



Characterization of an engineered cellulose based membrane by thiol dendrimer for heavy metals removal

Manuel Algarra^{a,*}, María Isabel Vázquez^b, Beatriz Alonso^c, Carmen María Casado^c, Juan Casado^d, Juana Benavente^{b,*}

^a Dept. Inorganic Chemistry, Faculty of Science, University of Málaga, 29071 Málaga, Spain

^b Grupo de Caracterización Electrocinética en Membranas e Interfases, Dpto. Física Aplicada I, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

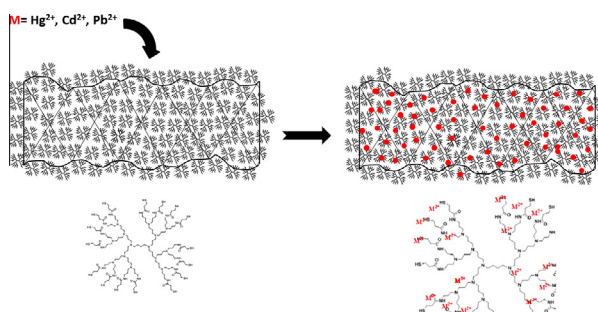
^c Dpto. Química Inorgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

^d Dpto. Química Física, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

HIGHLIGHTS

- Thiol polypropylenimine (DAB-3-(SH)₁₆) dendrimer engineered cellulosic support membranes.
- Chemical, elastic and electrical characterizations of original and engineered membranes.
- Diffusive permeability reduction of heavy metal (Cd²⁺, Hg²⁺ and Pb²⁺) solutions.
- Potential application in electrochemical devices for heavy metal water remediation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 November 2013

Received in revised form 13 May 2014

Accepted 19 May 2014

Available online 27 May 2014

Keywords:

Thiolated DAB dendrimer
Engineered cellulosic membrane
Diffusive permeability reduction
Heavy metals remediation

ABSTRACT

Diaminobutane based poly(propyleneimine) dendrimer functionalized with sixteen thiol groups, DAB-3-(SH)₁₆, was successfully embedded in a swollen cellulosic support in order to achieve an easily handle engineered membrane. The membrane was characterised by physicochemical, electrical and transport measurements, and the effect of the dendrimer was established by comparing these results with those obtained for the original cellulosic support. Results show that dendrimer inclusion improves the membrane elastic behaviour (Young modulus increase around 20%), while a significant reduction in the permeation of toxic heavy metals (Cd²⁺, Hg²⁺ and Pb²⁺) was also obtained, which avails the possible application of dendrimer-modified membrane in electrochemical devices for water remediation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Membrane processes such as ultrafiltration, nanofiltration and reverse osmosis are nowadays currently applied to sea and brackish water desalting [1,2], while liquid supported membranes and polymer inclusion membranes have been proposed for treatment of industrial wastewater and metal cations recovery [3,4]. In fact,

heavy metal contamination of natural and wastewaters has become an important environmental problem, being cadmium, nickel, lead, mercury, copper and zinc the most hazardous [5,6]. Among the strategies proposal for metal ions removal from water, diffusive separation by heavy metal contaminated water passes through a membrane is a simple technique applicable to electrochemical devices.

Regenerated cellulose (RC) is a natural material used in membrane manufacture due to their high hydrophilicity and rather good chemical and solvent resistance. Particularly, RC membranes exhibit very high swelling degrees when they are in contact with

* Corresponding authors. Tel.: +34 952131929; fax: +34 952132000.

E-mail addresses: malgarra67@gmail.com (M. Algarra), j_benavente@uma.es (J. Benavente).

aqueous solutions [7,8], which can favor the inclusion of different substances in cellulose cross-linked structure and confer them particular characteristics able to affect the mass transport across the membranes [9,10].

Dendrimers and their derivatives are substances with diverse analytical, biomedical and environmental applications [11–15] due to their unique molecular structure, easy functionalization and manipulation of their terminal groups [16–21]. Dendritic polymers basically consist of a multi-functional core, high degree of repeated branching units and high density of surface functional groups [22]. A commercial poly(amidoamine) dendrimer (PAMAM) has been used in separation systems for recovery heavy metals from aqueous solution by means of chelating agents in pollution remediation processes. Particularly, aqueous heavy metal solutions treated with PAMAM previous to pass them through a membrane (ultrafiltration technique) has been proposed for water and soil remediation [23–27]. Other researchers have obtained functionalized membranes with PAMAM, hydroxyl PAMAM and carboxyl PAMAM for CO₂/N₂ separation and as models for adsorption of dye molecules [28–31]. Recently, raw PAMAM, aromatic PAMAM and PAMAM coated with polyethylene glycol have been used in the modification of polymeric reverse osmosis membranes for Ba²⁺, Na⁺ and As³⁺ recovery [32–34] and other contributions on dendrimers immobilization have also been proposed [35–37]. In this context, in a previous work we analyzed the possible use of a fifth generation thiol poly(propyleneimine) dendrimer coated with CdSe and embedded in a hydrophilic cellulosic membrane as cadmium sensor in liquid media [10], where the fluorescence character of the modified dendrimer allows us to confirm its presence in the structure of the cellulosic support.

