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Fabrication of ion-exchange ultrafiltration membranes for water treatment I. Semi-interpenetrating polymer networks of polysulfone and poly(acrylic acid)

Chamekh Ould M'Bareck[a,*], Quang Trong Nguyen[b],
Stephane Alexandre[b], Irène Zimmerlin[c]

[a] *Université de Nouakchott, F.S.T: P. B. 5026, Nouakchott, Mauritania*
[b] *P.B.M., UMR 6522, CNRS Université de Rouen, 76821 Mont-Saint-Aignan, France*
[c] *M2C, UMR 6143, CNRS Université de Rouen, 76821 Mont-Saint-Aignan, France*

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Abstract

This paper reports a simplified, efficient and economical method for fabricating ion-exchange ultrafiltration membranes for pollutant removal from water. To obtain these membranes by the phase inversion method, polysulfone (PSf) and poly(acrylic acid) (PAA) were separately dissolved in dimethylformamide (DMF), then the two solutions were mixed in desired proportions. The membranes have an asymmetric structure and rugous surface, as demonstrated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses. Their ion-exchange capacity was in the 0.70–1.0 meq/g range. The retention ratio of lead ions (Pb^{2+}) and Ponceau S dye were 99% and 90%, respectively, in the ultrafiltration process under 0.5×10^5 Pa (0.5 bar), with an average pure water flux of 18 L/(m^2 h). These performances, obtained at such a low pressure, make the fabricated membranes attractive for water treatment.

Keywords: Membrane preparation; Water treatment; Ultrafiltration; Lead ion; Ponceau S dye; Polysulfone; Poly(acrylic acid)

1. Introduction

Nowadays, water sources are overexploited and badly protected in many regions of the world. Demography and human activity are inducing, on one hand, an increase of water demand and, on the other hand, the misuse and mismanagement of water resources [1]. All over the world, water sources are being exposed to pollutant contamination. Industrial and agricultural activities, hunting, overexploitation and lack of awareness in the local population are different parameters which affect in a complex way the maintenance of water resources.

Heavy metal ions constitute one form of dangerous pollutants soluble in water. Exposure to low concentrations of heavy metal ions may provoke: loss of weight and audition, diarrhea, muscular weakness, growth retardation, cardiovascular abnormalities, cancers, renal insufficiency and sleeping disturbances [2–4].

Lead is known for its high toxicity. It is contacted by ingestion or inhalation via air, food and water. In air, it is present as fume or as dust, whereas in food and water it is present as salts or as complexes. After its ingestion or inhalation, the non-excreted fraction is mainly stored in the blood, soft tissues, bones and teeth. Its biological half-lifetime in the blood has been estimated to be 20–40 days. Its implication in many diseases is more and more acknowledged. Damages to the kidney system, anaemia and deterioration of the nervous system constitute the principal health risks attributed to lead presence in the human body [5,6].

The phenomena of eutrophication and ecosystem destabilization are currently observed in many countries [7–10]. Nevertheless, scientists are developing techniques in order to better control the drinking water quality and protect the water environment [11–15].

Since their first appearance two centuries ago, membranes have seen a great development in various industrial and fundamental science domains. Some authors consider that membrane technology reached its maturity in the early 1980s. Today, there

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[*] Corresponding author. Tel.: +222 677 16 51; fax: +222 525 39 97.
E-mail address: chamec@univ-nkc.mr (C.O. M'Bareck).

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is no doubt that the use of membrane processes is increasing in all fields. They are widely used in water desalination, wastewater treatment, the removal of heavy metal ions, nitrates, phosphates, pesticides, phenols and many other micropollutants. They are also used in the fabrication of chemical and food products, and they are playing an important part in environmental protection [16–20].

The core of a membrane process is the membrane itself. Depending on the membrane nature and characteristics, a process (e.g. a pressure-driven or an electro-membrane process) and operating conditions are to be chosen. Among the processes, ultrafiltration has a large potential for applications in various fields: biotechnology, pharmacy and water treatment. The new development of applications relies on the availability of membranes having high permeabilty and high fouling and chemical resistances. Fouling resistance and high permeability would be obtained by improvements in the membrane hydrophilicity, while chemical resistance would come from the intrinsic properties of the polymer materials.

