CELLULOSE CHEMISTRY AND TECHNOLOGY

WATER PURIFICATION BY PHOTO-ELECTRODIALYSIS USING PMMA-L-CYSTEINE NANOPARTICLE MEMBRANES COMBINED WITH SEMICONDUCTORS

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The present work combines the solar energy with the environmental protection through the membrane selectivity for metallic ions. Firstly, we prepared new cationic and anionic polymeric membranes for ions separation. The membranes were prepared using PMMA/L-cysteine noted PM-CYST plasticized by dioctyle phthalate (DOP), or a mixture of cellulose triacetate (CTA), polyethyleneimine (PEI) and DOP. All synthesized membranes were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). In the second part, we prepared two new semiconductors *n*-$Sr_2Fe_2O_5$ and *p*-$CuFeO_2$ and their photo-electrochemical characterizations were undertaken. As application, the transport of Pb^{2+} using synthesized membranes coupled with the synthetized photoelectrodes was studied. The photo-catalytic results indicate that the combined hetero-system *n*-$Sr_2Fe_2O_5$/*p*-$CuFeO_2$ enhances considerably the electrons transfer. The diffusion flux of Pb^{2+} increases considerably when the electrode is exposed to visible light. The results show that the diffusion percentages of Pb^{2+} increase by 68% under solar energy and 79% using a LED lamp.

Keywords: membranes; nanoparticles; polymers; semiconductor; *n*-$Sr_2Fe_2O_5$, *p*-$CuFeO_2$ photo-electrochemistry

INTRODUCTION

The protection of the environment from the effects of pollution is related principally to the elimination of toxic metals and requires the use of new technologies known as clean, efficient, durable and less expensive. Water pollution control has become a priority even for developing countries. Currently, environmental research is focusing on conventional separation methods, including ion exchange resins,[1] reverse osmosis[2] and desalination methods.[4] Most of the conventional separation and metallic concentration processes used in hydrometallurgy, such as precipitation, ore leaching or liquid–liquid extraction are currently reconsidered in view of their possible substitution with processes using synthetic membranes. In order to recycle and reuse wastewater, one of the solutions that seem very promising is the installation of membrane filtration systems capable of ensuring the purification of effluents. The majority of these processes use organic membranes based on several polymers.[4-6] Many papers have been published using polymeric membranes based on cellulose triacetate (CTA).[7-16] Recently, Arous *et al.*[17-20] combined polymeric membranes with semiconductors to improve the performance of metal ion transfer/diffusion.

Nanotechnology is an innovative field of research that has accomplished a great deal in the last decades. In the simplest terms, it deals with materials and devices with nanometer dimensions. Nanotechnology leverages the properties of nanoparticles into a wide range of applications, spanning a vast number of industries. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly ameliorated using nanosorbents,[21] nanocatalysts,[22] bioactive nanoparticles,[23] nanostructured catalytic membranes and nanoparticles enhanced filtration systems, among other products and processes.

Polymer nanospheres have received increasing attention in a number of research fields. Among various polymers, poly(methyl methacrylate) (PMMA) has been widely investigated for a variety of applications. However, the surface of PMMA prevents adhesion to other substances, limiting its applications. Therefore, functionalization of the PMMA would provide the polymer with more practical applications.

In this work, we present a successful new strategy to activate the PMMA surface by grafting an amino acid, L-cysteine ($C_3H_7NO_2S$), which contains three functional groups: amine ($-NH_2$), carboxylic (- COOH), and thiol (-SH).

The present work deals with two attractive aspects, economic and environmental, based on the membrane selectivity for metal ions. The principal objective of this work is the development of enhanced polymeric membranes at a low cost, based on PMMA/L-Cysteine as a polymeric matrix and semiconductors. A further objective of this paper is the treatment of wastewater polluted by heavy metals, principally Pb^{2+}, and to evaluate the usage possibility of treated wastewater in irrigation.

