



Permeability and chemical analysis of aromatic polyamide based membranes exposed to sodium hypochlorite

Axel Ettori^{a,b,c,*}, Emmanuelle Gaudichet-Maurin^c, Jean-Christophe Schrotter^c, Pierre Aimar^{a,b}, Christel Causserand^{a,b}

^a Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 118 route de Narbonne, F-31062 Toulouse cedex 09, France

^b CNRS, Laboratoire de Génie Chimique, F-31062 Toulouse, France

^c Veolia Environnement Research and Innovation, Water Research Center, Chemin de la digue, BP76, 78603 Maisons-Laffitte cedex, France

ARTICLE INFO

Article history:

Received 20 December 2010

Received in revised form 15 February 2011

Accepted 22 March 2011

Available online 29 March 2011

Keywords:

Polyamide

Ageing

Chlorine

Hydrogen bonding

Pure water permeability

ABSTRACT

In this study, a cross-linked aromatic polyamide based reverse osmosis membrane was exposed to variable sodium hypochlorite ageing conditions (free chlorine concentration, solution pH) and the resulting evolutions of membrane surface chemical and structural properties were monitored. Elemental and surface chemical analysis performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), showed that chlorine is essentially incorporated on the polyamide layer of a commercially available composite RO membrane, when soaked in chlorine baths, presumably through a two step electrophilic substitution reaction governed by the concentration of hypochlorous acid (HOCl), at pH values above 5. Deconvolution of the FTIR vibrational amide I band experimentally confirmed previous assumptions stated in the literature regarding the weakening of polyamide intermolecular hydrogen bond interactions with the incorporation of chlorine. An increase in the fraction of non associated C=O groups (1680 cm^{-1}) and a decrease of hydrogen bonded C=O groups (1660 cm^{-1}) were observed with an increase in the concentration of the free chlorine active specie. The relative evolution of pure water permeability was assessed during lab-scale filtration of MilliQ water of a membrane before and after exposure to chlorine. Filtration results indicate polyamide conformational order changes, associated with the weakening of polyamide intermolecular H bonds, as observed with the increase in the packing propensity of the membrane, dominant for HOCl doses above 400 ppm h. In addition, water–sodium chloride selectivity capabilities permanently decreased above this HOCl concentration threshold, further suggesting polyamide chain mobility. However, under controlled exposure conditions, i.e., HOCl concentration, operating conditions (applied pressure or permeation flux) can be improved while maintaining similar RO membrane separation performance.

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1. Introduction

Aromatic polyamide thin films, synthesized by interfacial polymerization, are currently the base of commercially available composite reverse osmosis membranes (RO). This polymer acts as the membrane active layer in applications including seawater desalination, water reclamation and reuse, and several other purification processes [1–3]. During the course of their use, RO membrane selectivity and production capabilities progressively abate, significantly affecting their operating lifetime onsite. Fouling, consisting namely of contributions from colloidal cake fouling,

biofouling and inorganic deposition (scaling) or combination of these, is considered to be the main cause for the decrease of membrane operation efficiency, e.g., with a reduction of permeation flux [4–7]. Chemical cleaning is performed periodically to mitigate membrane performance loss. Generally, alkaline and acidic based cleaning agents (generic or formulated) are used on-site [8]. Sodium hypochlorite, a disinfecting agent commonly used during chemical backwashes of ultrafiltration or microfiltration membranes [9,10], has been assessed as a means to control RO membrane biofouling [11]. However, the ubiquitous reactivity of aromatic polyamide with chlorine is evident from ample published literature on this topic [12–15]. Membrane manufacturers unanimously recommend minimizing exposure, such that free chlorine concentration be below 0.1 mg L^{-1} , as can be found on RO membrane technical data sheets [16,17].

Chlorination of aromatic polyamide has been studied on model compounds, namely benzamide, acetamide and derivatives, mim-

* Corresponding author at: Veolia Environnement Research and Innovation, Water Research Center, Chemin de la digue, BP76, 78603 Maisons-Laffitte cedex, France. Tel.: +33 5 61 55 76 19; fax: +33 5 61 55 61 39.

E-mail address: axel.ettori@veolia.com (A. Ettori).

icking main polyamide chemical functions [18,19]. Admittedly, the reaction mechanism involves a two-step electrophilic substitution, consisting of an N-chlorination (a reaction extensively studied on amines and amides [20,21]), reversible and instantaneous, followed by a ring-chlorination, an irreversible reaction, occurring on the meta-substituted phenylenediamine aromatic cycle through Orton rearrangement and yielding no chain cleavage [22]. This reaction is favored at acidic pH, where the hypochlorous acid and aqueous chlorine, free chlorine specie are dominant [19,23]. A direct ring chlorination pathway has also been suggested as cited in the article of Glater et al. (1994) [18] although the reaction involves aqueous chlorine and requires the presence of a catalyst such as a Lewis acid, known to govern electrophilic aromatic substitution reactions [24].

Polyamide RO membrane solute rejection and water transfer were monitored in pilot test studies to assess the impact of exposure to chlorine and monochloramine, when added into the influent groundwater or surface water upstream of the RO modules [11,25,26]. These studies particularly reported solute rejection loss with increasing free chlorine contact time during long term filtration and ageing studies.

