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Study of polyamide composite reverse osmosis membrane degradation in water under gamma rays

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ABSTRACT

This study aims to investigate the impact of irradiation on the behavior of Polyamide (PA) composite reverse osmosis (RO) membranes. Irradiations were performed for two doses (0.1 and 1 MGy) in wet conditions under an oxygen atmosphere, with a gamma ^{60}Co source. Irradiation effect on RO membranes performances (NaCl rejection, permeability) was studied before and after irradiation. ATR-FTIR, XPS, AFM, FESEM microscopy, ion chromatography were also used to characterize structural modifications. Results show that NaCl rejection of RO membranes irradiated at 1 MGy decreased until 64% and permeability increased by a factor of three. Nevertheless, membranes irradiated at 0.1 MGy did not exhibit any change in theirs permselectivity properties. Advanced analysis techniques confirmed that the firsts effects of gamma rays on RO membranes occurred between 0.1 and 1 MGy. Results emphasize that gamma rays effects on the RO membranes led to the breaking of amide and ester bonds at 1 MGy. These breakings resulted in loss of hydrogen bonds between polyamide chains, and consequently to a relaxation of the polyamide network. Finally, modifications of the polysulfone layer underneath were highlighted. Both relaxation of the polyamide network and modifications of the polysulfone layer could be involved in the drop of the permselectivity properties.

1. Introduction

Nuclear power industry provides 3% of the world's energy, while in France it reaches roughly 80% [1]. As a result, nuclear facilities generate a significant amount of radioactive liquid effluents needing further treatment to meet environmental requirements. Evaporation, precipitation and ion exchange are most commonly used in industrial scale for the decontamination of these effluents [2]. However, membrane processes for decontamination have shown a significant growth in the past decades since they exhibit many advantages over conventional processes [3]. Among them reverse osmosis might be suitable for radioactive liquid waste treatment [4].

Reverse osmosis is a well-known process extensively used in desalination to produce drinking water [5,6], and in other applications [7,8]. Reverse osmosis membranes are Thin Film Composite (TFC) materials usually made of a superposition of three layers: an active one with aromatic polyamide supported by a polysulfone microporous layer and a non-woven polyester bottom structure. However, accurate information about the composition of commercial TFC RO membranes remains unknown through manufacturer data. Only a limited number of studies have carried out characterizations of some commercial RO membranes. Most commonly, studies focus mainly on the characterization of PA active layer, since the active layer governs separation properties [9–11].

As widely reported in the literature, organic materials are known to undergo degradations under gamma radiations [12]. Particularly for nuclear industry, gamma rays effects on polymer are studied on Ion Exchange Resin (IER) regarding long term behavior [13] and polymer materials for their stability [14,15]. Gamma rays are highly penetrating ionizing radiations that could induce a production of radical species into the polymers structure. Evolution of these species via radical or ionic mechanisms leads to crosslinking or relaxation reactions and gas production [16]. Only few studies focus on polyamide degradations under irradiation, and comparisons between studies are difficult because of the wide variety of polyamide type materials and irradiation conditions. Moreover, behavior of linear polyamide under irradiation is most commonly studied to estimate radiolytic yields, gas production, radical species and degradation mechanisms instead of modification of separation properties for membrane processes [17–20].

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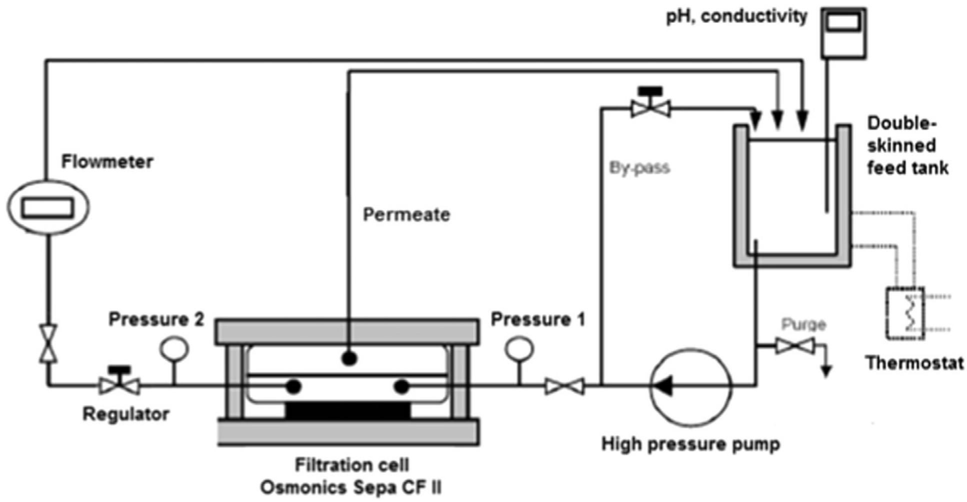

Fig. 1. Experimental set-up for filtration experiments.