In this paper, we prepared by a chemical route two new semiconductors: $Sr_2Fe_2O_5$ (*n* type) and $CuFeO_2$ (*p* type). In parallel, we synthesized a novel class of plasticized polymeric membranes modified by polyelectrolytes. The combination between membranes and semiconductors was subsequently carried out for the purification of Pb polluted water.

EXPERIMENTAL

Chemicals

All chemicals used in this work were of analytical reagent grade and used as received, without any further purification. $PbCl_2$ (99.99%), tetrahydrofuran (THF) (GC ≥99%), chloroform, polyethyleneimine (PEI) were purchased from Fluka Company. Dioctyl phtalate (DOP) was a product of Carlo Erba Company. The reagents as potassium persulfate (KPS, Sigma-Aldrich, 98%), and L-cysteine ($C_3H_7NO_2S$, Sigma Aldrich) were used without any purification. The monomer methyl methacrylate (MMA) (Acros Organics, 99%) was distilled before use. The aqueous solutions were prepared by dissolving the different reagents in double-distilled water.

Synthesis of PMMA nanoparticles grafted with L-cysteine

The PMMA nanoparticles grafted with L-cysteine were prepared by emulsion polymerization of methyl methacrylate, in the presence of L-cysteine in an aqueous solution.

Two different samples, containing 0.01 g and 0.05 g of L-cysteine, labeled PM-CYST1 and PM-CYST2, respectively, were synthesized by free-radical emulsion polymerization using an optimized version of the method reported in the literature.[24-25]

Briefly, 6 mL of MMA in 80 mL of distilled water, containing 0.01 g and 0.05 g of L-cysteine were added to a three-neck round-bottom flask, equipped with a water condenser, thermometer and nitrogen gas. The mixture solution was stirred vigorously at approximately 400 rpm and heated to 70 °C under nitrogen gas. After stabilization of the temperature, 0.10 g of KPS as an initiator was added, and the emulsion polymerization was allowed to proceed for 60 min. Next, the colloidal solution obtained was filtered through glass wool to remove all the polymer agglomerates. In order to remove impurities and unreacted monomers, the polymer nanospheres were isolated by centrifugation and washed with distilled water three times. The L-cysteine grafted PMMA nanospheres obtained from the two reaction mixtures have an average diameter of 220 nm.

Preparation of membranes

Plasticized polymeric membranes were prepared using the same procedure as described by Sugiura *et al.*[7] Briefly, 0.2 g of PM-CYST or 0.1 g of cellulose triacetate (CTA) and 0.1 g of polyelectrolyte (PEI) were dissolved in 30 mL of tetrahydrofuran (THF) and stirred for 4 h. Then, 0.1 mL of DOP was added under vigorous stirring during 2 h. The solutions were transferred in a circular glass container and left for a slow evaporation during 24 h. The resulting membranes were extracted by addition of double-distilled water and dried at 40 °C.

Synthesis of $Sr_2Fe_2O_5$ and $CuFeO_2$ semi-conductors

The brownmillerite $Sr_2Fe_2O_5$ was prepared by the nitrate route from $Fe(NO_3)_3$ $9H_2O$ (Merck, 99.5%) and $Sr(NO_3)_2$ (Merck, >99.5%). The stoichiometric mixture was dissolved in water and the solution was slowly evaporated on a sand bath. The powder was ground, pressed into pellets and heated at 950 °C for 6 h, with average compactness of 75%. The delafossite $CuFeO_2$ was synthesized by nitrate decomposition; the detailed preparation procedure is given elsewhere.[26]

The phases were identified by XRD analysis (Ital Structures Diffractometer APD2000). UV-Visible spectra of the oxides were recorded with a Specord 200 Plus Spectrophotometer. Photo-electrochemical (PEC) characterization was done in a standard cell using an auxiliary Pt electrode (2 cm^2) and a saturated calomel electrode (SCE). The variation of the interfacial capacitance was measured at 10 Hz using a PGZ 301 Potentiostat.

