



Catalytic effect of iron on the tolerance of thin-film composite polyamide reverse osmosis membranes to hydrogen peroxide



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ABSTRACT

Hydrogen peroxide (H₂O₂) is potentially an attractive alternative to chlorine-based (hypochlorous acid and monochloramine) antifouling agents in reverse osmosis (RO) because H₂O₂ does not form toxic disinfection byproducts and is tolerated by polyamide (PA) membranes up to high concentrations. However, aqueous H₂O₂ solutions are corrosive and iron corrosion products activate H₂O₂ to reactive oxygen species (ROS) that can degrade the PA separation layer. The impact of iron oxides on membrane stability was studied in the presence of H₂O₂ in two different systems: a corrosion-resistant system (constructed with plastic components) and an all-steel system. Tests in the all-steel system were conducted under enhanced corroding conditions and in deionized (DI) water. H₂O₂ concentrations were 2.0 mM (68 mg/L) or 10 mM (340 mg/L). Corrosion was enhanced by adding 10 mM Cl⁻ or suppressed by adding phosphate buffer. Membrane performance was evaluated by determining salt rejection and the water flux. Under corrosion-suppressed conditions, membranes were stable during the 8-d test. In the all-steel testing system containing 10 mM Cl⁻ ion as corrosion promoter, the membrane tolerance was significantly diminished. In DI water, corrosion was relatively slow but degradation of the membranes was noticeable. Kinetic data of pCBA degradation indicated that membrane damage was caused by ·OH radicals. Quenching of the ·OH radical by methanol, and X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) data are consistent with the hypothesis that Fenton reactions caused cleavage of the polyamide cross-linkages.

1. Introduction

Reverse osmosis (RO) is widely used to recover freshwater from saline sources and wastewater effluent, mainly because RO membranes remove a broad spectrum of organic and biological contaminants as well as salts [1,2]. A major operational challenge of RO treatment is membrane fouling, i.e., coating of the membrane with insoluble chemical and colloidal materials and bacterial biofilms that diminish product water quality, membrane permeability and the energy efficiency of the RO system [3–7]. To avoid the formation of biofilms, microbial attachment and growth are often inhibited by amending the feed water with chlorine-based disinfectants, typically hypochlorous acid (HOCl) or monochloramine (MCA) [8]. However, chlorine-based disinfectants can form toxic disinfection by-products (DBPs) [9,10] and degrade the PA separation layer [11–13]. Thus, there is a significant need to find benign, nonchlorine-based disinfectants. Hydrogen peroxide (H₂O₂) does not produce toxic by-products and PA membranes withstand relatively high H₂O₂ exposures and are therefore studied as a potential alternative to

chlorine-based disinfectants [14,15]. Because H₂O₂ is readily decomposed by bacterial peroxidases, disinfection with H₂O₂ is relatively inefficient and requires relatively high concentrations [15–18]. Efficient removal of established biofilm was found to require the application of 0.5% H₂O₂ at high pH in combination with a surfactant [19].

Applying oxidative biocides for fouling control in RO systems requires an understanding of the biocidal efficacy of the biocides and the tolerance of PA membrane to oxidants [11,12,20,21]. This study focused on the tolerance of a commercial RO membrane to withstand exposure to H₂O₂ in the presence of iron oxides formed during corrosion. RO membranes can withstand exposure to concentrated H₂O₂ in DI water [14,22] but little is known about the influence of water quality on the tolerance of PA membranes to H₂O₂ exposure.

The tolerance of a membrane to exposure of an oxidant, D_{max} , is commonly expressed as the exposure the membrane withstands when in contact with the oxidant without suffering a loss of performance. For constant $[C_{ox}]$, the tolerated cumulative exposure, D_{max} , is given by (Eq. (1)):

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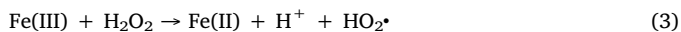
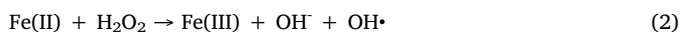
E-mail address: reinhard@stanford.edu (M. Reinhard).

$$D_{max} = [C_{ox}] \times t_{max} \quad (1)$$

where t_{max} defined as the time the membrane is exposed to $[C_{ox}]$ while performing within acceptable specifications. In practice, this definition is referred to as the C*T concept and tolerances are specified in “ppm-h”. This definition implies that doubling $[C_{ox}]$ lowers t_{max} by a factor of two. However, data to assess the validity of this concept are scarce [14]. For example, a commercial RO membrane was specified to withstand 200–1000 h of exposure to 1 mg/L hypochlorite. Resistance to oxidative attack also depends on water quality [23].

In all-steel flat-sheet membrane test systems, corrosion of steel components by MCA solutions led to the accumulation of rust (iron oxide) particles at the surface of membranes and to the destruction of membranes [20]. Iron oxides can be expected to accumulate on RO membranes treating brackish water and seawater [24]. Gabelich et al. [21] found that ferrous iron [Fe(II)] accelerated the degradation of PA membranes exposed to hypochlorous acid and MCA. Based on mechanistic considerations, these authors suggested the formation of the extremely reactive amidogen radical ($\cdot NH_2$) and the hydroxyl radical ($\cdot OH$) in a Fenton-like process. Radicals generated by rust particles were suspected to damage the PA layer in the presence of MCA [20]. The flux increased by approximately 30% following the exposure of 70 mg/L MCA for 6 h.