In this work, a diaminobutane based poly(propyleneimine) dendrimer functionalized with sixteen thiol groups, DAB-3-(SH)₁₆, was included in a regenerated cellulose support in order to obtain a nano-engineered modified membrane. Original and modified membranes were characterised by physicochemical and diffusion measurements to see the effect of the dendrimer by comparing the results obtained with both membranes. Particularly, elastic and chemical information was obtained from tensile-strength/elongation curves and Raman spectroscopy, while changes in electrical resistance were associated to differences electrolytes uptake;

moreover reduction in toxic heavy metals (Cd²⁺, Hg²⁺ and Pb²⁺) permeabilities were determined from diffusion measurements. Difference in this parameter supports the possible application of this engineered membrane in electrochemical device for water remediation.

2. Materials and methods

2.1. Dendrimer

The thiolated dendrimer DAB-3-(SH)₁₆ was synthesized by treatment of the third diaminobutane based poly(propyleneimine) dendrimer DAB-3-(NH₂)₁₆ with an excess of 3-mercaptopropionyl-N-hydroxysuccinimide ester in dichloromethane solution at room temperature, according to the procedure already published [38]. Fig. 1 presents a scheme of the studied dendrimer with the sites for cation anchorage.

2.2. DAB-3-(SH)₁₆ dendrimer inclusion in the support membrane

A flat regenerated cellulose (RC) swollen membrane from Cellophane Española, S.A. (Burgos, Spain) with a content of 0.04 kg m⁻² of regenerated cellulose (sample RC/4) was used as support. The swelling degree of this membrane, $S_w = (\Delta x_w - \Delta x_d) / \Delta x_d$, where Δx_d and Δx_w represent the thickness of dry and wet samples, is $S_w = (79 \pm 4)\%$. Pieces of the RC-4 membrane were immersed in a water solution of the dendrimer for 2 h and dried at room temperature (sample RC/4+dendrimer). Fig. 2 shows a scheme of the easy to hand nano-engineered RC/4+dendrimer flat membrane.

2.3. Raman measurements

1064 nm FT-Raman spectra were obtained in an FT-Raman accessory kit (FRA/106-S) of a Bruker Equinox 55 FT-IR interferometer. A continuous-wave Nd-YAG laser working at 1064 nm was employed for excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back-scattering configuration with a standard

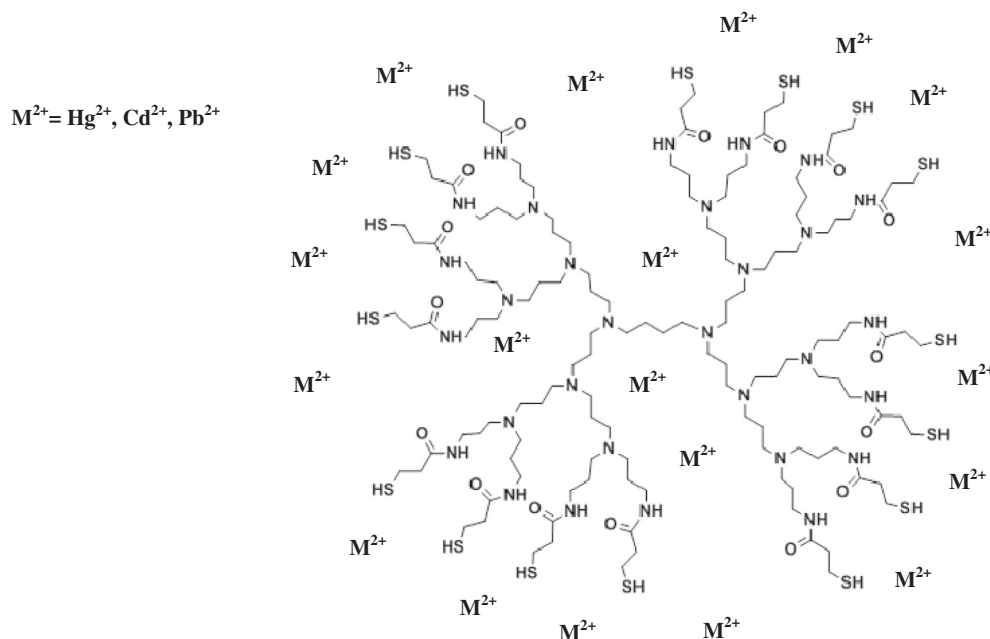


Fig. 1. Molecular representation of the interaction of DAB-3-(SH)₁₆ dendrimer with M²⁺.

