectra of acryl-PVA cation exchange membranes (Purolite C150) for different values of Cu^{2+} concentration: *a* Purolite C150 powder, *b* membrane without Purolite C150, *c*

membrane with Purolite C150 blank, *d* membrane with Purolite C150, concentration 1.5 g/L, *e* membrane with Purolite C150, concentration 3 g/L

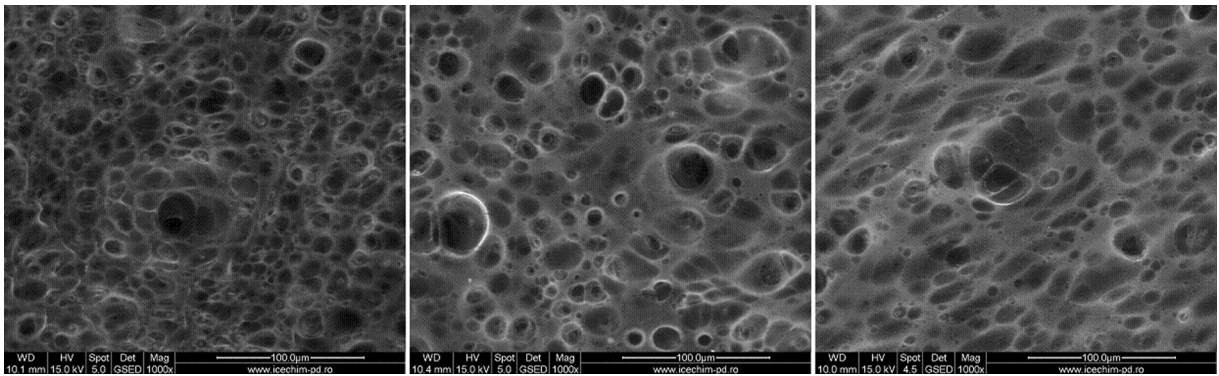


Fig. 4 ESEM images of prepared membranes: **a** without ion exchange resin, **b** with Purolite C150, and **c** with Purolite A100

exchange membranes (Marder et al. 2004; Abou-Shady et al. 2012).

A very low extraction percent demonstrated that there was low transport through the membrane, in accordance with the calculation of the transport number.

3.4 Membrane Characterization

3.4.1 FT-IR Spectroscopy

The chemical structure of bicomponent acrylic-PVA anion- and cation-exchange membranes (non-used membranes and used membranes at constant value of current and different values of concentration) was investigated by the Fourier transform infrared (FT-IR)

spectroscopy (see Figs. 2 and 3). The samples were examined before and after exposure to electro dialysis process.

Bicomponent polymer membranes based on mixtures of acrylonitrile copolymers and PVA, obtained by phase inversion, in which small quantities of anion (Purolite A100) or cation exchange resin (Purolite C150) were introduced, were characterized by FT-IR in order to study the composition and chemical structure of the membranes.

From Fig. 2, it was observed that a peak appears at $2,770\text{ cm}^{-1}$ in the spectra of the loaded anion exchangers (Purolite A100), which may be due to O-H and N-H stretching vibrations. At the same time, the peak at $2,925\text{--}2,937\text{ cm}^{-1}$ interval is related to the

Fig. 5 Impedance spectra of the acryl-PVA anion exchange membrane (Purolite A100) at various values of Cu^{2+} concentration

