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Effect of gamma irradiation at intermediate doses on the performance of reverse osmosis membranes

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HIGHLIGHTS

- Irradiation of RO membranes at intermediate dose (0.2 and 0.5 MGy).
- For a dose rate of 0.5 kGy h^{-1} RO membranes are radiation resistant until 0.2 MGy.
- Cleavages of polymer bonds in the active layer at 0.5 MGy.
- Decrease in permselectivity properties of the membrane at 0.5 MGy.
- High oxygen consumption between 0.2 and 0.5 MGy related to the membranes degradation.

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ABSTRACT

The goal of this study is to explain the degradation of Polyamide (PA) composite reverse osmosis membrane (RO) in function of the irradiation dose. Irradiations were performed with a gamma ^{60}Co source in wet conditions and under oxygen atmosphere. For different doses of 0.2 and 0.5 MGy with a constant dose rate of 0.5 kGy h^{-1}, RO membranes performances (NaCl retention, permeability) were studied before and after irradiation. ATR-FTIR, ion chromatography and gas chromatography were used to characterize structural modification. Results showed that the permeability of RO membranes irradiated at 0.2 MGy exhibited a small decrease, related to scissions of the PVA coating. However, retention did not change at this dose. At 0.5 MGy, permeability showed a large increase of a factor around 2 and retention began to decrease from 99% to 95%. Chromatography measurements revealed a strong link between permselectivity properties variation, ion leakage and oxygen consumption. Add to ATR-FTIR observations, these results emphasized that the cleavages of amide and ester bonds were observed at 0.5 MGy, more precisely the loss of hydrogen bonds between polyamide chains. By different analysis, modifications of the polysulfone layer occur until a dose of 0.2 MGy.

1. Introduction

As widely reported in the literature, degradations of organic materials are studied under gamma rays to assess the effect of irradiation on the structure or properties of different polymers as PVC or PET (Colombani et al., 2009; Mariani et al., 2007). The effect of gamma irradiation results in radical production on the polymer structure, that could further react and lead to crosslinking, scission reaction or gas production (Clough et al., 1991). Gamma irradiation is commonly employed for modifications of polymers surface and grafting (Bhattacharya, 2000). It is also used to simulate the behavior of a polymer in true condition for long time behavior as for nuclear or aerospace industry (Clavreul, 1997; Plaček et al., 2008). Another utilization concerns the stability of polymer materials within a certain dose range for sterilization (Buchalla et al., 1995; Goldman et al., 1996).

In this study, reverse osmosis (RO) membranes stability is studied within a large dose range. RO membranes are thin films 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. The interest in the behavior of RO membranes under gamma irradiation is related to the Fukushima Daiichi accident. Recently, RO was used in this framework to treat contaminated

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Table 1
Sum up of irradiations conditions carried out in the study.

Dose (MGy)	Dose rate (kGy h^{-1})	Type of glass tube	Membrane size	Conditions	Number of glass tube
0.1–0.2–0.5–1	0.5	sealed	sample	oxygen+water	2 for each dose (total 8)
0.1–0.2–0.5–1	0.5	opened	membrane	air+water	2 for each dose (total 8)

seawater but nowadays no feedback regarding materials lifetime have been communicated. According to the literature, first effects of gamma irradiation on membranes occur for a dose of 0.1 MGy with variations of membrane permeability and selectivity added to changes in the polyamide and polysulfone layer chemical composition (Chmielewski and Harasimowicz, 1997; Nakase et al., 1994; Oliveira et al., 2012). However, some studies were carried out with accelerated electrons but not with gamma irradiation which may results in different effects (Chmielewski et al., 2005). Moreover, the radionuclides spectra of the contaminated water in Fukushima Daiichi reveal mainly gamma and beta emitters. Our previous study have shown that RO membranes permeability increased by a factor around 3 and NaCl retention droped from 99% to 64% at a dose of 1 MGy with a dose rate of 0.5 kGy h^{-1} under gamma irradiation (Combernoux et al., 2015). However the behavior of RO membranes within the range of 0.1 and 1 MGy have not been studied yet. Consequently, this work investigated the behavior of RO membranes at 0.2 and 0.5 MGy. Evolution of the permeability and selectivity as well as chemical properties of both polyamide and polysulfone layer were assessed under gamma rays. The aim of the present paper was to find accurately the degradation threshold of such materials within the dose range of 0.1 and 1 MGy.