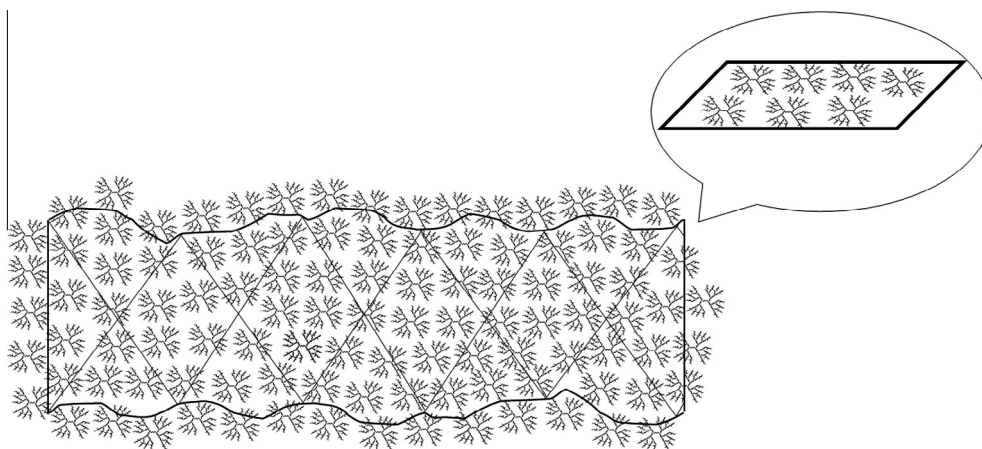


Fig. 2. Schematic representation of the coated RC/4 membrane by DAB-3-(SH)₁₆ dendrimer.

spectral resolution of 4 cm⁻¹. 2000 scans were averaged for each spectrum.

2.4. Elastic measurements

Measurements for the elastic characterization of membranes were performed with a force digital gauge (Mark-T, ES20 model) connected to a computer, with a maximum tension of 100 N, length accurate of ±0.01 mm and a strength rate of 10 mm/s. Samples of the same size (1 cm width × 4 cm length) of both membranes were used and measurements carried out with the membranes placed in a water tank.

2.5. Impedance spectroscopy measurements

The test cell for impedance spectroscopy (IS) measurements consisted of a Teflon support on which two Pt electrodes were placed and screwed down. The electrodes were connected to an Frequency Response Analyzer (Solartron 1260, England) and measurements were recorded for 100 data points with frequency ranging between 1 Hz and 10⁷ Hz, at a maximum voltage of 0.01 V. Impedance measurements were performed with dry and wet samples of both RC/4 and RC/4+dendrimer membranes; wet samples mean immersed for 24 h in a 1 mM solution of the different electrolytes (CdCl₂, PbCl₂ and HgCl₂), which allows us to determine differences associated to the uptake of the different cations in the membrane electrical parameters as well as the dendrimer effect.

The impedance is a complex number, $Z = Z_{\text{real}} + j Z_{\text{img}}$, which can be separated into real and imaginary parts by algebra rules. Membrane electrical parameters can be determined by analyzing the impedance plot (Z_{real} versus $-Z_{\text{img}}$) by considering an equivalent circuit formed by a parallel association of a resistance (R) and a capacitor (C), which is related to Z_{real} and Z_{img} by the following expressions [39]:

$$Z_{\text{real}} = \left(R / [1 + (\omega RC)^2] \right), Z_{\text{img}} = - \left(\omega R^2 C / [1 + (\omega RC)^2] \right)$$

where ω represents the angular frequency ($\omega = 2\pi f$). Complex systems usually present a distribution of relaxation times and the resulting plot is a depressed semi-circle, which is associated to a non-ideal capacitor or constant phase element (CPE) [39].

2.6. Salt diffusion measurements

Diffusion measurements allow the determination of the diffusive permeability (P_s) and they were performed in a dead-end test cell similar to that previously described [40]. The membranes were

placed in the middle of two symmetric half-cells separating two different solutions, one donor ($c_d = 0.001$ M of CdCl₂, PbCl₂ and HgCl₂, respectively) and distilled water as receiving solution (initially, $c_r = c_r^0 = 0$), and concentration-polarization at the membrane/solution interfaces was minimized by using two Teflon-covered magnetic stirrers at a stirring rate of 540 rpm. Variation in the conductivities of the solutions in feed and receiving half-cells were recorded versus time by means of two conductivity cells, each one placed in one half-cell, and connected to two digital conductivity-meters (Crison GLP 31). Conductivity-concentration calibration curves for each electrolyte were used for receiving concentration determination. Measurements were carried out at room temperature (25 ± 2) °C and standard pH (5.8 ± 0.3).

