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Structure and properties of heterogeneous and homogeneous ion-exchange membranes subjected to ageing in sodium hypochlorite

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ABSTRACT

The effects of sodium hypochlorite (NaClO) on ion-exchange membranes were carefully investigated and discussed with the aim to assess one of their possible causes of ageing. A thorough comparison was carried out for the degradation of ion-exchange membranes with different structures, *i.e.* homogeneous and heterogeneous ones, as well as with different functional groups, *i.e.* anionic (bearing $-\text{CH}_2\text{N}^+\text{R}_3$ groups) and cationic (bearing $-\text{SO}_3^-$ groups) ones. An artificial ageing protocol was implemented, which consisted in immersing four types of membranes, homogeneous AMX-SB and CMX-SB as well as heterogeneous, MA-41 and MK-40 in aqueous NaClO solutions at constant pH and concentration for different times over a 700 h period. The physico-chemical, structural, and mechanical properties of each sample were investigated, before and after ageing, by means of complementary analytical techniques, namely conductivity, ion-exchange capacity, water uptake, and thickness measurements, as well as SEM, ATR-FTIR, TGA, and tensile strength tests.

The results demonstrated that ageing mechanisms were different for anion-exchange membranes and cation-exchange membranes; however, ageing was similar among homogeneous and heterogeneous membranes of the same type (anionic or cationic). Sodium hypochlorite provoked a degradation of the quaternary ammonium sites of anion-exchange membranes and chain scission of the poly(styrene-*co*-divinylbenzene) backbone from anion and cation-exchange membranes through chain radical oxidation. No significant degradation was found for the polymer binder of membranes investigated in this paper.

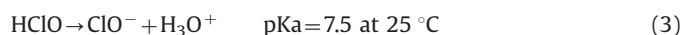
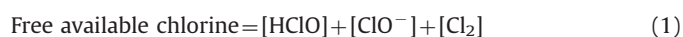
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1. Introduction

Conventional electrodialysis (ED) with ion-exchange membranes (IEMs) is applied for demineralization, purification, and concentration of electrolyte solutions. During the past years, several ED applications have been developed, mainly in the food and drug industry, in the chemical process industry as well as in waste water treatment and production of high quality water [1–4]. In the food industry, ED is used in dairy products, fruit juice, sugar, wine, among others [2,5]. Such solutions are highly nutritious media in which microorganisms may cause spoilage or colloidal matter, inorganic compounds or macromolecules form fouling at the interface or into the membrane [6–9]. In this regard, the effective cleaning-in-place (CIP) of membranes is crucial to prevent fouling and growth of microorganisms that could contaminate the product to be analyzed [10]. CIP is necessary to optimize the membrane performance and minimize the process costs.

CIP protocols are traditionally performed using acids and bases; sometimes however, the employment of stronger cleaning agents, like oxidants, might be necessary to achieve a complete cleaning in ED for food industry applications. Oxidation degrades the functional groups of proteins, which makes them more sensitive to hydrolysis at high pH [11,12]. Sodium hypochlorite (NaClO) is the most common oxidant used in reverse osmosis, ultrafiltration, and microfiltration membrane processes at alkaline pH and 200 ppm [12–14]. Nevertheless, contact with NaClO is suspected to play an important role in membrane ageing [15–26].

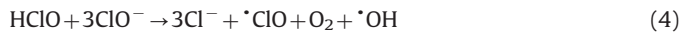
The chemistry of aqueous NaClO solutions is complex and pH dependent. Free available chlorine is the sum of aqueous $\text{Cl}_{2(\text{aq})}$, HClO , and ClO^- concentrations and is a measure of the amount of chlorine species that can oxidize organic or inorganic compounds. NaClO dissociates in water according to the following equilibrium equations:



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The ageing due to NaClO has been previously addressed for membranes based on polysulfone (PSf) and PSf modified with poly(vinylpyrrolidone) (PVP). According to Gaudichet-Maurin [18], exposure to NaClO produces chain breaking of the PSf macromolecules. The mechanism of degradation relies on radical oxidation when hydroxyl radicals $\cdot\text{OH}$ are present in the solution [26], which occurs when hypochlorous acid (HClO) and hypochlorite ions (ClO^-) are the predominant species [19]:



Causserand et al. [19] have then found that degradation of PSf membranes is greater when pH ranged from 8 to 10 than for higher or lower pH values. Arkhangelsky et al. [20] have proposed that polyethersulfone (PES) membranes suffer partial scission of the sulfonyl C–S bond with the formation of phenyl sulfonate, at pH 7.2 and in the presence of sufficient hypochlorite, which leads to enlarged pore sizes and increase in the membrane charge. Yadav et al. [23] have found that PES membranes suffer damage at both pH 9 and 12, however the damage is greater at pH 9.

In a recent study, Prulho et al. [24] have stated that the soaking of PES/PVP blends in hypochlorite solution at pH 8 provokes the oxidation of the aromatic rings into phenol groups. The oxidation of PES in the blend involves the primary oxidation of PVP, and it is accompanied by chain scission and cross-linking reaction.