Spectroscopic analysis of commercially available composite RO membranes, namely Fourier transform infrared red (FTIR) and X-ray photoelectron spectroscopy (XPS), were used to study aromatic polyamide chemical modifications with exposure to chlorine [15,27]. Results of these studies support the chlorination mechanism of aromatic polyamide, presented previously, and IR polyamide band modifications were correlated to the evolution of membrane transfer properties with varying chlorine ageing conditions (free chlorine concentration and solution pH). Membrane performance alterations, as observed in pilot studies and in a recent work on the NF/RO rejection of trace pharmaceutically active compounds, such as carbamazepine and ibuprofen [28], can thus be related to intrinsic aromatic polyamide property modifications during chlorine ageing. In a study on the evolution of aromatic polyamide specific vibrational IR bands, Kwon et al. hypothesized that the incorporation of chlorine results in the weakening of aromatic polyamide intermolecular hydrogen bond (H bond) interactions, presumably with the substitution of N-H...O=C by N-Cl O=C [29,30]. The disruption of these physical interactions, classified as weak interactions [31], was further believed to promote local chain mobility, accounting for the water flux variations with applied pressure and/or permeation of sodium chloride, as reported in lab-scale filtration studies [29].

H bond interactions have been shown to contribute to aliphatic polyamide structural order and phase transition properties, as reported in studies on semicrystalline and fully amorphous nylons [31–35]. The effect of stress, heat and solvent-induced changes on conformational order and enhancement of chain motion and free volume was demonstrated with various spectroscopy techniques and X-ray diffraction crystallography and was shown to be related to the disruption of intermolecular H bonds. In the study of the underlying risk of a loss of polyamide-based RO membrane selectivity capabilities, there is a strong need to demonstrate that exposure of these membranes to free chlorine results in the weakening of H bond interactions within the aromatic polyamide structure.

The purpose of the present study was to assess structural modifications of rigid aromatic polyamide RO membranes exposed to varying chlorine ageing concentrations. Membrane hydraulic resistance, a membrane property influenced (amongst others) by the physicochemical interactions with enviroing species, and by chain conformation of the polymer used as the filtration active layer, was monitored during ultrapure water filtration tests performed under high-pressure. Correlation between membrane transfer property modifications and the increase of the fraction of non-associated carbonyl groups, an H bond acceptor, obtained by curve fitting of IR spectra is also discussed. Sodium chloride rejection was monitored

Table 1
Free chlorine (HOCl and ClO⁻) content as a function of pH.

	pH 5.0	pH 6.9	pH 8.0	pH 12
% HOCl	100	78	22	0
% ClO ⁻	0	22	78	100

on initially pristine then aged membranes to provide additional insights of polyamide based RO membrane transfer property modifications with exposure to chlorine.

2. Experimental

2.1. Material

Experiments were performed with high-pressure composite reverse osmosis membranes SW30HRLE-400 (Dow FILMTEC™). According to the manufacture, these membranes have a thin active layer made of fully aromatic crosslinked polyamide synthesized on a polysulfone porous layer supported by a polyester backing layer.

2.2. Sample preparation

All membrane samples were extracted from an 8" spiral wound module, stored at 4 °C. These samples were then thoroughly rinsed with MilliQ water and soaked in MilliQ water baths for 24 h to remove preservation agents prior to characterization and/or ageing (total organic carbon of baths after immersion was below 0.5 mg CL⁻¹). Water baths were periodically renewed and a final bath was stored overnight at 4 °C. Samples used for polymer chemical and elemental composition (determined by attenuated total reflection Fourier transform infrared spectroscopy ATR-FTIR, and X-ray photoelectron spectroscopy XPS) were in addition dried in a vacuum before analysis.

2.3. Chlorine solution and accelerated ageing method

The chlorine solution was prepared by diluting a 111 gL⁻¹ NaOCl commercial bleach solution in MilliQ water (resistivity of 18.2 MΩ cm) to the desired concentrations, ranging from 0.54 to 54 mM NaOCl (i.e., 40–4000 mgL⁻¹). Free chlorine concentration (mainly hypochlorite ion at natural sodium hypochlorite pH, ca. pH of 11.5–12.0) of a diluted aliquot was spectrophotometrically determined ($\lambda_{\max} = 292 \text{ nm}$, $\epsilon_{\max} = 348 \text{ M}^{-1} \text{ cm}^{-1}$).

The pH of the solution was adjusted by addition of hydrochloric acid 37% (v/v) (Acros Organics) to the desired pH of 6.9 or 8.0 corresponding to pH conditions found in seawater desalination plants. The process was monitored with a pH meter (WTW, Sensitix 41). Additionally, ageing was performed at pH 5.0 and 12, where hypochlorous acid and hypochlorite ion are, respectively, dominant, to provide complementary insights on the chlorine reaction mechanism of polyamide based RO membranes. Contents of free chlorine species at each pH are given in Table 1 (obtained from the free chlorine fraction vs. pH diagram and spectrophotometrically verified for HOCl [$\lambda_{\max} = 230 \text{ nm}$, $\epsilon_{\max} = 111 \text{ M}^{-1} \text{ cm}^{-1}$] and ClO⁻ [$\lambda_{\max} = 292 \text{ nm}$, $\epsilon_{\max} = 348 \text{ M}^{-1} \text{ cm}^{-1}$]).

Ageing experiments were performed at 20 ± 3 °C by soaking, in static conditions, membrane samples in 1 L borosilicate glass beakers covered with Parafilm™ and stored in a dark area to reduce natural chlorine reaction with light or air. Contact time, unless specified otherwise, was set to 1 h. The total exposure of membrane to chlorine was expressed as ppm h.

On average, less than 5% variation of the free chlorine concentration was noticed (by comparison of the values measured before and after immersion of the membrane samples).

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