3. Results and discussion

Possible chemical changes in the cellulosic support membrane as a result of both dendrimer inclusion and heavy metal uptakes after membrane immersion for 24 h in water or 1 mM of the studied electrolytes (CdCl₂, PbCl₂ and HgCl₂) were analyzed by Raman spectroscopy. Fig. 3 displays the Raman spectra of three samples, which correspond to: RC/4 (a) and RC/4+dendrimer (b) dry membranes, while Fig. 3(c) shows the spectra of this latter sample after immersion in the HgCl₂ aqueous solution (wet membrane sample). As can be observed, the spectrum of the RC/4+dendrimer does not

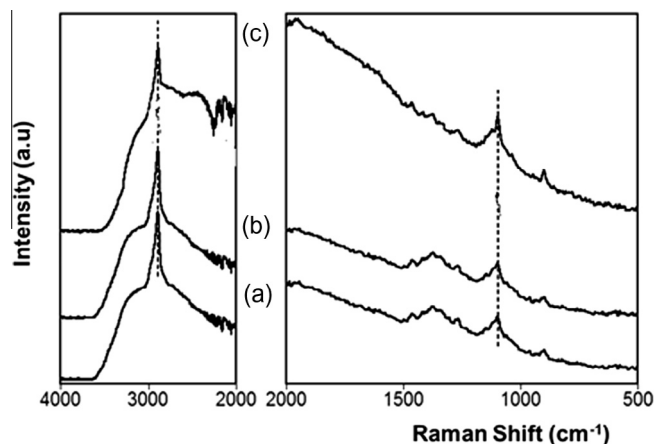


Fig. 3. 1064 nm FT-Raman spectra of: (a) RC/4 dry membrane, (b) RC/4+dendrimer dry membrane, (c) RC/4+dendrimer membrane embedded in a 10⁻³ M HgCl₂ aqueous solution.

undergoes any appreciable transformation when compared with the original RC/4 support; however, as a result of its immersion in a water solution of HgCl_2 , some changes in the spectral background are observed which are specially notable in the region around 1400 cm^{-1} , but they do not reveal chemical transformation in the RC/4+dendrimer membrane but electrolyte absorption driven by physical forces.

Moreover, very similar Raman spectra for the RC/4+dendrimer membrane embedded of HgCl_2 and CdCl_2 aqueous solutions can also be observed in Fig. 4, indicating that no changes in the membrane chemical structure have taken place, but some differences exist in the spectrum of the RC/4+dendrimer membrane with PbCl_2 , although no new bands assignable to the formation of new chemical structures are detected. The change in spectral background in the PbCl_2 case might be again an indication of the involvement of distinctive physical phenomena (reversible from a chemical point of view).

To estimate physical changes in the cellulosic support associated to the presence of the dendrimer, elastic and electrical characterization of RC/4 and RC/4+dendrimer membranes in conditions related with membrane applications (aqueous solutions) were considered.

Measurements of membranes elastic response were performed with the samples submerged in a water bath to check the effect of the presence of the dendrimer and its maintenance in the hydrophilic cellulosic support under such conditions (contact with aqueous solutions). Fig. 5 shows the normal stress–strain curves (F/S vs $\Delta L/L_0$) obtained for both membranes, where clear differences can be observed. This fact is rather interesting since it demonstrates the stability of this highly hydrophilic engineered membrane even in aqueous environments. Young modulus was obtained from the slope of the linear part of the curves, which corresponds at low elongations, and the following values were determined: $E(\text{RC}/4) = (24.5 \pm 1.8)\text{ MPa}$ and $E(\text{RC}/4+\text{dendrimer}) = (39 \pm 6)\text{ MPa}$. These results indicate that both hydrated samples can be considered as soft plastics ($E < 70\text{ MPa}$) and the presence of the dendrimer increases the Young modulus ($\sim 20\%$) and length at break ($\sim 8\%$).

Impedance spectroscopy measurements also permit us to get information on the presence of the dendrimer in the cellulosic structure and its effect on a characteristic physical parameter (electrical resistance) or a material specific parameter (conductivity) by analysing the impedance plots [39,41]. Variations of Z_{real} values (related to electrical resistance/conductivity) with the applied frequency (Bode plot) are presented in Figs. 6 and 7. Particularly, Fig. 6 shows a comparison of the experimental values

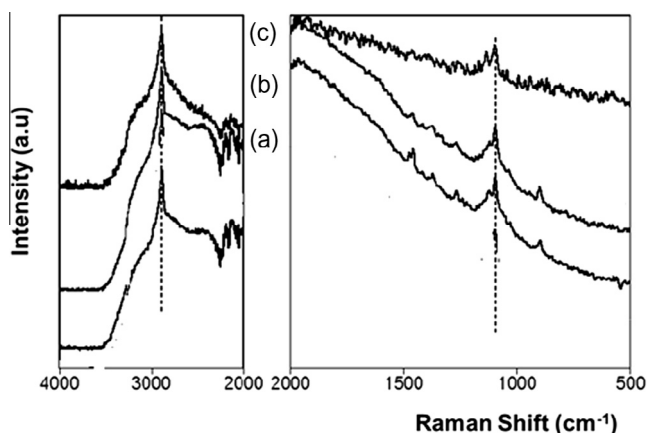


Fig. 4. 1064 nm FT-Raman spectra of membranes embedded of different electrolytes 10^{-3} M aqueous solution: (a) the RC/4 membrane and HgCl_2 ; (b) RC/4+dendrimer membrane and HgCl_2 ; (c) RC/4+dendrimer membrane and CdCl_2 ; (d) RC/4+dendrimer membrane and PbCl_2 .

