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Irradiation effects on RO membranes: Comparison of aerobic and anaerobic conditions

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ABSTRACT

In this study, the investigation of the degradation of polyamide composite reverse osmosis membrane under gamma irradiation was carried out in aerobic and anaerobic conditions. A gamma ^{60}Co source was used to reach irradiation doses ranging from 0.1 to 1 MGy, with a constant dose rate of 0.5 kGy h^{-1}. The RO membranes degradation was assessed using XPS and ATR-FTIR for the chemical modification of the membrane active layer. Ion chromatography, pH measurement and gas chromatography were also used to identify and quantify the species release in aqueous and gaseous phases. Results showed a difference in the degradation of the membrane active layer and support layer between aerobic and anaerobic conditions. The different analysis performed suggested that the breakage of amide bonds was significantly higher in aerobic conditions rather than in anaerobic. This observation was confirmed by the measurement of an increasing amount of release species in aqueous and gaseous phase in aerobic conditions. Ester bonds scissions were highlighted as soon as the dose reached the value of 0.1 MGy in both conditions indicating an important sensitivity of the PVA-type coating of the RO membrane towards irradiation. Nevertheless, investigation of the top 10 nm surface of the active layer composition by XPS showed that the scissions of amide and ester bonds were similar in both conditions. Finally, all these results underlined a difference in the degradation mechanisms of the RO membranes: in anaerobic conditions, the degradation was limited to the top surface of the membrane and reductive species were involved in the degradation reactions.

1. Introduction

Reverse osmosis (RO) is extensively used in desalination processes to product drinking/pure water, and to treat industrial wastewater [1,2]. Recently, RO was used in the framework of Fukushima-Daiichi accident to treat contaminated seawater [3]. This process uses dense organic membranes that are typically composed of a superposition of three layers: a top skin layer in aromatic polyamide supported by a polysulfone microporous layer and a non-woven polyester bottom structure [4]. However the accurate composition of the commercial organic RO membranes is not given by the manufacturers.

As widely documented in the literature, organic materials are sensitive to gamma irradiation [5–7]. In an industrial process of radioactive liquid waste treatment one should expect to the degradation of the RO by the irradiation induced by the radionuclides in the effluents [8]. The radionuclides spectra of the contaminated water in Fukushima Daiichi, and more generally for nuclear accidents like Chernobyl, shows mainly gamma and beta emitters, as ^{137}Cs, ^{90}Sr and ^{131}I [9,10]. In this case the longtime behavior of polymer regarding irradiation can be simulated by the use of gamma irradiation [11].

Gamma irradiation of polymer generally lead to the production of radicals species inside the polymers that can damage the structure by ionic or radicals reactions. Regarding RO membranes, the degradation path identified lead to scission of organic bonds in the polymer structure that may result in an increase in the permeability and a decrease in the salt rejection [12]. These degradations were observed for dose ranging from 0.1 to 1 MGy with gamma irradiation and more than 2 MGy for accelerated electrons [13].

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However, these studies focus on irradiation in aerobic conditions either under air either under pure oxygen. The literature shows that polymer behavior with or without oxygen may lead to different results [14,15]. For example, the irradiation of polyethylene with oxygen led to chain scission whereas crosslinking is observed in absence of oxygen [16]. Oxygen is also involved in the increase of the ageing speed of the polymers [17]. Indeed, oxygen can quickly diffuse in the polymer and react with the radicals produced after irradiation [18]. These reactions could result in the formation of peroxide groups that are highly reactive and likely to react to form more stable products like alcohols, ketones, aldehydes or esters [19].

Several studies have been carried out on the degradation of polyamide [20–23] or polysulfone [6,24] in presence or absence of oxygen. However RO organic membranes are more sophisticated polymers and this point has not been assessed yet for such composite system. This potential behavior difference with or without oxygen may be considered with full attention since it could lead to an improvement of the process if the membrane degradations are reduced in absence of oxygen.

