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Impact of in situ physical and chemical cleaning on PVDF membrane properties and performances

M.F. Rabuni [a], N.M. Nik Sulaiman [a], M.K. Aroua [a], Ching Yern Chee [b], N. Awanis Hashim [a,*]

[a] Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

HIGHLIGHTS

- The effect of cleaning process at mild conditions towards PVDF membrane stability is investigated.
- Two commonly used cleaning agents (NaOH and NaOCl) were found to reduce PVDF membrane stability.
- The protein retention performance of membrane is reduced subsequent to membrane cleaning process.
- The stability of PVDF membrane was affected even at a chemical concentration of 0.01 M.

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ABSTRACT

Appropriate selection of cleaning agent is an important factor to achieve a better cleaning efficiency and this topic has become an ongoing discussion. This work assesses the impacts of sodium hydroxide (NaOH) and sodium hypochlorite (NaOCl) aqueous solution towards polyvinylidene fluoride (PVDF) stability at the typical concentrations used in membrane cleaning. The cleaned membranes were characterised using field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR), pure water flux measurement, contact angle, protein retention and tensile testing. Membrane cleaned at elevated temperature and higher concentration presented a higher water flux than the virgin membrane which can be a worrying sign of alteration in membrane properties. The FTIR spectra indicated that the alteration in chemical composition of the membrane causes a reduction in the degree of hydrophilicity. The mechanical properties of the membrane were compromised based on the declination of tensile strength. The findings from this work suggest that the usage of NaOCl as compared to NaOH causes a more detrimental effect towards the stability of the PVDF membrane.

1. Introduction

At present, polyvinylidene fluoride (PVDF) has appeared as a favourable material for membrane fabrication due to its outstanding chemical, thermal and mechanical characteristics (Hashim et al., 2011; Liu et al., 2011; Zhang et al., 2009). However, pure PVDF exhibits high hydrophobicity which makes it easily fouled during the filtration process compared to hydrophilic material. For that reason, it is frequent to do modification on PVDF membrane to turn it into hydrophilic properties (Kim et al., 2009; Liu et al., 2011). One of the common methods to modify membrane is by the incorporation of hydrophilic additives during membrane preparation (Fontananova et al., 2006; Hajibabania et al., 2012). The additive is added to introduce hydrophilic functional group to the structure that will aid water permeation. Despite its enhanced property, fouling is still unavoidable. Fouling could be described into two types, external and internal fouling. External fouling occurs when certain impurities or constituents known as foulants are deposited on the membrane surface. The internal fouling takes place by the adsorption and deposition of solutes and small particles within the internal structure of membranes, e.g., adsorption of foulants to pore-walls and pore narrowing or blocking (Wang et al., 2014). This phenomenon contribute to a decrement in membrane flux and permeability, thus lead to a poor separation performance (Puspitasari et al., 2010).

Since fouling remains an inevitable event, consequently, membrane cleaning is accepted as a compulsory procedure during the filtration operation in order to restore membrane flux and performance. There are several ways to clean membrane with each depending on the types of foulant (Hilal et al., 2005; Porcelli and Judd, 2010). The fouled membrane could be physically cleaned via backwashing or flushing. This method can potentially eliminate

* Corresponding author. Tel.: +60 37967 5206; fax: +60 37967 5319.
E-mail address: awanis@um.edu.my (N. Awanis Hashim).

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the cake layer that has been deposited on the surface layer. However, physical cleaning is ineffective in the case where foulants were adsorbed into the membrane layer or pore plugging by means of chemical reaction that occurred between the foulants and membrane material. Accordingly, chemical cleaning is the proper approach to remove irreversible foulant for optimum restoration of the flux.

There have been many studies conducted with regards of fouling, yet, only a small number of research were committed to study PVDF membrane ageing that are caused by chemical cleaning (Hajibabania et al., 2012; Levitsky et al., 2011; Puspitasari et al., 2010). Sodium hydroxide (NaOH) and sodium hypochlorite (NaOCl) are both commonly used in the membrane cleaning study (Kimura et al., 2004; Lin et al., 2010; Regula et al., 2013; Suárez et al., 2012; Wang et al., 2010). For instance, caustic solution was found to be efficient in restoring flux of membrane that had been fouled with humic acid (HA) (Srisurichan et al., 2005). Cleaning was also performed with aqueous NaOH (1 wt%) on a submerged rotating membrane bioreactor system that was severely fouled (Zuo et al., 2010). Subsequent to cleaning, distinct membrane pores can be observed given that the alkaline solution successfully removes the organic contaminants of protein, together with the microorganisms that lie inside and on the surface of the membrane. Levitsky et al. evaluated the effects of cleaning a bovine serum albumin (BSA) fouled PVDF membrane using NaOCl (Levitsky et al., 2011). In general, all cleaned membranes presented a higher permeability than the virgin membranes which implies an enhanced hydrophilicity of the membrane. In another study, hydrochloric acid (HCl), NaOH and NaOCl were used for cleaning process of membrane fouled with coke particles (Madaeni et al., 2011). The result shows both NaOH and NaOCl, performed a flux recovery of more than 75% while HCl produced a lesser result. Other than analysing the efficacy of chemical cleaning for membrane water flux recovery, the changes in polymeric membrane stability following the cleaning process was also studied (Arkhangelsky et al., 2007). It was found that the membrane exposed to hypochlorite experienced a decline in its elasticity, tensile strength, and elongation at break. An intriguing remark was made by the author whereby a reduction in mechanical strength was detected even at hypochlorite concentration that is considered as "safe-cleaning" conditions. In our recent study, we too, showed the exposure to strong alkaline solution even at mild condition could be detrimental to PVDF membrane (Rabuni et al., 2013).

