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Characterization and cleaning of anion-exchange membranes used in electrodialysis of polyphenol-containing food industry solutions; comparison with cation-exchange membranes

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ABSTRACT

This paper concerns the mechanisms of aging of ion-exchange membranes (IEMs) during their use in electrodialysis (ED) of food industry solutions containing polyphenols (PPs), as well as their cleaning. The study focuses on anion-exchange membranes (AEMs); their behavior is compared with that of cation-exchange membranes (CEMs). First, physicochemical static characteristics, structural, morphological and tensile strength parameters are determined for new AEMs and two batches of used AEMs at different duration of their use in industry, subjected to regular "Cleaning In Place". Second, non-aggressive and economic *ex-situ* static cleaning methods involving the application of NaCl at 35 g L^{-1}, a reconstituted seawater and a water-ethanol mixture acidified with H_2SO_4 were examined. During the cleaning process, the evolution of physicochemical parameters, such as ion-exchange capacity (IEC), electrical conductivity (κ_m) and contact angle (θ), were followed. It is shown that the application of NaCl solution has a negligible effect on IEC and κ_m; when soaking the membranes in the reconstituted seawater, κ_m even slightly decreases; however, there is a significant increase in these parameters when soaking the membranes in the acidified water-ethanol solution. As for the mechanism of fouling, PPs are the main responsible constituents. Apparently, they form dense colloidal nanoparticles not permeable for ions within membrane meso- and macropores, not penetrating into micropores. A modification of the micro-heterogeneous model under this assumption allows an adequate description of membrane conductivity and explains the fact that the membrane pore size increases with the duration of membrane utilization, while the apparent volume fraction of the inter-gel solution (f_{2app}) decreases. CEMs are found less prone to fouling. The soaking of CEMs in the water-ethanol solution leads to an increase in IEC and f_{2app} by 33% and 60%, respectively, as well as to doubling κ_m and decreasing θ by 23%, after a 120 h. treatment.

1. Introduction

Cation-exchange (CEMs) and anion-exchange (AEMs) membranes, which are permeable to cationic and anionic species, respectively, are widely used as separating films in various electromembrane devices. Conventional electrodialysis (ED) is one of the most important processes based principally on the specific action of ion-exchange membranes (IEMs); it is applied mainly in food [1] and drug industries, in chemical process industry and in waste water treatment and high quality water production [2–6]. In food industry, ED is generally used for tartaric stabilization of wines, deacidification and treatment of fruits juices [7,8], in dairy applications, for the demineralization of whey or the removal and fractionation of whey proteins [9–12]. All these solutions are rich in organic and inorganic matters, colloidal particles, microorganisms and macromolecules that could be negatively/positively charged or neutral. The complex composition of foodstuffs increases the risk of membrane fouling during effluents treatments. That concerns especially the solutions containing several organic components such as proteins, polyphenols, organic acids, etc., which could precipitate or form complexes, aggregates or chelates under unfavorable conditions (pH, temperature, chelating agents, etc.) [3,13,14]. Fouling represents one of the most important efficiency limitative phenomenon in ED processes; it increases the IEMs electrical resistance, decreases their mechanical resistance and their selectivity, and leads

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consequently to an increase in the process cost and a reduction in the membrane lifetime [13,15–20]. In order to reduce the harmful effects of fouling, several *in-situ* chemical washing operations in industries, such as high-quality rinse-water, alkali, acids and surfactant solutions, are regularly or even daily used [21]. These solutions could be used separately or alternatively like in « Cleaning In Place » (CIP) operations that are traditionally carried out by alternating acid-base washings once a day [10]. This method could be efficient for the removal of organic deposits from the membrane surface [22] by increasing the solubility of ionizable compounds or provoking saponification reactions in contact with lipidic matters, etc. However, prolonged exposure of IEMs to alkali and acidic solutions reduce their lifetimes because of applying extreme pH which affects the membrane stability, structure and properties [23,24].

Knowledge of the mechanisms of membrane fouling during ED by the components of feed solution as well as response of IEMs on the CIP operations is very important for a more effective implementation of electroseparation and purification processes. There is an essential difference in the behavior of AEMs and CEMs due to different nature of their functional groups, different state and interactions of foulant components with the membrane matrix and functional groups [15,25–29], which affect the rate and type of fouling [18,30]. Our earlier studies investigated the dynamics and mechanisms of membrane aging and fouling in industrial ED treatment of the whey [19] and organic acid solutions [15]. Paper [31] was devoted to CEMs fouled in food solutions containing polyphenols together with some organic acids; in addition, several cleaning methods deferring from the conventional acid-base procedure in industry were tested. It was found that a water-ethanol mixture had promising results.

