Development of cellulose-polypyrrole microfiber membranes and assessment of their capability on water softening

C Barrera¹, A Arrieta¹, N Escobar², P Gañan² and C Castro²
¹ Grupo de Investigación de Desarrollo y Aplicación de Nuevos Materiales – DANM, Universidad Pontificia Bolivariana, Montería, Colombia.
² Universidad Pontificia Bolivariana, Medellín, Colombia.

E-mail: alvaro.arrieta@upb.edu.co

Abstract. The application of conducting polymer composite for water softening is based on the use of pyrrole’s electrochemical properties joined with the flexibility and relatively high surface areas associated with cellulose fibers, to develop a new hybrid material that exhibits the inherent properties of both components. This hybrid would allow to promote an ion exchange reaction between the composite membrane and the hard water. The cellulose membranes obtained from banana plant agricultural waste (raquis), were uniform with individual and well separated fibers. The fibers were encapsulated by a continuous coating of polypyrrole by an in situ oxidative chemical polymerization. The amount of polypyrrole deposited on the fiber increased by increasing the monomer concentration, behavior that was identified through the observation of differences on the intensity of the light to dark color shift that coated the fibers after the polymerization. The ion removal capability of the membrane coted with the conducting polymer was tested using an experimental device, finding reductions on the conductivity for hard water within 23 to 66 μs/cm after 6 hours of the assay.

1. Introduction

Conducting polymers (CP) represent a novel generation of organic materials which possess electrical and optical properties similar to the metals and inorganic semiconductor, but with the properties related to conventional polymers such as: ease of synthesis, flexibility, chemical inertness, low density, low cost, processability, among others [1, 2]. Different studies in the last few years has been focused on the applications of conducting polymers in electronic, environmental, biologic, as well as other fields, due to the variety of properties these materials possess [3, 4]. The CP’s property of interest in this research is the electrochemical property, which can be defined as the ion exchange CPs undergo when they are subjected to an electrical stimulus in an electrolytic cell [5]. This property makes these materials an excellent possibility to develop ion exchange membranes with important applications in water softening. The development of polypyrrole-cellulose membrane provides the opportunity to generate new hybrid materials that exhibit the properties of the combined components. In this case the flexibility, resistance and surface area offered by the cellulose fibers, strengthened with the electrochemical properties of polypyrrole [6, 7].

2. Materials and methods

The cellulose membranes used in the experiments were provided by the Pontificia Bolivariana University’s research group GINUMA. Pyrrole and other reactants were purchased from Sigma-
Aldrich. Conducting Polypyrrole-cellulose composites were obtained through in situ oxidative polymerization using two different procedures. In the first procedure the pyrrole was added directly to the cellulose fibers and in the second one, a solution of pyrrole with the dopant ion was prepared, and then this solution was added on the fibers. A complete description of the methods, reagent and concentrations used in each method is shown in table 1.

Both procedures were done for membranes with cylindrical and disk shapes and repeated three times for each method and shape analyzed. After polymerization the composite membranes were thoroughly washed with a solution 1:1 methanol/water in order to remove the excess of monomer, dopant ion or oxidant agent.

Table 1. Procedures followed to obtain the Polypyrrole-cellulose composites membranes.

| Method          | First step of procedure                                                                 | Time of contact with the fibers | Second step of procedure                                           | Time of contact |
|-----------------|----------------------------------------------------------------------------------------|---------------------------------|-------------------------------------------------------------------|-----------------|
| Direct deposition| Same amount of Pyrrole 98% and a solution of sodium p-toluen-sulfanate 2M (dopant ion), was added on the fiber to completely cover them. | 45 min. Under ultrasonic treatment | 1 ml of aqueous solution of ammonium persulfate 2M (oxidant agent), was added. | 24 h            |
| Solution deposition | Solution of Pyrrole 1M with sodium p-toluen-sulfanate 2M (dopant ion), mixed by ultrasonic treatment, and then added on the fiber to completely covered them. | 45 min | 1 ml of aqueous solution of ammonium persulfate 2M (oxidant agent), was added. | 24 h |

2.1. Characterization of the Polypyrrole-cellulose material
Membrane surface topography and the coating level of the fibers were imaged using a JEOL JSM-6490L Scanning electron microscope, operating at 15 kV and 80 A. Analysis was then performed on the cross section area of the samples. The structural characterization of composite material was performed using a Nicolet 6700 FT-IR Spectrometer. Spectra were recorded at the range of 4000 to 400 cm⁻¹ by accumulating 32 scans.

2.2. Ion removal by the polypyrrole-cellulose membrane
For this experiment a factorial design with two levels and two factors was used. An experimental device proposed by the research groups DANM and GINUMA, shown in figure 1, was used to assess the composite membranes’ ion removal application. As a hard water sample, a solution of 500 ppm of magnesium chloride and 500 ppm of calcium chloride was prepared.

A conventional three electrode configuration was used. The composite membranes were used as work electrodes. These three electrodes were placed in the upper container of the device, connected to potentiostat-galvanostat 2263 PARSTAT through which was loaded with a potential current of -0.5V to the immersed membrane being tested. The decreased conductivity of the hard water was measured with a conductimeter 315i WTW. Three membranes from each method and shape used were tested for six hours and the average value was calculated as the mean value.
3. Results and discussion
The cellulose membrane fibers obtained from agricultural waste were successfully encapsulated by a continuous coating of polypyrrole. The natural color of cellulose membranes before the polymerization was white, and after the chemical in situ polymerization of pyrrole on the fiber, all the membranes turned black. This dark color is characteristic of polypyrrole and shows the polymer deposition on the cellulose fibers. Preliminary assays with different concentrations of monomer and dopant ion shows that the amount of polypyrrole deposited on the fiber increased with increasing these two reactant concentrations. However, at higher concentrations of the monomer than the concentrations of the dopant ion, the solution gets a certain grade of immiscibility, requiring harder agitation.

