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

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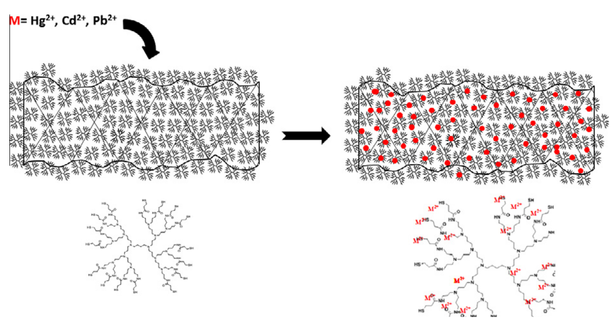
HIGHLIGHTS

- 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 (Cd^{2+}, Hg^{2+} and Pb^{2+}) solutions.
- Potential application in electrochemical devices for heavy metal water remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

Diaminobutane based poly(propyleneimine) dendrimer functionalized with sixteen thiol groups, DAB-3-$(SH)_{16}$, was successfully embeded 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 toxics heavy metals (Cd^{2+}, Hg^{2+} and Pb^{2+}) was also obtained, which avails the possible application of dendrimer-modified membrane in electrochemical devices for water remediation.

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

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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 CO_2/N_2 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 Ba^{2+}, Na^{+} and As^{3+} 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 (Cd^{2+}, Hg^{2+} and Pb^{2+}) pemeabilities 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-$(NH_2)_{16}$ with an excess of 3-mercaptopropanyl-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 Brucker 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

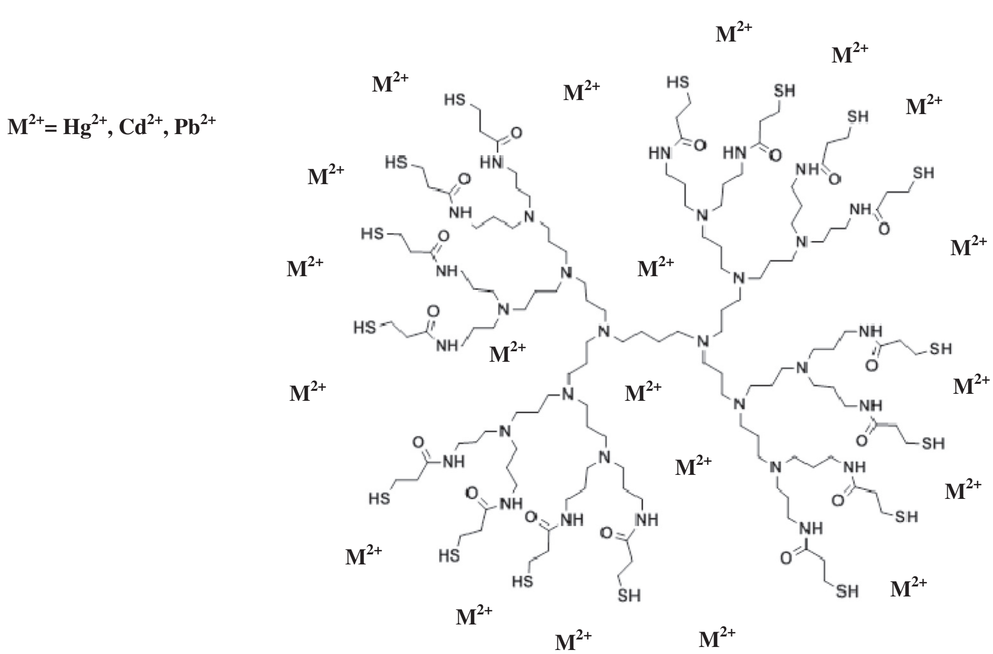

Fig. 1. Molecular representation of the interaction of DAB-3-$(SH)_{16}$ dendrimer with $\mathbf{M^{2+}}$.