Polysulfone is apparently the best material that can be used for the fabrication of membranes for pressure-driven processes. This is due to its reasonable price, its good film forming ability and its thermal, mechanical and chemical resistances. However, the asymmetric polysulfone membranes made by phase inversion are mainly good for ultrafiltration, i.e. they have no selectivity to small dissolved organic molecules and salts. The commercial nanofiltration membranes that reject soluble salts use a conventional polysulfone asymmetric support, onto which a very thin layer of polyamide is synthesized by interfacial polycondensation of polyacid chloride and polyamine [21]. The preparation method is complex and the membranes obtained are chemically fragile. Phase inversion membranes selective to salts can be obtained from highly sulfonated aromatic polysulfones (PSf) but these hydrophilic membranes are well swollen in aqueous media and become mechanically fragile [22]. It is important to us to find a simple method that makes it possible to fabricate, at low price, membranes that reject salt/organic pollutant molecules while keeping the PSf advantages.

This work is dedicated to the fabrication of asymmetric ion-exchange ultrafiltration membranes based on PSf. The chemical and physical properties of the prepared membranes were studied: morphology, swelling ratio, ion-exchange capacity and the ratio of immobilized polyelectrolyte. Many techniques were employed to achieve this aim: optical microscopy (OM), scanning electronic microscopy (SEM), atomic force microscopy (AFM) and atomic absorption spectroscopy (AAS) techniques. Filtration tests were performed on the prepared membranes to assess the potential of the membranes in water purification under low pressures.

2. Experimental

2.1. Polymer properties

Polysulfone (PSf) and poly(acrylic acid) (PAA) were supplied by Aldrich and dimethylformamide (DMF) by Prolabo. All polymers and chemical products were used as supplied, without any further purification. The molecular weights of PAA, PSf and Ponceau S were 450,000, 26,000 and 760 g/mol, respectively.

2.2. Membrane preparation

PSf and PAA were dissolved in DMF in a glass reactor equipped with a mechanical stirrer and thermostated at 90 °C for more than 3 h. The PSf concentration was 20 wt.% and that of PAA was 5 wt.%. Afterwards, the two solutions were mixed together in known proportions, and stirred for 30 min to form the casting dopes. The de-bubbled casting dope was cast on a glass plate with a laboratory-made Gardner knife (265 μm). The cast liquid film was left for evaporation in air for 20–30 s and finally immersed in a coagulation bath containing a sufficient volume of MilliQ water at 23 °C. The membranes were thoroughly washed with water and stored in a dilute sodium azide solution till their use.

2.3. Scanning electronic microscopy and optical microscopy

The SEM images were obtained with a Cambridge Instruments^{TM} model 200 microscope. In order to obtain good membrane cross-section images, the samples were frozen in liquid nitrogen at −190 °C, fractured and coated with a thin gold film. The images were obtained at 20 kV voltages and different magnification factors.

The optical microscopy images were recorded via a Sony^{TM} 3CCD camera adapted to a Leica^{TM} DMLM microscope. All membranes were observed in their swollen (wet) state. Both transmission and reflection images of the membranes could be obtained.

2.4. Atomic force microscopy

AFM imaging in the contact mode was done with a "Nanoscope II" from Digital Instruments^{TM} (Santa Barbara, USA) using a 140 μm scanner. The cantilevers used were characterized by a spring constant of 0.06 N/m. A standard pyramidal tip in silicon nitride was used. The measurements were carried out in air and at a constant force in the 10^{-9} to 10^{-8} N range.

2.5. Ion-exchange capacity measurement

The ion-exchange capacity was determined after alternative sample conditionings in 0.1 M NaOH and 0.1 M HCl for an immersion time of at least 4 h. In H^+ form, the sample was equilibrated in water for at least 12 h to remove the free hydrogen ions and afterwards immersed in NaCl 0.1 M for 4 h. The released H^+ ions in the NaCl medium were titrated by NaOH 0.01 M. The immobilization ratio for the membrane PAA is defined as the ratio of the actual ion-exchange capacity to the theoretical ion-exchange capacity that would be obtained if the PAA in the initial blend in solution was kept entirely in the membranes.