Analysis

The metal concentrations were determined by sampling aliquots (0.5 mL) at different time intervals from both the feed and strip solutions, and analyzed with an atomic absorption spectrometer (Perkin-Elmer A700 using a specific lamp for lead at a wavelength of 216.9 nm). Conventional TGA was performed using TA instruments TGA-Q 500 thermogravimeter under N_2 atmosphere from 30 to 600 °C and a heating rate of 10 °C/min. The elaborated membranes were kept in a vacuum oven for several days at 40 °C until the solvent was removed. The FTIR/ATR spectra were recorded at room temperature with a Perkin-Elmer (Spectrum One) Spectrometer, using 32 scans at a resolution of 2 cm^{-1}. Scanning electron microscopy (SEM) images of the membranes were obtained using a JOEL JSM 7100-F Microscope operating at 10 kV.

Diffusion of metallic ions using synthetic membranes

The nature of the ionic membrane has been studied using two supports with different chemical and physical characteristics: (PMMA + L-Cystein + DOP) as a cationic membrane and (CTA + PEI + DOP) as an anionic membrane. We also used n-$Sr_2Fe_2O_5$ and p-$CuFeO_2$ in n/p short-circuited configuration to ensure the creation of electrical field as transference gradient forces. The photo-electrodeposition catalyzes the diffusion process as evidenced from Pb^{2+} concentrations. This system is applied after the separation and diffusion across a polymer inclusion membrane (PIM) combined with the semiconductors (Fig. 1).

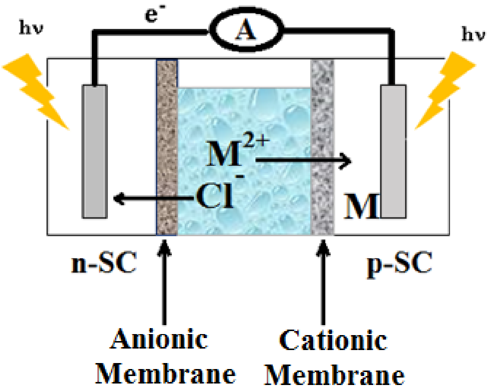

Figure 1: Photo-electrodialysis cell: (anode) $Sr_2Fe_2O_5$ and (cathode) $CuFeO_2$

RESULTS AND DISCUSSION

Characterization of membranes by FTIR

Figures 2 and 3 illustrate the FTIR spectra of the (PMMA + L-Cysteine + DOP) cationic membrane and of the (CTA + PEI + DOP) anionic membrane, respectively.

The main features of these spectra are the absorption band located around 1726 cm^{-1}, attributed to stretching vibrations of the carbonyl group (C=O) of PMMA and CTA. The presence of amine type groups (N–H) of PEI appeared at 3004 cm^{-1}. The bands at 1264 and 1244 cm^{-1} correspond to the stretching modes of C–O–C asymmetric single bonds and the bands detected at 1076 cm^{-1} correspond to the stretching modes of C–O–C symmetric single bonds of PMMA and CTA. These bands appeared at 1244 and 1076 cm^{-1} for DOP. Less intense bands at 2948 cm^{-1} are attributed to C–H bonds stretching modes. These results are in accordance with those reported in our previous works.[27-28]

Characterization of membranes by TGA

Figures 4 and 5 show the thermal behavior of, respectively, (PMMA + L-Cysteine + DOP) and (CTA + PEI + DOP) membranes, which decompose in two stages. The first mass loss (~48-52%) occurring at 200–300 °C represents the main thermal degradation of the L-cysteine and plasticizer (DOP). The second one starting at 350 °C is due to the complete degradation of PMMA or CTA polymers.