Consequently, the aim of this study is to compare the behavior of RO membranes after irradiation with or without oxygen. More precisely, this difference will be assessing for different doses. The different doses chosen were 0.1, 0.2, 0.5 and 1 MGy since this range lead to observe noticeable effects in presence of oxygen. Degradation of the RO membranes will be characterized by complementary analytical methods: FTIR-ATR, XPS, ion chromatography and gas chromatography. These analytical techniques enable to evaluate both degradation of the membrane (top surface and intermediate layer) and the species released from the membrane after 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. The thickness of the flatsheet resulted from a contribution of the different layers: the membrane (~100 nm), the polysulfone intermediate layer (~200 μm) and the polyester non-woven layer (~200 μm) for a total of around 500 μm according to Coronell et al. [25].

2.2. Sample preparation for irradiation

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 irradiation experiments. Membranes 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 prior to be pouring into the glass. No significant amount of liquid water in the glass tube was lost during this process. Irradiation tubes were emptied of atmospheric air by vacuum aspiration. The vacuum absolute pressure was limited to 15 mbar to maintain the sample moisture content. Then irradiation tubes were backfilled with pure oxygen for aerobic conditions and pure argon for anaerobic conditions. This operation was repeated three times to remove the residual air before sealing the tube at absolute pressure around 900 mbar.

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 industrial facility (Ionisos, Dagneux). This facility provided a constant dose rate, approximately 0.5 kGy h^{-1}. The total dose was set to 0.1, 0.2, 0.5 and 1 MGy. Irradiation was performed at room temperature 24 °C ± 3. The cumulated energy absorbed in the sample itself was measured by dosimeters with a known response to irradiation, proportional to the exposure time, as described elsewhere [26]. Furthermore, the samples were irradiated homogeneously by rotating them during exposure. Irradiation time ranged from few days to several months according to the total absorbed dose targeted.

2.4. Membrane characterization after irradiation

Samples used for polymer characterization (attenuated total reflection Fourier transform infrared spectroscopy ATR-FTIR, X-ray photoelectron spectroscopy XPS) were dried in vacuum for at least 48 h before analysis.

2.4.1. 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). The background spectrum was recorded prior to each experiment to avoid contribution of carbon dioxide, water vapor and diamond crystal to the spectrum. The membrane active layer or support layer was then pressed tightly 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.

2.4.2. X-ray photoelectron spectroscopy (XPS)

XPS experiments were performed on an ESCALAB 250 XPS Spectrometer (Thermo Electron Corporation) using Al Kα monochromatic X-ray source (1486,6 eV). The analysis area was a 40 μm diameter. Survey scan were collected for binding energy ranging from 0 to 1200 eV. High resolution scans were obtained by averaging 10 scans for C(1s), O(1s), N(1s) peak with a resolution of 0.1 eV. The sample charging was compensated by an electron flood gun operated at 2 eV. High resolution spectra were subtracted by Shirley-type background. The deconvolution of high resolution spectra was conducted using CasaXPS software with Gaussian-Lorentz functions.

2.4.3. Characterization of leaching species during irradiation in presence of water

The water inside irradiation glass tubes was analyzed by ion chromatography in order to follow leaching species (formates, acetates, oxalates, phthalates, chlorides, sulfates, ammonium, methyl amine and nitrates) from the RO membrane. These compounds are commonly studied in the case of the radioactive nuclear wastes storage [27,28]. Some are specific of degradation of the polymers constituting the membrane.

2.4.4. Radiolysis gas measurement by gas chromatography

The gas analysis was performed with a gas chromatography equipped with a thermal conductivity detector (Varian, CP3800). The capillary column used is a 13 × molecular sieve (Varian, 2 m × 2 mm) and permits to separate H_2, O_2 and N_2. The oven temperature and the detector temperature were set at 140 °C and 120 °C, respectively. The acquisition time is about 6 min.