A limited number of studies reported the effect of gamma irradiation on TFC RO or NF membranes [21–24]. According to these papers, first effects of gamma rays degradation occur above the dose of 0.1 MGy,[1] with variations of membrane permeability and selectivity. These results show some similitude with those from studies carried out on the ageing of RO membranes under chlorine exposition [25]. Only Nakase et al. [24] have reached higher doses and found out a link between structural and separation properties. However, their study was carried out with accelerated electron and not gamma rays which depending on conditions may result in different effects [26]. Finally, the interest in RO membranes for nuclear effluents treatment is related to the Fukushima-Daiichi accident. Indeed, one step of the radioactive water decontamination process was carried out with RO membranes. Consequently, the aim of the present work is to study the modifications of physical and chemical properties of both polyamide and polysulfone layers, and link them to separation performances for two doses (0.1 and 1 MGy) of gamma rays. The 0.1 MGy dose was defined in accordance with the literature on RO membranes. A 10 factor was then applied to set the upper dose of 1 MGy in order to effectively observe noticeable effects of gamma irradiation on RO membranes. These two thresholds were also in accordance with the feedback from IER degradation studies under gamma irradiation.

2. Materials and methods

2.1. Materials

Reverse osmosis membranes SE (GE Osmonics) were used in this study. Membranes were purchased with a size of 19 cm × 14 cm, in order to fit with the SEPA CFII cell and suit the irradiation glass tube size. This membrane was used because it may be suitable for the treatment of an effluent defined by one of our industrial support.

A cross-flow filtration cell (SEPA CFII, GE Osmonics) was used for membrane performance measurement (NaCl rejection and permeability). A feed spacer of 1.2 mm and a permeate collector surrounded membrane sample inside the cell and provided 138 cm^2 of effective surface filtration. Feed solution was incorporated into a 4 L stainless steel thermostated cylindrical tank. A constant feed solution temperature of 25 °C ± 0.5 was kept by adjusting the chiller temperature set point. pH (Mettler Toledo, FiveGo) and conductivity (Hannah Instrument, HI9865) of the feed solution were also monitored. Feed solution circulation through the filtration cell was carried out by hydracell pump (Wanner Engineering). Applied pressure was adjusted by a back pressure regulator (Tescom) and measured by two pressure gauges (Keller). Feed flow rate across the filtration cell was adjusted with a by-pass valve to obtain a recirculating flow around 250 L h^{-1}. Fig. 1 provides an illustration of the experimental setup used in the study.

2.2. Sample preparation

In the following, the term "membrane" will design an entire membrane, whereas the term samples will refer to cut membranes.

All membranes were rinsed with pure water (resistivity 15 MΩ cm) and soaked in pure water baths for 24 h at 8 °C to remove preservation agents before both irradiation and/or filtration experiments. Samples used for polymer characterization (attenuated total reflection Fourrier transform infrared spectroscopy ATR-FTIR and X-ray photoelectron spectroscopy XPS) were dried in vacuum for at least 48 h before analysis.

Membranes for characterization experiments were cut into 4 bands and then placed into a 100 mL glass tube, and 20 mL of pure water was added to the glass so that samples were entirely immerged. Nitrogen bubbles were used to remove dissolved oxygen and carbon dioxide from water before to be poured into the glass. Irradiation tubes were emptied of atmospheric air by vacuum aspiration. Vacuum absolute pressure was capped at 15 mbar to limit the sample moisture content. Then irradiation tubes were backfilled with pure oxygen for aerobic conditions. This operation was repeated three times to remove the residual air before sealing the tube at an absolute pressure around 900 mbar.

Membranes for filtration experiments were directly and entirely placed into 250 mL glass tubes. Pure water purged with nitrogen bubbles was poured into the glass to totally immerge membranes samples. These samples were not sealed and water was naturally gas saturated with atmospheric conditions.

Before and after irradiation experiments, samples were stored into a MilliQ water bath at 8–10 °C. Water baths were periodically renewed during the storage. In order to avoid artefact measurement, all irradiation samples were doubled.

2.3. Irradiation conditions

Gamma irradiation was carried out using ^{60}Co source in an industrial facility. This irradiation conditions were chosen regarding

[1] 1 Gy (Gy) is a unit traditionally use in irradiation. A gray represent the dose absorbed by the material and corresponding to 1 J kg^{-1}.