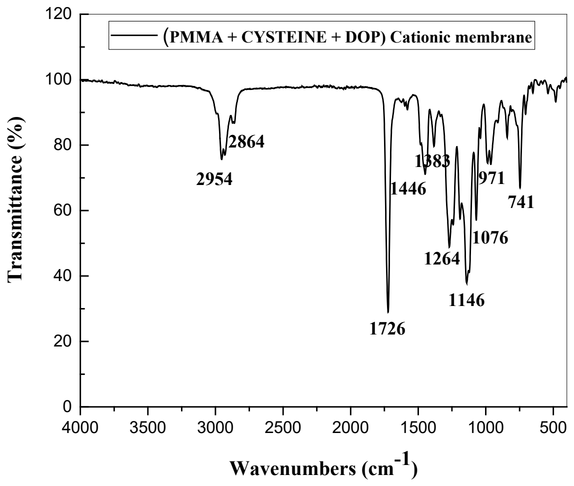

Figure 2: FTIR spectrum of (PMMA + L-Cysteine + DOP) cationic membrane

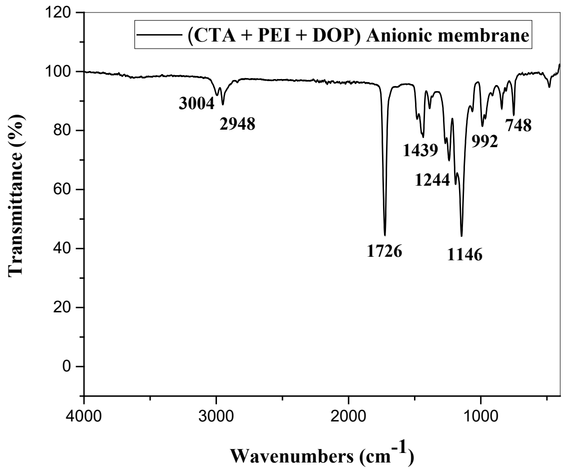

Figure 3: FTIR spectrum of (CTA + PEI + DOP) anionic membrane

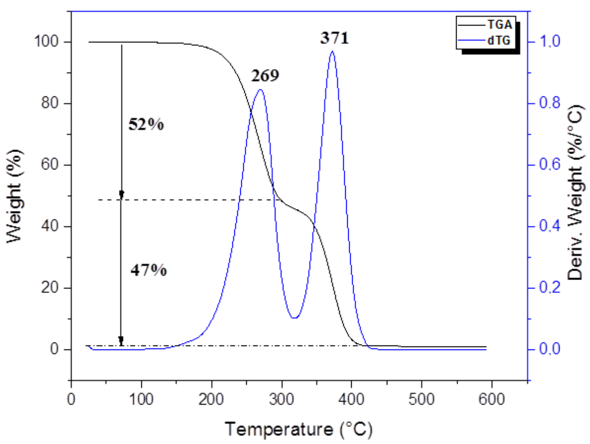

Figure 4: Thermogravimetric analysis (TGA) and DTG curve of (PMMA + L-cysteine + DOP) cationic membrane

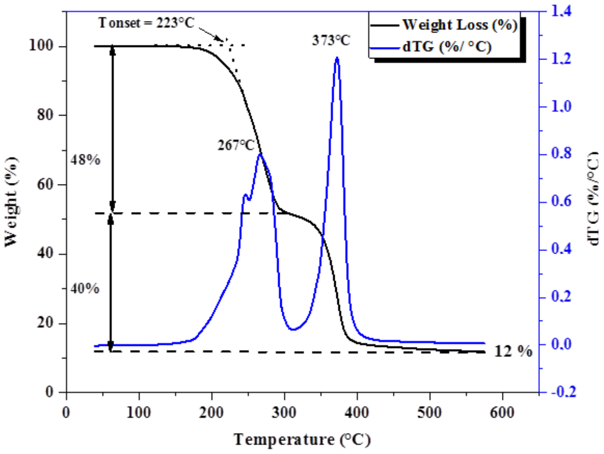

Figure 5: Thermogravimetric analysis (TGA) and DTG curve of (CTA + DOP + PEI) anionic membrane

The degradation process of the membrane (CTA + PEI + DOP) follows two main stages. This membrane exhibits thermal stability up to 210 °C. A mass loss of about 48 wt% was recorded during the first step of degradation, which extends over the temperature range between 210 °C and 300 °C, with a T_{max} around 267 °C and T_{Onset} at 223 °C. This stage is attributed to the evaporation of a part of the plasticizer DOP and polyelectrolyte PEI. During the second stage of degradation, ranging from 350 °C to 400 °C, the membrane lost 40% of its mass, with a T_{max} at 373 °C. This weight loss is characteristic of the degradation of the polymer CTA.