All of the previous works mentioned above have demonstrated that the chemical cleaning to be relatively satisfactory in recovering membrane flux. The efficiency of cleaning has been mostly discussed with regards to its flux recovery and rejection performance rather than to scrutinise the effects of the chemical used towards the stability of the membrane material itself. Thus, it has not been realised that the membrane deteriorates throughout the cleaning process. There have long been suspicions that NaOH and NaOCl could be detrimental to PVDF. However, not many works had been done to investigate the effect of these cleaning agents on PVDF membrane. To our knowledge, discussions on the effects of chemical exposure on the PVDF membrane intrinsic properties primarily in repetitive fouling and cleaning cycles are only available in limited references (Hajibabania et al., 2012; Puspitasari et al., 2010; Wang et al., 2010). It was observed that cyclical filtration and cleaning has changed the PVDF membrane stability. Previous research usually involved a longer cleaning time and relatively high dose of chemical exposed to the fouled membrane. Furthermore, there is a lack of detailed study on the comparison of NaOH and NaOCl used to clean fouled PVDF membrane. The compatibility of cleaning agents and the membrane material is vital to ensure a longer and improved membrane lifespan. Therefore, in this work, we aim to investigate the effect of repeated chemical cleaning of fouled PVDF membranes analogous to cyclical chemical cleaning processes for membrane system in real industry-related application. It is also worth to state that the main difference between this and earlier studies is the application of the comparatively mild-cleaning conditions i.e. shorter cleaning time and relatively lower chemical concentration.

2. Experimental

2.1. Materials

Commercial flat sheet ultrafiltration (UF) PVDF membrane with 100 K molecular weight cut-off (MWCO) was purchased from Sterlitech Corporation (USA). Due to the proprietary nature of the commercial membrane formulations, information on the type of hydrophilic additive used for PVDF modification cannot be disclosed. Throughout this work, ultrapure water (Milli-Q) was used for rinsing, preparation of sample solution and membrane water flux measurement. NaOCl with 4.99% available chlorine was obtained from Fisher Scientific (Malaysia) and NaOH was purchased from R&M Chemicals (Malaysia). Bovine serum albumin (BSA) in a form of lyophilised powder with a molecular weight of approximately 66 kDa was purchased from Sigma Aldrich (Malaysia). The protein solution was prepared by mixing the BSA solid powder in Milli-Q water.

2.2. Methodology

The filtration experiments were conducted with the cross-flow filtration module (Solteq membrane bench filtration (Model TR 32), Malaysia). Prior to filtration experiment, the membrane was rinsed to remove any preservative on its surface and soaked in Milli-Q water for approximately one day. A sequence of experiments was carried out as depicted in Fig. 1.

Throughout this study, the cleaning process was performed in-situ (without removing the membrane from the module). Physical cleaning of the fouled membrane was conducted by means of hydraulic via forward flush. The ultrapure water was allowed to flow along the membrane for 20 min with a velocity of approximately 5 m/min. In principle, this process could remove a constructed layer of contaminants on the membrane surface through the creation of turbulence. Afterwards, cleaning with chemical was conducted in similar approach, by allowing the cleaning solution to flow across the fouled membrane surface at different cleaning conditions. The parameters in chemical cleaning procedure were selected in accordance with the commonly employed membrane cleaning conditions (i.e. chemical concentration, cleaning period and temperature) documented in earlier works (Chen et al., 2006; Regula et al., 2014) and also based on the recommended cleaning protocol/guidelines by several membrane manufacturers. In this work, three different concentrations were tested (0.01, 0.05 and 0.1 M) and the cleaning period were 10, 20, 40 and 60 min. The effect of different temperature on cleaning performance was investigated by cleaning the membrane at room condition (25 ± 2 °C) and 50 ± 2 °C.

For comparison purposes, membrane cleaning was conducted with both NaOH and NaOCl. After the chemical cleaning process, the filtration system was rinsed for 15 min with pure water. During oxidative (NaOCl) cleaning experiments, a little amount of sodium bisulphite was added to remove traces of NaOCl prior to another cycle of BSA filtration. To evaluate the flux recovery, the ratio of the specific flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$) of permeate flux for cleaned membrane, J_c, to the initial flux of virgin membrane, J_v, was calculated and described as cleaning efficiency (C_e) and is