From these experimental investigations, NaClO seems to be more harmful at pH 7 or 8. This represents a problem in practical applications as potable water or food solutions generally lie within the same pH range.

In this regard, IEM suppliers advise not to use strong oxidizing agents as they could affect the membrane stability. Even though NaClO is not traditionally applied to the IEM CIP, great needs for sanitization in the ED treatment of food solutions might lead to the use of NaClO since it is one of the most efficient chemicals in terms of membrane cleaning and disinfection [16]. Therefore, the consequences of NaClO employment on IEM degradation are worth being investigated.

This work lies within the scope of a research project aiming to explore the effects, causes, and mechanisms of IEM ageing in ED for food industry applications [27–31]. In our more recent papers, ageing of cation-exchange membranes (CEMs) [30] and anion-exchange membranes (AEMs) [30,31] was investigated in two different applications of industrial ED. Membranes suffered a significant decrease in the ion-exchange capacity and an important damage in the functional polymer chains, when performing ED for the treatment of organic acids [30], in which diluted oxidizing solutions might be used to clean and sanitize the ED stack. On the other hand, no significant loss of the ion-exchange capacity or degradation of the functional polymer chains was detected on membranes used for whey demineralization [31]; ageing comes from a progressive loss of the polymer binder, thus leading to the formation of non-charged pores that change the permselectivity and the mechanical properties of the membranes. In this case, CIP is performed with acidic and alkaline solutions. The aim of the current study is to assess the possible causes of IEM ageing in the presence of NaClO.

Depending on their structure, IEMs may be classified into homogeneous membranes and heterogeneous ones. Homogeneous membranes are prepared by introducing an ion-exchange moiety directly into the structure of the constitutive polymer. This leads to a relatively even distribution of the charged groups over the entire membrane matrix. Heterogeneous membranes are prepared by mixing a fine ion-exchange resin powder with a polymer binder. This results in a structure where the ion-exchange groups are clustered and very unevenly distributed in the membrane matrix. Most heterogeneous membranes have relatively low

production costs but they have a higher electrical resistance, due to the longer pathway of the mobile ion in the heterogeneous structure [1]. To the best of our knowledge, thorough studies on the differences or similarities in the stability and durability of both kinds of membranes remain scarce.

This paper constitutes a fundamental investigation of the effects of hypochlorite on heterogeneous and homogeneous IEM properties. As the membrane lifetime is accounted for several thousands of hours, real-time experimentation is impossible, and ageing protocols must be developed to shorten experimental time. Herein, the artificial ageing protocol consists in immersing each membrane in NaClO at constant pH and concentration for different times. Physico-chemical, structural and mechanical properties of each sample are then investigated by means of complementary analytical techniques. This experimental investigation reveals significant issues concerning IEM structure and long-term behavior. The approach is based upon the interpretation of the membrane characterization through a systematic analysis of new samples and aged ones.

2. Experimental

2.1. Membranes

For the ageing experiments, well-known and frequently used IEMs were investigated. Neosepta[®] CMX-SB and AMX-SB from Tokuyama Soda (Japan) are homogeneous CEMs and AEMs, respectively. They are made of functionalized polystyrene (PS) crosslinked with divinylbenzene (DVB) and mixed with finely powdered poly(vinyl chloride) (PVC), which are coated on a PVC cloth used as a reinforcing material [32].

Cationic MK-40 and anionic MA-41 from the Shchekinoazot (Russia) were used as heterogeneous IEMs. They consist in fine polymer particles of ion-exchange resin anchored to a polyethylene matrix and reinforced by caprone fitted fabrics [33]. The ion-exchange resin also consists in functionalized PS crosslinked with DVB. Both types of CEMs possess sulfonate fixed sites, and both types of AEMs possess quaternary ammonium fixed sites.

As a starting point, heterogeneous MA-40 and MA-41 were specifically treated according to the manufacturer. Each sample was wiped with tetrachloromethane and then, immersed during 6 h in ethanol to eliminate the impurities. Afterwards, samples were successively immersed in several NaCl solutions, *i.e.* 2 M, 1 M, 0.5 M, and 0.1 M, for 24 h in each case.

Then, all samples were conditioned following the French standard NF 45-200 [34] in order to stabilize their physico-chemical properties, to remove any impurities that may come from their manufacturing process and to achieve a reproducible initial condition for all membranes before characterization.

This procedure consisted in immersing the samples in solutions of different natures. AEMs were first treated 1 h with 0.1 M HNO_3 , rinsed with water, and carefully dried with filter paper. Then, they were immersed for 1 h in 0.1 M HCl, and rinsed by immersing in 0.1 M NaCl. The procedure was repeated twice, and finally the membrane was stored in 0.1 M NaCl.

CEMs were immersed in 0.1 M HCl, rinsed with water, and dried with filter paper. Then, they were immersed in 0.1 M NaOH, and rinsed by immersing them in 0.1 M NaCl. The procedure was repeated twice as well, and the membrane was kept in 0.1 M NaCl, before the ageing treatment.

2.2. Ageing protocol

Membrane samples of 40 cm² were soaked in 400 mL of the ageing solution during 20, 60, 100, 200, 300, and 700 h.

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