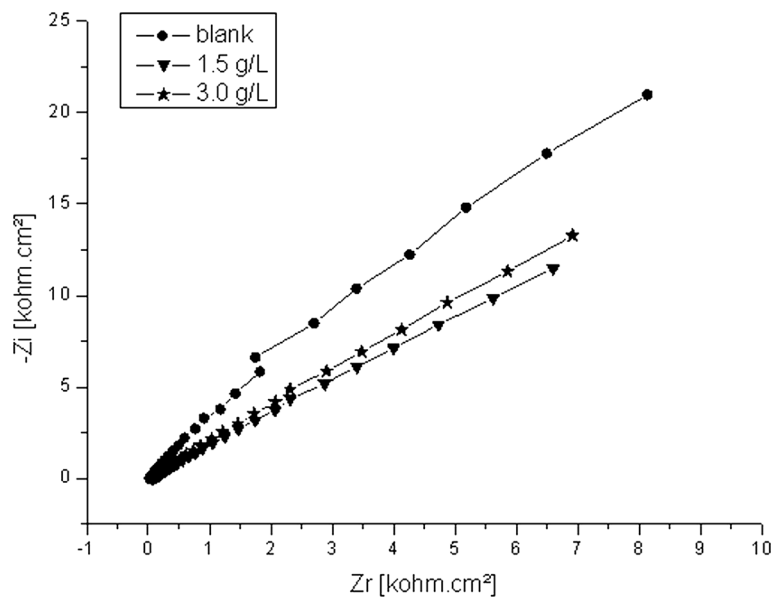
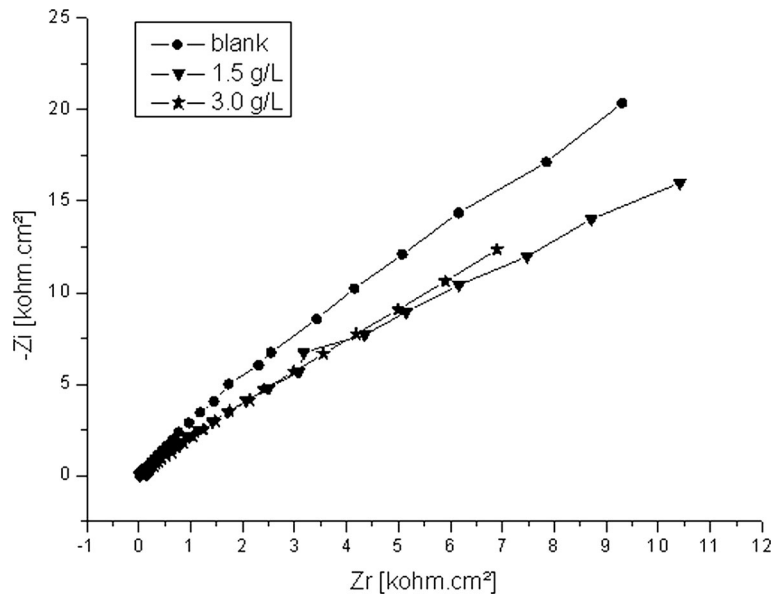


Fig. 6 Impedance spectra of the acryl-PVA cation exchange membrane (Purolite C150) at various values of Cu^{2+} concentration



stretching vibrations of the ring C–H bands of the resin (cross-linked polystyrene) (Purolite C150; Fig. 3).

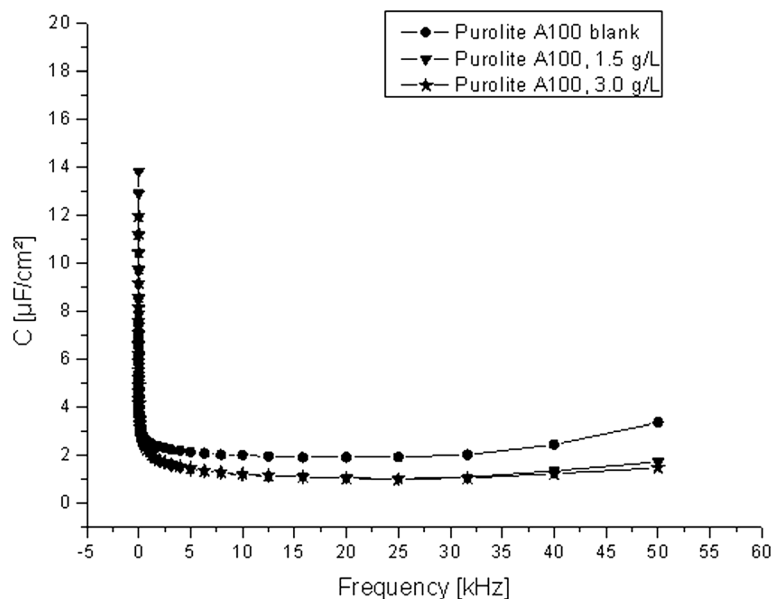
In Figs. 2 and 3, the large band at around $3,500\text{ cm}^{-1}$ are assigned to OH groups in PVA. The specific absorption band of polyacrylonitrile from copolymer occurs at $2,244\text{ cm}^{-1}$, which may be assigned to the stretching vibrations of cyan group ($-\text{C}\equiv\text{N}$).