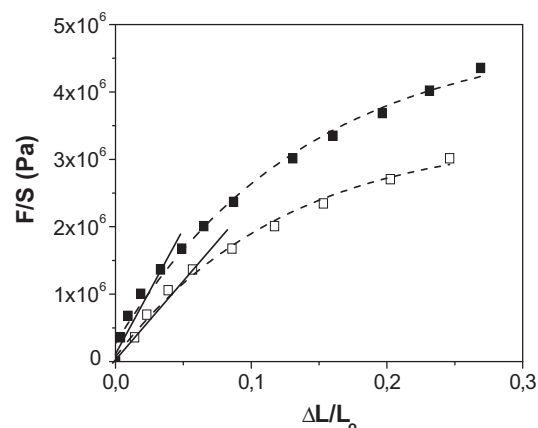


Fig. 5. Normal stress versus strain curves for hydrated membranes RC/4 (□) and RC/4+dendrimer (■).

obtained for RC/4 and RC/4+dendrimer membrane samples in hydrated state (after 24 h in distilled water), where slight differences in both interface and bulk membrane contribution can be observed, which is a confirmation of dendrimer inclusion into the cellulosic support structure already obtained from normal stress–strain curves but also of surface coverage; the increase in Z_{real} values for the RC/4+dendrimer membrane is concordant with its more rigid structure due to the dendrimer inclusion but it also indicates the stability of the engineered membrane under adverse conditions (aqueous environment plus alternating electric field).

The effect of dendrimer on Z_{real} values can clearly be observed in Fig. 7, where a comparison of the impedance values for the original and the dendrimer modified membranes, RC/4 and RC/4+dendrimer, after 24 h immersed in each electrolyte solution is shown. In this case, a reduction in Z_{real} values for the RC/4+dendrimer samples embedded with each one of the electrolytes studied is an indication of the higher number of charges and, consequently, the entrapment of heavy metal cations by the RC/4+dendrimer membrane. Moreover, higher entrapment of Hg^{2+} cation (or stronger interaction) could be expected taking into account the slightly lower experimental values shown in Fig. 7c.

Diffusive electrolyte transport in a membrane caused by a concentration gradient ($\Delta c = c_d - c_r$) is usually characterized by its permeability (P_s), which is the parameter indicating the total or partial restriction that the membrane offers to the transport of a

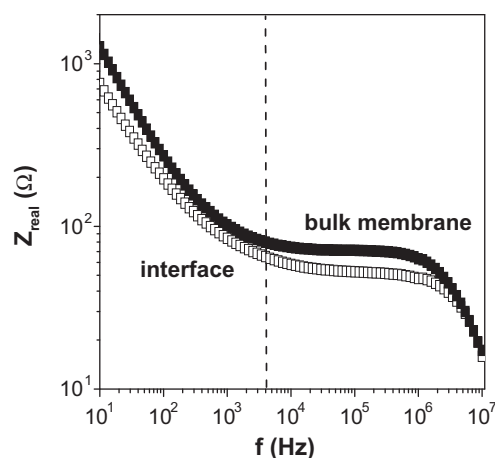


Fig. 6. Bode plots for RC/4 (□) and RC/4+dendrimer (■) membranes after 24 h immersion in distilled water.

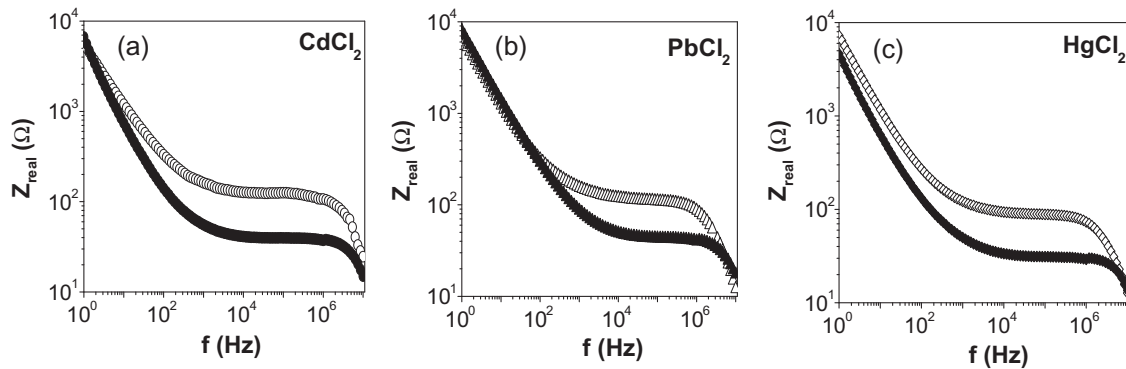


Fig. 7. Comparison of Bode plots for RC/4 membrane (open symbols) and RC/4+dendrimer membrane (dense symbols) after 24 h immersion in (a) CdCl₂, (b) HgCl₂ and (c) PbCl₂.

