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Impacts of sodium hydroxide and sodium hypochlorite aging on polyvinylidene fluoride membranes fabricated with different methods

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ABSTRACT

This study compared the effects of chemical aging on the polyvinylidene fluoride (PVDF) membranes fabricated with the methods of non-solvent induced phase separation (NIPS) (named NIPS-PVDF) and thermally induced phase separation (TIPS) (named TIPS-PVDF). The chemical solutions of sodium hypochlorite (NaClO) and sodium hydroxide (NaOH) were chosen at the concentration of 5000 mg/L. The equivalence of 5 and 10 years was respectively selected as the time of aging. The physicochemical evolutions of membrane aging are characterized on the base of morphology analysis, chemical components, permeation ability and mechanical properties. The aging of NIPS-PVDF membrane led to the elimination of surface hydrophilic additives, while NaOH focused on the dehydrofluorination process resulting in the formation of conjugated chains of polyene on the skeleton structure. The chemical components of the surface of TIPS-PVDF membrane were removed continuously during the aging processes of both NaClO and NaOH, which was caused by the saponification of surface additives and the chain scissions of skeleton structure, but without producing any obvious conjugated chains of polyene. All the aging processes led to the increase of contact angle and the decrease of mechanical properties, and the permeability was reduced first and increased later due to the enlargement of surface membrane pores and membrane block. With the influence of membrane aging, selectivity of membrane was decreased (except coliform bacteria). At the beginning of filtration, the turbidity and particle count were at relatively high levels and declined with the filtration process.

Introduction

Micro/ultrafiltration (MF/UF) is known as a high effective technology for drinking water treatment in removing suspended particles, colloids, and microorganisms (Liden et al., 2016; Bergamasco et al. 2011). At present, there is a growing interest in using polymer hollow fiber membranes in the drinking water treatment for micro/ultrafiltration, which can afford stable and good permeate water (Ravereau et al. 2016; Konieczny et al. 2009; Ma et al. 2014). Many kinds of polymers such as the polyvinyl chloride, polyacrylonitrile, aromatic polysulfones, and polyvinylidene fluoride are used

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for membrane material (Regula et al. 2014; Zhang et al. 2016a). More recently, polyvinylidene fluoride (PVDF), a semi-crystalline polymer, has appeared as a favorable material for polymer membrane material due to its outstanding characteristics in chemical resistance, mechanical strength, flexibility and thermal stability (Jung et al. 2016; Zhao et al. 2016; Zhang et al. 2016b). Polyvinylidene fluoride membrane can be fabricated mainly using several methods, including the methods of electro-spinning, non-solvent induced phase separation (NIPS), and thermally induced phase separation (TIPS) (Kim et al. 2016). NIPS and TIPS are two common methods widely used in fabricating various MF/UF membranes. Electro-spinning is used to fabricate nanofiber membranes for membrane distillation (Jung et al. 2016; Xu et al. 2014). The membranes prepared with the NIPS method typically exhibit an integrally skinned asymmetric structure when membranes prepared with the TIPS method show a highly porous and symmetric structure. These two membranes can be used for various applications because of their different characteristics (Xiao et al. 2015).

One of the main problems associated with drinking water micro/ultrafiltration treatment process is membrane fouling, which is susceptible to the modification of membrane properties, such as permeate flux, pore size distribution, and hydrophilicity, and may influence the characteristics of membrane filtration (Hwang et al. 2015; Kimura et al. 2014; Yu et al. 2016). To restore the membrane flux and properties, chemical cleaning is routinely performed during the operation process of filtration (Regula et al. 2013). The corrosive chemical agent, sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH), are still popular due to their high efficiency and acceptable price (Ravereau et al. 2016).

However, it has been reported by some researchers that the caustic environment would impact PVDF (Ravereau et al. 2016; Rabuni et al. 2015; Zhang et al. 2017; Hashim et al. 2011). For instance, the PVDF material became brittle in the extremely caustic environment for the chemical attacking from NaOH (Antón et al. 2015; Ross et al. 2000). It was explained as a dehydrofluorination reaction, which removed hydrogen fluoride unit from polymer chain structure and forming carbon–carbon double bonds (Ross et al. 2000; Zhang et al. 2006). But most of the experiments were carried out under the very strong caustic condition of 12 mol/L, high temperature of 80°C, or long exposure time of a few months (Rabuni et al. 2015; Zhang et al. 2017; Hashim et al. 2011). The reaction must be much more reactive than the relatively low concentration at ambient temperature (Hashim et al. 2011).