In our previous studies [15,19,31], the application of the microheterogeneous model developed in Refs. [32] has given useful results allowing a quantitative interpretation of structural changes in IEMs occurring during their long-term use in ED processes. According to modern theoretical concepts [33–36], due to phase separation in charged water-swollen polymers, ion and water transport in ion-exchange membranes occurs through hydrophilic pores/channels confined within a hydrophobic polymer matrix. The ions in the pores form an electrical double layer (EDL) where they are distributed according to the Poisson-Boltzmann law: the concentration of counterions is high near the charged walls, while that of co-ions is very low there. If the pore size is sufficiently large, there is a region in the pore center, which contains electrically-neutral solution identical to the bathing solution. The amount of the electroneutral solution in a membrane gives an idea of its structure: the volume fraction of this solution (denoted as f_2) quantifies the presence of large pores. The microheterogeneous model assumes that an ion-exchange membrane can be considered as a multiphase system. At least, two phases are distinguished (Fig. 1): (1) the swollen gel phase, which involves polymer chains with fixed functional groups whose charge is compensated by the counterions within the EDL, and (2) the inter-gel electrically neutral solution. The gel phase is a microporous media: the size of pores there is so small ($<$ 2–3 nm) that the EDLs formed at the opposite pore walls are overlapping. The model is widely used in scientific research [37,38] including our previous works [15,19,39]. The main interest represents the simple relationship between the membrane conductivity (κ_m) and the conductivities of the gel phase (κ_g) and electroneutral solution (κ_s) filling the inter-gel spaces: according to [32],

$$\kappa_m = (f_1 \kappa_g^{\alpha} + f_2 \kappa_{int}^{\alpha})^{1/\alpha} \qquad (1)$$

where f_1 and f_2 are the volume fractions of the membrane gel phase and inter-gel spaces, respectively, $f_1 + f_2 = 1$; α is a structural parameter, which varies between -1 and $+1$. The extreme values of α refer to two possible extreme mutual arrangements of two phases in relation to the transport axis: the connection in series and in parallel, respectively. The value of κ_{int} in the case of conventional non-fouled IEM equilibrated with an electrolyte solution (such as NaCl) is assumed equal to the conductivity of the external bathing solution, κ_s. The latter is taken to be approximately proportional to the external solution concentration, C. When $|\alpha|$ is not too far from zero (< 0.2), and the concentration is in the range $0.1\ C_{iso} < C < 10\ C_{iso}$, Eq. (1) may be approximated as [32]:

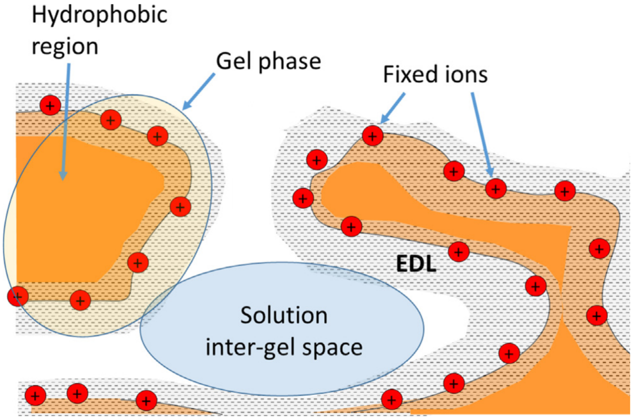

Fig. 1. Schematic representation of the membrane structure and the terms of microheterogeneous model [32]. The concentration of counterions in the electrical double layer (EDL) is essentially higher than that of co-ions; the inter-gel spaces are filled with the electrically neutral solution identical to the external bathing solution.

$$\log(\kappa_m) \approx f_2 \log(C) + \text{const} \qquad (2)$$

C_{iso} is the electrolyte concentration at the isoconductance point (where $\kappa_m = \kappa_g = \kappa_s$), const $= f_1 \log(\kappa_g)_{C=C_{iso}}$.

This study focuses on AEMs used in an industrial ED treatment of the same food solutions as in Ref. [31]; as well, we examine the possibility of AEMs cleaning. The behavior of AEMs is compared with that of CEMs aged and cleaned in the same conditions. The emphasis is on the role of PPs not present in industrial feed solutions applied in Refs. [15,19]. In particular, we will see that the concentration dependence of κ_m evolves with time differently in the cases where PPs are present in feed solution or not. We give an interpretation to this phenomenon by assuming that it is due to formation of dense colloidal nanoparticles in the membrane pores. For the first time, a modification of the microheterogeneous model [32] is proposed in order to take into account the presence of PP colloidal nanoparticles.

2. Experimental

2.1. Anion-exchange membranes

For characterizations and cleaning methods, specific and confidential AEM samples were provided by an industrial from ED units used in food processing. A batch of new AEM(n) and two batches of used AEM(u) at two different use durations in ED modules were studied in this work. Membranes are constituted by a poly(styrene-co-divinylbenzene) (PS-DVB) copolymer with quaternary ammonium functional sites and reinforced by PVC cloth (for privacy reasons, we cannot give the exact reference of the membranes). Before any experiment, AEM(n) were stabilized according to the French standard NF X 45-200 [40], and AEM(u) were directly stored in a 0.1 M NaCl solution in their fouling state. The samples notations used in this paper are presented in Table 1.

2.2. Membrane characterization

Physicochemical, morphological and structural parameters and tensile strength properties of new and used AEM samples were