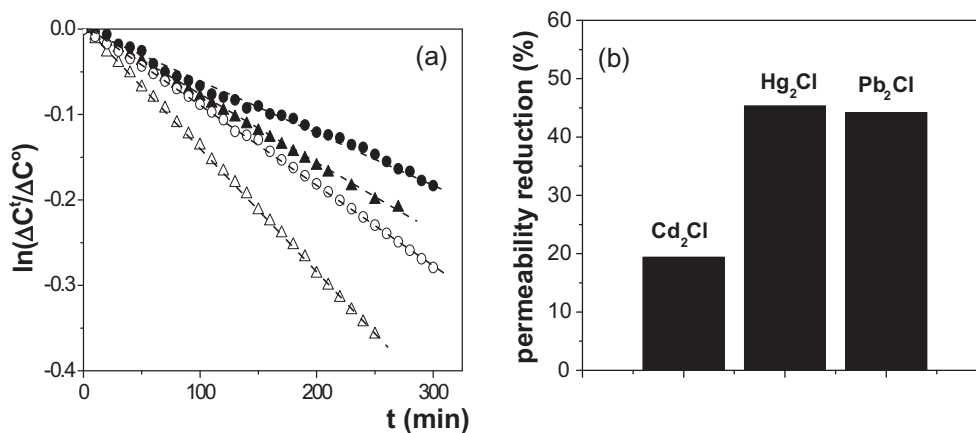


Fig. 8. (a) Time dependence of relative electrolyte concentration difference in the solutions at both membrane sides with: RC/4 support membrane (○) CdCl₂ and (△) PbCl₂ solutions; RC/4+dendrimer engineered membrane (●) CdCl₂ and (▲) PbCl₂ solutions. (b) Permeability reduction for CdCl₂, PbCl₂ and HgCl₂ solutions as a result of dendrimer inclusion in the support membrane.

particular solute. In steady-state condition, the flux of mass per membrane area (J_s) is related with the difference of concentrations between both membrane surfaces by Fick's first law [1]:

$$J_s = (dn/dt)(1/S) = P_s(c_d - c_r) = P_s \Delta c \quad (1)$$

where S indicates the membrane area. Since $dn/dt = (1/V_0)(dc/dt)$, Eq. (1) can be expressed as:

$$dc_r/(c_d - c_r) = (S/V)P_s dt \quad (2)$$

where V is the volume of the solution, while dn and dt represent the mass crossing the membrane in an elemental period of time, respectively. Taking into account the mass continuity:

$$c_d^0 + c_r^0 = c_d^t + c_r^t = cte \quad (3)$$

where c_d^0 and c_r^0 indicate the concentrations of initial donor and receiving solutions (time $t = 0$), while c_d^t and c_r^t correspond to these concentrations at a certain time t ; then, the following expression is obtained [7]:

$$\ln[\Delta c^t/\Delta c^0] = -2(S/V) \cdot P_s \cdot t \quad (4)$$

Fig. 8a shows time evolution of the concentration ratio for each membrane and electrolyte studied where significantly lower values for the RC/4+dendrimer membrane with the same electrolyte can be observed, which indicates a reduction in the solute celerity through the engineered membrane. The effect of a membrane on solute transport can be quantified by determining its diffusive permeability, P_s , which is determined from the slopes of the linear

relationships according to Eq. (4). A decrease in diffusive permeability through the RC/4+dendrimer membrane when compared with the RC/4 original sample was obtained for all the studied electrolytes, which is associated to the reduction in free volume among the cellulosic chains due to the presence of dendrimer. Permeability reduction ($PR = (P_s^{RC/4} - P_s^{RC/4+dendrimer})/P_s^{RC/4}$) for the different electrolytes is indicated in Fig. 8b. As can be observed, this effect is lower for the CdCl₂ solution (~20%) than for HgCl₂ and PbCl₂ ones (~45%), which could also open the possibility of heavy metal discrimination in case of electrochemical devices application.

4. Conclusions

In summary, innovative and simple thiol DAB-dendrimer incorporation in a highly hydrophilic cellulosic support by immersion in an aqueous solution has permitted us to obtain a nano-engineered system with potential application in heavy metal water remediation. As a result of DAB-dendrimer incorporation, elastic behaviour of the cellulosic support was improved by increasing Young modulus of wet samples (~20%) and a slight uptakes of heavy metals of environmental interest (Cd, Hg and Pb) according to the results supported by two different chemical and physical techniques (Raman and impedance spectroscopy analysis). Moreover, the reduction in diffusive permeability across the DAB-dendrimer engineered membrane obtained for different chloride salts (CdCl₂, HgCl₂ and PbCl₂) demonstrate its control on the transport of these contaminant metal ions when incorporate in remediation devices.

Permeability reduction supports the possible application of dendrimer-engineered cellulosic membranes in electrochemical devices used in water remediation associated to heavy metal contamination.

Acknowledgments

The authors would like to thanks to Andalucía Tech Program (Universidad de Málaga, Spain) and the CICYT (MINECO, Spain, research project CTQ/2011-27770 FEDER funds) for partial financial support. Spanish Ministerio de Ciencia e Innovación (Project CTQ2009-12332-C02-01) is also acknowledged.