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 fitting with the SEPA CFII cell and suit irradiation glass tube size. A commercial cross-flow filtration cell (SEPA CFII, GE Osmonics), used to characterize liquid permeability and NaCl retention and permeability, is described in a previous study (Combernoux et al., 2015).

2.2. Sample preparation

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.

Membranes for material characterization were cut into 4 samples strips placed into a 100 mL glass irradiation tube containing 20 mL of pure water so that samples were entirely immerged. Nitrogen was gently bubbled in water to remove dissolved gas (mainly oxygen and carbon dioxide). Irradiation tubes were emptied of atmospheric air by vacuum aspiration. Vacuum absolute pressure was limited to 15 mbar to avoid water vaporization. Then irradiation tubes were backfilled with pure oxygen for aerobic conditions. This operation was repeated three times to remove residual air before sealing the tube at absolute pressure around 900 mbar. In addition, glass tubes containing only pure water were also prepared following the same procedure. This glass tubes represented blank samples.

Flat sheet membranes for filtration experiments were directly and entirely placed into 250 mL glass tube. Gas-purged pure water was poured into the glass to immerged totally membrane samples. These samples were not sealed and water was naturally gas saturated with atmospheric conditions. Before and after irradiation experiments, samples were stored into 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 (Ionisos, Dagneux). This facility provides a constant dose rate, around 0.5 kGy h^{-1}. A sum up of irradiation conditions carried out in this study is given in Table 1. Irradiations were performed at room temperature. The cumulated energy absorbed in the sample itself was measured by dosimeters as described by Rébufa et al. (Rébufa et al., 2015). Furthermore, the materials were irradiated homogeneously by rotating them during exposure. Irradiation time ranges from few days to several months according to the total absorbed dose targeted.

2.4. Membrane characterization

2.4.1. Permeability and salt retention

Membrane compaction was carried out according to the conditions given by the manufacturer. The feed tank was filled with pure water at pH∼6. Pure water filtration was then carried out at low applied pressure of 5 bar to accommodate the membrane. Afterwards, the applied pressure was increased to 32 bar for membrane compaction and maintained constant for at least 24 h until water flux remained constant. Pure water permeability was then measured. The second step was the measurement of NaCl retention. A 0.5 g L^{-1} NaCl (Sigma Aldrich, analytical grade) solution was added to the feed tank for salt retention measurement with a transmembrane pressure (TMP) of 28 bar. Concentrations of both feed and permeate were deducted from conductivity measurements with calibration curve, in order to calculate the observed retention with Eq. (I):

$$R_{obs} = 1–C_p/C_r \quad (1)$$

where R_{obs} represents the observe retention (%), C_p the permeate concentration (mol L^{-1}) and C_r the retentate concentration (mol L^{-1})

2.4.2. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR experiments were carried out using iS50 FTIR spectrometer (Nicolet) equipped with an ATR element (diamond crystal plate) and Omnics 9.2 software (Thermo Electron Corporation). Samples were dried for 48 h before analysis to remove the water in the membrane. Background spectrum was recorded prior to each experiment to avoid the contribution of carbon dioxide, water vapor and diamond crystal to the spectrum. The membrane active layer was then pressed gently against the crystal plate for analysis. Each spectrum resulted in an average of 56 scans from the range 4000–800 cm^{-1} at 1 cm^{-1} resolutions. ATR corrections were applied after measurement.