A limited number of studies presented data on membrane stability in H_2O_2 . Abejón et al. [22] reported that a commercial BE PA membrane (Woongjin Chemical) tolerated 35% (wt/wt) H_2O_2 for up to 80 h (31,000,000 ppm-h) while Ling et al. [14] studying an ESPA2 membrane observed a tolerance of 744,000 ppm-h. Differences are likely due to different membrane characteristics (BE vs. ESPA2) and the different feed water quality [14,22,25]. While in clean systems PA membranes are relatively tolerant to H_2O_2 , damage can be severe if iron species oxide species are present [14]. H_2O_2 activation can occur via the classical Fenton (Eq. (2)) or the Fenton-like chain reaction (Eq. (3)) [26]:



In membrane testing systems, sodium chloride salts are commonly used to quantify rejection. However, chloride salts are not suited as performance indicators in corrosive solutions because they promote corrosion [27,28] and enhance rust formation [29]. In this study, we substituted chloride salts with a phosphate buffer solution because phosphate ions inhibit corrosion [14,30] or acesulfame (ACE). ACE is a small (MW 162.99 Da), negatively charged organic compound.

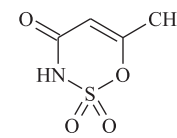
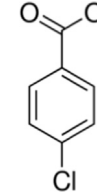
The primary objective of this study was to study the catalytic effect of iron oxides on the degradation of PA membranes, specifically the activation of H_2O_2 via iron oxides via the Fenton reaction. Membrane stability was studied under “corrosion-resistant,” mildly corrosive (in deionized DI water) and in corrosion-enhanced conditions (in the presence of chloride ions). The mechanism of membrane degradation was studied by quantifying the degradation of an $\cdot OH$ probe (*para*-chlorobenzoic acid) under different corrosion conditions. Experiments were conducted at relatively high H_2O_2 concentrations (up to 340 mg/L) to limit the duration of the degradation experiments to less than two weeks.

2. Materials and methods

2.1. Chemicals and membranes

Acesulfame (ACE) and *para*-chlorobenzoic acid (p-CBA) were purchased from Sigma-Aldrich Pte. Ltd., Singapore. The physicochemical properties of the compounds are shown in Table 1. Corresponding mass-labeled internal standard ACE-d4 was purchased from Toronto Research Chemicals, Inc., Canada. HPLC grade methanol, ammonium

Table 1
Physicochemical properties of acesulfame and pCBA.

Compound	Chemical structure	Molecular formula	Molecular weight	log K_{ow}	pK _a
ACE		C ₄ H ₅ NO ₄ S	162.99	-1.33	2.0
pCBA		C ₇ H ₅ O ₂ Cl	156.57	2.65	3.98

acetate, hydrogen peroxide (H_2O_2) (30% wt/wt), sodium phosphate and sodium chloride were purchased from Sigma-Aldrich Pte. Ltd, Singapore.

Samples of the commercial PA thin film composite (TFC) cross-linked membranes: ESPA2 (Hydranautics Oceanside, CA, USA) were obtained as a gift from Public Utility Board, Singapore. ESPA2 is a low-pressure reverse osmosis (LPRO) membrane and is used at the Bedok NEWater water reclamation plant (Singapore). The properties of the ESPA2 membrane are shown in Table 2. Membranes were stored at 4 °C in the dark until use.

2.2. Flat-sheet membrane testing systems

Experiments were conducted in three different systems with varying levels of corrosion control (Table 3): under strongly corrosive conditions in an “all-steel” flat-sheet membrane testing system (constructed with stainless steel cells and a stainless steel tank as described previously [32,33]) in 10 mM NaCl solution. The combined presence NaCl (as the rejection indicator) enhanced corrosive conditions, caused rapid decomposition of H_2O_2 in the feed tank, the accumulation of corrosion products (rust) on the membrane surface and rapid loss of membrane performance. To slow corrosion, NaCl was replaced with ACE in DI water (referred to as “the all-steel system in DI water”). To suppress corrosion to the maximum extent possible, a new testing system was built using inert plastic components where possible. In addition, to measure rejection, NaCl was replaced with phosphate buffer, a corrosion inhibitor. This system is referred to as the “corrosion-resistant system.” The schematic of the all-steel test systems corresponds to the “corrosion-resistant” system, except for modifications described previously [14] and summarized below.

Construction of the “corrosion-resistant” test system was described in a previous communication [14]. The list of the major non-stainless steel components is indicated in Table S1. Briefly, the stainless steel tank was replaced with a 50-L polyethylene tank; stainless-steel tubing was replaced with polytetrafluoroethylene (PTFE) tubing wherever possible and polyethylene valves were used on the low pressure (permeate) side. Crossflow membrane test cells (Model CF042D) made

Table 2
Properties of the ESPA2 membrane.

Membrane	Manufacturer	NaCl Rejection (%)	Permeability at 20 °C (L/m ² h bar)	Contact Angle (°)
ESPA2	Hydranautics	99.6	5.2 ± 0.2	53

Data are from Fujioka et al. [31].

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