References

- [1] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, 1992.
- [2] R.W. Baker, *Membrane Technology and Applications*, John Wiley & Sons, England, 2004.
- [3] C. Fontàs, R. Tayeb, S. Tingry, M. Hidalgo, P. Seta, Transport of platinum(IV) through supported liquid membrane (SLM) and polymeric plasticized membrane (PPM), *J. Membr. Sci.* 263 (2005) 96–102.
- [4] C. Gherasim, G. Bourceany, R. Olariu, C. Aresene, A novel polymer inclusion membrane applied in chromium(VI) separation from aqueous solutions, *J. Hazard. Mater.* 197 (2011) 244–253.
- [5] R. Güell, E. Anticó, S.D. Kolev, J. Benavente, V. Salvadó, C. Fontàs, Development and characterization of polymer inclusion membranes for the separation and speciation of inorganic As species, *J. Membr. Sci.* 383 (2011) 88–95.
- [6] M. Hofman, R. Pietrzak, Copper ions removal from liquid phase by Polyethersulfone (PES) membranes functionalized by introduction of carbonaceous materials, *Chem. Eng. J.* 215–216 (2013) 216–221.
- [7] D.L. Gilbert, T. Okano, T. Miyata, S.W. Kim, Molecular diffusion through collagen membranes, *Int. J. Pharm.* 47 (1988) 79–85.
- [8] J.D. Ramos, C. Milano, V. Romero, S. Escalera, M.C. Alba, M.I. Vázquez, J. Benavente, Water effect on physical–chemical and elastic parameters for a dense cellulose regenerated membrane. Transport of different aqueous electrolyte solutions, *J. Membr. Sci.* 352 (2010) 153–159.
- [9] M.I. Vázquez, V. Romero, J. Hierrezuelo, R. Rico, J.M. López-Romero, M.R. López-Ramírez, J. Benavente, Effect of lipid nanoparticles inclusion on transport parameters through regenerated cellulose membranes, *J. Membr. Sci.* 370 (2011) 70–75.
- [10] M. Algarra, B.B. Campos, B. Alonso, C.M. Casado, J.C.G. Esteves da Silva, J. Benavente, Inclusion of thiol DAB dendrimer/CdSe quantum dots based in a membrane structure: surface and bulk membrane modification, *Electrochim. Acta* 89 (2013) 652–659.
- [11] D.A. Tomalia, A.N. Naylor, W.A. Goddard III, Starburst dendrimers: molecular level control of size, shape, surface, chemistry and topology, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 138–175.
- [12] J.M.J. Fréchet, Functional polymers and dendrimers: reactivity, molecular architecture, and interfacial energy, *Science* 263 (1994) 1710–1715.
- [13] J.M.J. Fréchet, D.A. Tomalia, *Dendrimers and Other Dendritic Polymers*, Wiley-VCH, Weinheim, 2001.
- [14] Y. Cheng, *Dendrimer Based in Drug Delivery Systems*, John Wiley & Sons, Hoboken, NJ, 2012.
- [15] C.N. Moorefield, S. Perera, G.R. Newkome, Dendrimer chemistry: supramolecular perspectives and applications, in: Y. Cheng (Ed.), *Dendrimer-based Drug Delivery Systems: From Theory to Practice*, John Wiley & Sons, Hoboken, NJ, 2012 (Chapter 1).
- [16] U. Boas, P.M. Heegaard, Dendrimers in drug research, *Chem. Soc. Rev.* 33 (2004) 43–63.
- [17] M. Algarra, B.B. Campos, M.S. Miranda, J.C.G. Esteves da Silva, CdSe quantum dots capped PAMAM dendrimer nanocomposites for sensing nitroaromatic compounds, *Talanta* 83 (2011) 1335–1340.
- [18] J.C.G. Esteves da Silva, M. Algarra, B.B. Campos, Synthesis and analytical applications of Quantum Dots coated with different generations of DAB dendrimers, in: B. Reddy (Ed.), *Advances in Nanocomposites-Synthesis, Characterization and Industrial Applications*, IN-TECH, 2011, pp. 23–38.
- [19] M. Algarra, B.B. Campos, B. Alonso, M.S. Miranda, A.M. Martínez, C.M. Casado, J.C.G. Esteves da Silva, Thiolated DAB dendrimers and CdSe quantum dots nanocomposites for Cd(II) or Pb(II) sensing, *Talanta* 88 (2012) 403–407.
- [20] G. Jie, J. Yuan, Quantum dots-based multifunctional dendritic superstructure for amplified electrochemiluminescence detection of ATP, *Biosens. Bioelectron.* 31 (2012) 69–76.
- [21] J.M. Oliveira, A.J. Salgado, N. Sousa, J.F. Mano, R.L. Reisa, Dendrimers and derivatives as a potential therapeutic tool in regenerative medicine strategies – a review, *Prog. Polym. Sci.* 35 (2010) 1163–1194.