The peak that appears at $1,735\text{ cm}^{-1}$ can be ascribed to C=O (stretching vibration), confirming the presence of OCOCH_3 group from vinyl acetate. The presence of

C=C in the cation exchanger (Purolite C150) was noticed at $1,636\text{ cm}^{-1}$.

The ring C–C stretching and the scissoring of the methylene groups ($\delta\text{-CH}_2$) appeared at about $1,453\text{ cm}^{-1}$ (Purolite C150). The peak that appears at $1,370\text{ cm}^{-1}$ may be due to C–N stretching vibrations. C–O–C asymmetric vibration from vinyl acetate appears at $1,235\text{--}1,238\text{ cm}^{-1}$ (stretching vibration). The peak that appears at $1,371\text{ cm}^{-1}$ may be due to CH_3 symmetric deformation vibration.

Fig. 7 Change of the impedance of the acryl-PVA anion exchange membrane (Purolite A100) system versus frequency, for different value of Cu^{2+} concentration



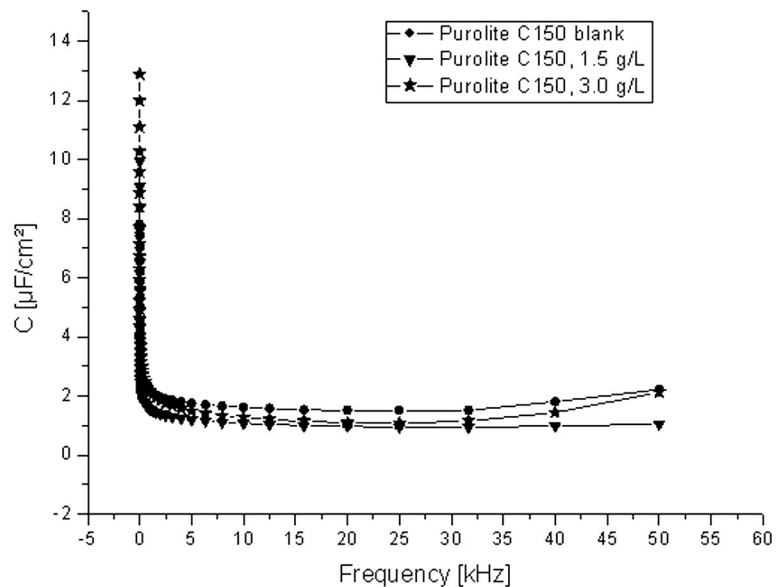
It was stated that symmetric and asymmetric vibrations of $-\text{SO}_3^-$ groups appeared at $1,039$ and $1,176\text{ cm}^{-1}$, respectively, and is due to the sulfonic acid group (Purolite C150).

The peak occurring in $1,024\text{--}1,031\text{ cm}^{-1}$ range is assigned to C-O (stretching vibration) and O-H (deformation vibration; ion exchange was carried out) (Purolite A100) (Tzanetakis et al. 2003; Dizge et al. 2009; Osaki and Tanioka 2002).

3.4.2 ESEM

The ESEM images for prepared membranes are shown in Fig. 4. The ESEM pictures for the membrane with and without ion exchange resins present macro- and micropores which indicate the occurrence of phase-separation in the polymer solution. The pores also indicate that the evaporation occurred fastly and confirm the uniformity of the membranes. For the ion exchange membranes, the pores offered a large surface area. As it can be observed, the pronounced heterogeneity of the ion exchange membranes was conducted by both ion exchange particle polarities. This fact explains also the good ion mobility and extraction values obtained on such a low amount of ion exchanger resin in the obtained membranes (Arthanareeswaran and Starov 2011; Chakrabarty et al. 2011; Boricha and Murthy 2009).