3.1. Characterization of the Polypyrrole-cellulose material
The results of comparing composite material obtained through the two procedures used (direct deposition and solution deposition); indicate that the use of the second procedure leads to a more uniform coating of the fibers as is shown in figure 2.

The images in figure 2 (b) and (d) show the enlargement of the adherence of the polypyrrole to the cellulose fibers. As can be seen in figure 2 (b) the direct deposition of the monomer and dopant ion on the cellulose membrane promotes agglomeration of the polymer. This result may be due to better integration of the initial reagent that can be achieved through the solution deposition procedure. Regarding the two different shapes of membranes analyzed, there was no variation found on the polymerization behavior between the cylindrical and disk shapes. The tendency to form agglomeration of the polymer for direct deposition was observed in both shapes.

The spectra obtained for the polypyrrole-cellulose composite membranes show characteristic broad band of cellulose O–H group around (3375-3210) cm$^{-1}$, which confirm the presence of cellulose in the composite materials analyzed. The typical spectral features of the polypyrrole are also reported in the literature [2, 8]. There are absorption bands around (1644-1415) cm$^{-1}$ for all the membranes tested; these bands are attributed to the C-C vibration in the pyrrole ring. The absorption bands, around (11121-1052) cm$^{-1}$, are characteristic of C-O functional groups. The differences of the wavelength of the bands in spectra indicate the different polypyrrole concentration obtained for the membranes analyzed. However, spectra show a similarity on the functional groups found for polypyrrole-cellulose membranes obtained through the same deposition method. There were not important differences on the final composition of membranes regarding the shape used, although there is a variation on the spectra registered regarding the deposition method, which can be attributed to the different concentration of Polypyrrol attached to the cellulose structure due to the procedure used.
3.2. Ion removal by the polypyrrole-cellulose membrane

The assay performed to test removal ion application by the composite membranes proved the applicability of the conducting polymer composite on water softening. The reduction on water sample conductivity shows a removal of ions responsible for water hardness. Individual membranes tested achieved conductivity reductions within 23 to 66 μs cm⁻¹ after 6 hours of the assay, which equals a reduction of 11.5 to 33 ppm of CaCO₃ for hard water.

On the other hand, variations in the ion removal efficiency among deposition methods and also regarding the membrane shapes used were found. The comparison of efficiency in ion removal for the two deposition procedures used show better results for composite membranes obtained through direct deposition. This variation on the ion removal action may be due to the amount of polypyrrole attached to the cellulose fibers, as was shown in the characterization analysis.

Finally, regarding the initial cellulose membrane shape used to support the polypyrrole; findings show that cylindrical shape does not possess the physical stability needed to be used in water softening. The level of swelling obtainable by the cylindrical shape makes these membranes easy to break and also affects the ion removal application because of the great amount of water in the membrane which reduces the concentration of the ions.

4. Conclusions

The resulting polypyrrole-cellulose membranes combined the electrochemical properties of Polypyrrole and the high surface area of cellulose fibers as expected. The amount of polymer added to the fibers was found to be dependent on the initial concentration of monomer and dopant ion used in the reaction. However, the relation between these two reactants must be further analysed given that at
monomer concentrations higher than the dopant ion a harder level of agitation is required in order to obtain a homogenous solution. Concerning to the two different procedure used for the reactants deposition on the fibers, a variation of the characteristics and conductive properties of the membrane was found. Although through solution deposition characterization analysis a more uniform coating of the fibers was obtained, it was through the direct deposition method that membranes showed better ion removal action, given the bigger amount of polymer added to the fibers. Regarding the shapes tested, findings show not only better physical stability for disk shaped membranes, but also better efficiency on ion removal. Finally considering all findings, the Polypyrrole-cellulose membranes obtained through direct deposition from the cellulose are called to be a new material that provides good properties for water softening. Further research should focus on the analysis of the optimal relation between monomer and dopant ion concentration and of the thermal and mechanical properties of the polypyrrole-cellulose membrane.

References
[1] Neves S and Fonseca C 2004 J. of Brazil Chemistry Society 15 395–9
[2] Guimard N, Gomez N and Schmidt C 2007 Progress in Polymer Sci. 3 876–921
[3] Müller D, Rambo C, Recouvreux D, Porto L and Barra G 2011 Synthetic Metals 161 106-11
[4] Merle G, Wessling M and Nijmeijer K 2011 J. of Membrane Sci. 377 1–35
[5] Arsalani N and Geckeler K E 1997 Reactive and Functional Polymers 33 167–72
[6] Johnston J H, Kelly F M, Moraes J, Borrmann T and Flynn D 2006 Current Appl. Phys. 6 587–90
[7] Johnston J H, Moraes J and Borrmann T 2005 Synthetic Metals 153 65–8
[8] Mecerreyes D, Stevens R, Nguyen C, Pomposo J, Bengoetxea M, Grande H 2002 Synthetic Metals 126 173–8.