Limited literature is available concerning degradation of the PVDF by hypochlorite (Ravereau et al. 2016; Regula et al. 2013; Zhang et al. 2017; Puspitasari et al. 2010). Most of the researchers focus on the altering of functional and mechanical properties, the mechanisms still focus on the dehydrofluorination, and some modifications of the functional properties have been found (Zhang et al. 2017; Hashim et al. 2011). With the decomposition of NaClO into Cl_2, ClO., and OH. free radicals, macromolecule chain scission and crosslinking of PVDF membranes were observed under the exposure to NaClO solution of the concentration of 4000 mg/L at 40°C, at three distinct pH values: 6.0, 7.5 and 11.5, during about 5 months (Ravereau et al. 2016; Regula et al. 2014). The temperature, concentration and exposure time are far from the chemical clean strength in the whole lifespan of most polymer membranes (Ravereau et al. 2016; Hashim et al. 2011; Ross et al. 2000). The removal or degradation of the surface hydrophilic additives of PVDF membrane is often presented by spectroscopy analysis, but the removal process is seldom observed, which would modify surface morphology and chemical characteristics of membrane (Robinson et al. 2016).

The effects of NaOH and NaClO aging on PVDF membranes fabricated by various methods have been published by several authors. For instance, Zhang et al. (2017) found that the effects of NaClO aging on PVDF membrane fabricated with the NIPS method would change the surface characteristics, permeability, retention ability and fouling behavior of membrane. Hashim et al. (2011) compared the effects of sodium hydroxide on PVDF membranes made of three kinds of commercial raw material (Solef 1015, Solef 6010, and Kynar 761) by the NIPS method. It demonstrated the decreases of different levels in mechanical integrity and crystallinity of PVDF membrane. Ravereau et al. (2016) compared the effects of NaClO aging on two PVDF base membranes fabricated by TIPS. One contained hydrophilic additives, and the other was additive free. The chemical modifications of PVDF membranes were observed, but the changes were too low to induce membrane embrittlement and porosity change. The polymer additives were completely destroyed, which led to the decrease of hydrophilicity and the improvement on membrane selectivity. The effects of chemical aging on membranes fabricated with the electro-spinning method, which was a nanofiber technology for membrane distillation (MD), had not been studied in details. It may impact the surface hydrophobic property, pore size and surface porosity of the membrane (Liao et al. 2013).

Research mentioned above mainly focus on harsh condition, only one type of PVDF membrane, whilst many kinds of PVDF membranes have been produced by manufacture, and single cleaning agent of NaClO or NaOH (Regula et al. 2014; Robinson et al. 2016). The comprehensive investigation is seldom reported. Rabuni et al. (2015) assessed the impacts of NaOH and NaClO cleaning on the stability of plate sheet PVDF membrane, and found the increase of contact angle and the decrease of protein retention, against with Ravereau et al. (2016) research results of the improvement in virus selectivity of membrane with chemical aging, which may be due to the differences in membrane kind and aging condition. Some researchers did not find water flux and polyethylene glycol retention change significantly after the PVDF membrane immersed in NaOH solution of 10 wt% for 1 month or NaOH solution of 1 wt% for 24 months, due to the aging condition not so harsh (Regula et al. 2014).

In the study, the effects of sodium hydroxide and sodium hypochlorite solutions on two PVDF hollow fiber membranes have been researched: one fabricated by the non-solvent induced phase separation process and the other by the thermally induced phase separation process. Since polymer membranes have a designed lifespan, in order to gain a better understanding of the relationship between aging extent and usage history, an equivalence of lifespan in the aging condition is introduced and varied. The changes of the chemical components and permeate water quality (instead of bovine serum albumin (BSA) or dextran) of membranes are monitored, and the links between each other are established.

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