- [22] F. Vogtle, G. Richardt, N. Werner, *Dendrimer Chemistry: Concepts, Syntheses, Properties, Applications*, Wiley-VCH, Weinheim, 2009.
- [23] A. Rether, M. Schuster, Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers, *React. Funct. Polym.* 57 (2003) 13–21.
- [24] M.S. Diallo, S. Christie, P. Swaminathan, L. Balogh, X. Shi, W. Um, C. Papelis, W.A. Goddard 3rd, J.H. Johnson Jr., Dendritic chelating agents. 1. Cu(II) binding to ethylene diamine core poly(amidoamine) dendrimers in aqueous solutions, *Langmuir* 20 (2004) 2640–2651.
- [25] M.S. Diallo, S. Christie, P. Swaminathan, J.H. Johnson Jr., W. Goddard, Dendrimer enhanced ultrafiltration. 1. Recovery of Cu(II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core and terminal NH₂ groups, *Environ. Sci. Technol.* 39 (2005) 1366–1377.
- [26] M.S. Diallo, W. Arasho, J.H. Johnson Jr., W.A. Goddard, Dendritic chelating agents. 2. U(VI) binding to poly(amidoamine) and poly(propyleneimine) dendrimers in aqueous solutions, *Environ. Sci. Technol.* 42 (2008) 1572–1579.
- [27] Y. Xu, D. Zhao, Removal of Cu(II) from contaminated soil using pamam dendrimers, *Environ. Sci. Technol.* 39 (2005) 2369–2375.
- [28] M.A. Barakat, M.H. Ramadan, M.A. Alghamadi, S.S. Algarny, H.L. Woodcock, J. Kuhn, Remediation of Cu(II), Ni(II), and Cr(III) ions from simulated wastewater by dendrimer/titania composites, *J. Environ. Manage.* 117 (2013) 50–57.
- [29] S. Duan, T. Kouketsu, S. Kazama, K.J. Yamada, Development of PAMAM dendrimer composite membranes for CO₂ separation, *J. Membr. Sci.* 283 (2006) 2–6.
- [30] T. Kouketsu, S. Duan, T. Kai, S. Kazama, K. Yamada, PAMAM dendrimer composite membrane for CO₂ separation: formation of a chitosan gutter layer, *J. Membr. Sci.* 287 (2007) 51–59.
- [31] S. Tomita, K. Sato, J. Anzai, Layer-by-layer assembled thin films composed of carboxyl-terminated poly(amidoamine) dendrimer as a pH-sensitive nano-device, *J. Colloid Interface Sci.* 326 (2008) 35–40.
- [32] S. Duan, F.A. Chowdhury, T. Kai, S. Kazama, Y. Fujioka, PAMAM dendrimer composite membrane for CO₂ separation: addition of hyaluronic acid in gutter layer and application of novel hydroxyl PAMAM dendrimer, *Desalination* 234 (2008) 278–285.
- [33] A. Sarkar, P.I. Carver, T. Zhang, A. Merrington, K.J. Bruza, J.L. Rousseau, S.E. Keinath, P.R.J. Dvornic, Dendrimer-based coatings for surface modification of polyamide reverse osmosis membranes, *J. Membr. Sci.* 349 (2010) 421–428.
- [34] Q. Zhang, N. Wang, L. Zhao, T. Xu, Y. Cheng, Polyamidoamine dendronized hollow fiber membranes in the recovery of heavy metal ions, *ACS Appl. Mater. Interfaces* 349 (2013) 1907–1912.
- [35] D. Hiraiwa, T. Yoshimura, K. Esumi, Interaction forces between poly(amidoamine) (PAMAM) dendrimers adsorbed on gold surfaces, *J. Colloid Interface Sci.* 298 (2006) 982–986.
- [36] Y. Gao, A.M. Sáez de Jubera, B.J. Mariñas, Nanofiltration membranes with modified active layer using aromatic polyamide dendrimers, *Adv. Funct. Mater.* 23 (2013) 598–607.
- [37] V. Katur, M. Eichler, E. Deigle, C. Stage, P. Karageorgiev, J. Geis-Gerstorfer, G. Schmalz, S. Ruhl, F. Rupp, R. Müller, Surface-immobilized PAMAM-dendrimers modified with cationic or anionic terminal functions: physicochemical surface properties and conformational changes after application of liquid interface stress, *J. Colloid Interface Sci.* 366 (2012) 179–190.
- [38] S. Connolly, S.N. Rao, D. Fitzmaurice, Characterization of protein aggregated gold nanocrystals, *J. Phys. Chem. B* 104 (2000) 4765–4776.
- [39] J. Benavente, Use of impedance spectroscopy for characterization of membranes and the effect of different modifications, in: N. Hilal, M. Khayet, Ch.J. Wright (Eds.), *Membrane Modification: Technology and Applications*, CRC Press, 2012.
- [40] L. Pelaez, M.I. Vázquez, J. Benavente, Interfacial and fouling effects on diffusional permeability across a composite ceramic membrane, *Ceram. Int.* 36 (2010) 797–801.
- [41] R.J. MacDonals, *Impedance Spectroscopy*, Wiley, New York, 1987.