Based on these figures, we can confirm that the synthesized cationic and anionic membranes exhibit good thermal stability.

Characterization of membranes by SEM

An important aspect of polymeric membranes is the microstructure of the materials, which determines the distribution of PM-CYST in the polymer matrix and ultimately affects the membrane transfer efficiency. SEM provides excellent qualitative information (dense or porous membranes) and is a quantitative analysis tool in measuring important subsurface features, such as porosity and layer thickness.

Figure 6 shows the morphology of the elaborated cationic membrane. The surface view of the membrane containing PMMA/L-cysteine/DOP reveals that it presents a porous structure. This membrane is characterized by well-defined pores, the distribution of the pores is nearly uniform (porosity = 60%). Figure 7 shows the morphology of the prepared PM-CYST nanoparticles. The observed spherical nanoparticles have an averaged diameter of 220 nm.

Diffusion of metallic ions using a membrane/semiconductor combination

The chemical nature of the membrane support is a fundamental operative parameter, which can influence the stability of the membrane, and therefore the Pb^{2+} diffusion flux.

The influence of the illumination source was studied using $Sr_2Fe_2O_5$ and $CuFeO_2$ as polarized electrodes in the extremities of each membrane. Figures 8 and 9 show, respectively, the transport percentages of Pb^{2+} obtained in the strip and feed phases, using two different illumination sources (LED lamp: 20 mW cm^{-2} and solar light: 100 mW cm^{-2}). The photo-electrodeposition catalyzes the diffusion process, as evidenced from the Pb^{2+} concentrations. Consequently, the equilibrium strongly lies to the right, *i.e.* the Pb deposition follows the Le Chatelier principle.