Fig. 8 Change of the impedance of the acryl-PVA cation exchange membrane (Purolite C150) system versus frequency, for different value of Cu^{2+} concentration



3.4.3 Electrochemical Impedance Spectroscopy Tests

The impedance data are depicted using the Nyquist plots (see Figs. 5 and 6). Figures 5 and 6 are two samples of a Nyquist plots using as coordinates, for OX the real part of impedance Z_r , while for OY the imaginary part, Z_i , of the impedance Z , for the acrylic-PVA anion exchange membranes and, respectively, for acrylic-PVA cation exchange membranes, tested after they have been subjected to two different values of copper ions concentrations comparing to its original state (the blank sample).

As one may see, the slope is lower for the membranes subjected to the ionic exchange (copper ions concentrations) indicating that these membranes may be used for their intended purpose. Moreover, the similarity of the two slopes indicated that the saturation concentration was not reached yet, these membranes being able to stand a higher concentration than the 3 g/L . The absence of the semicircular portion in the high-frequency region of plot indicated that the conduction is mainly due to the bulk ionic conduction.

The capacitive loop in low-frequency range starts linearly, but presents a finite limit at very low frequencies, (anomalous diffusion) depicting the electrical responses to interface phenomena originating from the ion-exchange membrane and the transport ions (Park et al. 2006; Benavente et al. 2001; Martinhon et al. 2006; Sistat et al. 2008; Hurwitz and Dibiani 2004; Moya 2010).

The dispersions of the capacitance with frequency for each concentration were essentially linear. Figures 7 and 8 show that the capacitance increases with the decrease in frequency and may be due to the contribution of increase in the interfacial layer resistance to total impedance. Moreover, the decrease in the capacitance values of the membranes subjected to the ionic exchange processes in comparison with the blank sample indicated that the ionic process takes place, the membranes becoming loaded in time with copper ions and act as loose capacitors with a value lower than that of the blank sample.

It was observed that the capacitance dispersions are very small, depending on the concentration of the electrolyte; if the concentration of Cu^{2+} in the electrolyte is higher, the capacitance is larger and the charge transfer resistance is lower. This capacitance is considered as being associated to the ionic changes coupled with the double layer at the interface membrane/metal (Park et al. 2006; Benavente et al. 2001; Martinhon et al. 2006; Sstat et al. 2008; Hurwitz and Dibiani 2004; Moya 2010; López-García et al. 2009).

4 Conclusion

Bicomponent polymer membranes with anion (Purolite A100) or cation exchange resin (Purolite C150) were used for the removal of Cu^{2+} from simulated wastewaters by applying electro dialysis.

The Cu^{2+} percent extraction and current efficiency depend on the concentration of the solution to be treated. At the constant current density of 8.58 mA/cm^2 , the percent extraction of the ionic species is higher (>81 %) and current efficiency is higher (>25 %) when higher concentrations are applied (3 g/L); this fact demonstrated an excellent separation properties of the studied membranes.

Infrared spectroscopy showed characteristic bands of ion exchanger resin from bicomponent polymer membranes. It was found that the occurrence of symmetric and asymmetric vibrations of $-\text{SO}_3^-$ groups are due to the sulfonic acid group (Purolite C150). It was observed that a peak appears at $2,770 \text{ cm}^{-1}$ in the spectra of the loaded anion exchangers (Purolite A100), which may be due to O-H and N-H stretching vibrations.

The impedance spectroscopy can provide useful information on the interfacial phenomena of bicomponent polymer membranes. It is found that the impedance

spectra (Nyquist plots) present a finite limit at very low frequencies; the straight lines could be associated with the diffusion effect of the transport ions; the capacitance increases with decreasing in the frequency and may be due to the contribution of increasing the resistance of interfacial layers to total impedance.

The removal of copper ions using electro dialysis has more advantages such as not using chemicals or causing sludge problems; the operation cost of this method can be reduced because of the recovery of copper, this deposited on the cathode lead.

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