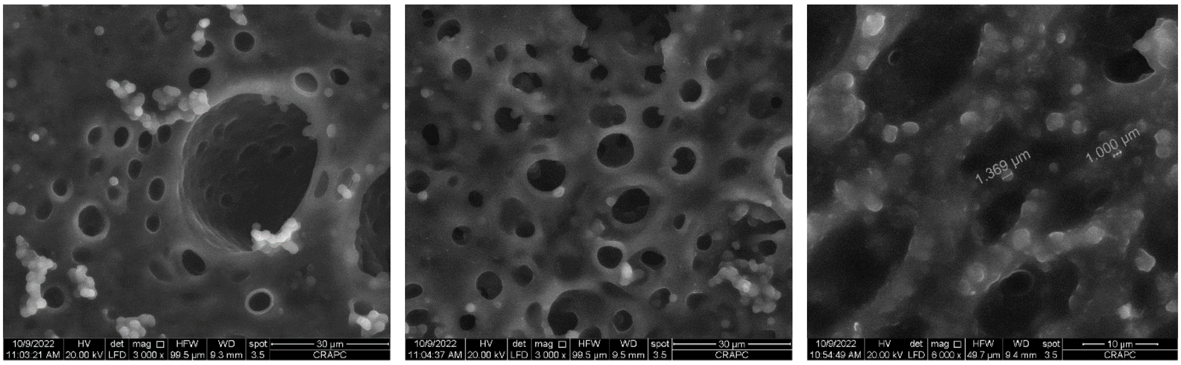

Figure 6: SEM images of (PMMA + L-cysteine + DOP) cationic membrane

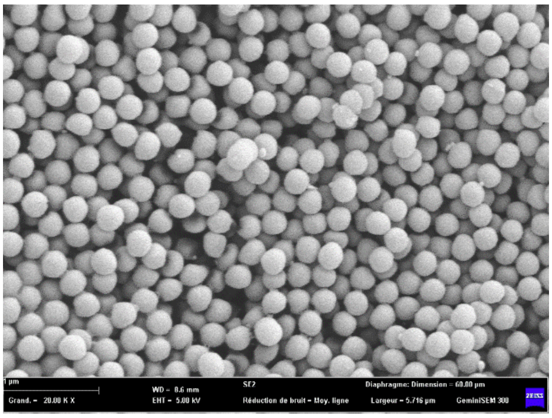

Figure 7: SEM image of PM-CYST nanoparticles

Figure 8 shows that the quantities of Pb^{2+} ions decrease strongly in the feed compartment by passing from the cationic membrane, thus confirming that the diffusion of metallic ions is an active process, where the charges of the polyelectrolyte plays an important role. We also note that a plateau region is reached after 5 hours, with a percentage of 20.96%. Such a result shows that, from 79.04% of Pb^{2+} transferred to the strip compartment, 23.42% was free and 55.62% reduced into Pb^0 (metallic state). It is clearly shown that the Pb^{2+} concentration in the strip phase (11.71 mg/L and 12.25 mg/L) depends highly on the nature of the illumination source. It is helpful to mention here that the photo electro-deposition of lead takes 2 hours, beyond which saturation is observed. It can be easily concluded that an enhancement of metal transfer has been obtained when the gradient of metal transfer was governed by the electrical field.

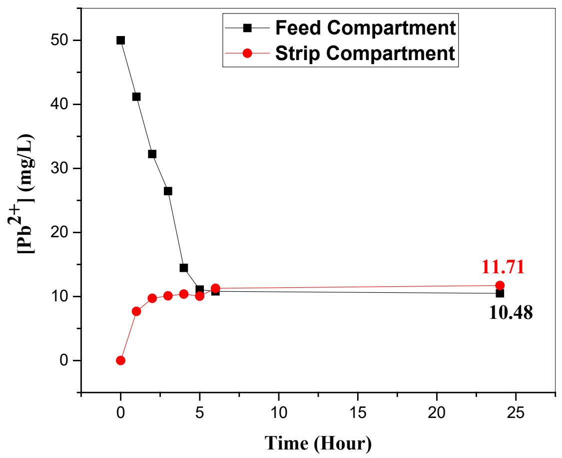

Figure 8: Evolution of lead ions concentration in the feed and strip compartments as a function of time using an artificial LED illumination source ([Pb^{2+}] = 50 mg/L, (PMMA + L-cysteine + DOP) cationic membrane)

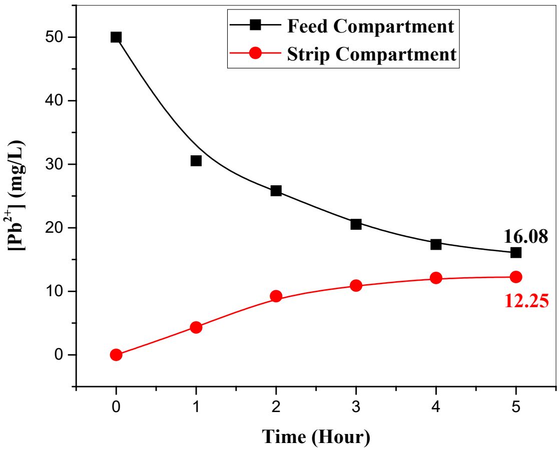

Figure 9: Evolution of lead ions concentration in the feed and strip compartments as a function of time using a solar illumination source ([Pb^{2+}] = 50 mg/L, (PMMA + L-cysteine + DOP) cationic membrane)

CONCLUSION

Mono-dispersed PMMA nanospheres grafted with L-cysteine have been successfully obtained. PMMA membranes modified by polyelectrolytes and plasticized by dioctylephthalate (DOP) have been prepared. These polymers + plasticizer + polyelectrolyte membranes were characterized using FTIR, TGA and SEM analyses. Our approach was to use n/p semiconductors in a short-circuited configuration to generate an electrical field as transference gradient force. This system was applied to the light-driven reduction of lead, after the separation and transport across a polymer membrane in combination with semiconductors (n-$Sr_2Fe_2O_5$ and p-$CuFeO_2$). The results showed that the Pb^{2+} photo-electrodeposition was significantly increased when using the hybrid system based on the combination of polymeric membranes and photo-electrodes. Also, very interesting results of the diffusion flux were obtained when the electrode was activated by solar illumination.

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