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Ageing of membranes for water treatment: Linking changes to performance

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ABSTRACT

Fouling and cleaning of membranes are well understood, but long-term changes (ageing) are not as established. A large body of literature has emerged on membrane ageing in the past 15 years. An array of changes in physical and chemical characteristics, as well as in membrane performance, has been attributed to ageing. The present review and analysis of published literature emphasize that research into membrane ageing is complex; it can only be comprehensively addressed by considering performance factors, chemical/physical membrane characteristics, and analytical methods in parallel, as well as the links between these. Of the performance factors, membrane resistance and breach frequency are widely discussed, but there is still debate over the membrane characteristics that cause them to change. Changing membrane fouling rate has been attributed to fewer causes, whereas membrane cleaning rate has not been linked to membrane characteristics. Chemical and physical changes in PVDF membranes can be understood using classic analytical techniques as well as methods that mimic membrane operation. Several research avenues emerged from the literature review. These include heightened attention to foulant effects, identifying the cause of changes to cleaning rate, and considering all performance factors simultaneously in economic assessment of membrane ageing.

Contents

Abbreviations: AFM, Atomic Force Microscopy; ATR–FTIR, Attenuated Total Reflectance – Fourier Transform Infrared [Spectroscopy]; BSA, Bovine Serum Albumin; CA, Cellulose Acetate; DSC, Differential Scanning Calorimetry; FESEM, Field Emission Scanning Electron Microscopy; FTIR, Fourier Transform Infrared [Spectroscopy]; GPC, Gel Permeation Chromatography; HA, Hydrophilic Additive; HF, Hollow Fiber; MALDI, Matrix-Assisted Laser Desorption Ionization; MF, Microfiltration; MIT, Membrane Integrity Testing; MS, Mass Spectrometry; MWCO, Molecular Weight Cutoff; NF, Nanofiltration; NMR, Nuclear Magnetic Resonance [Spectroscopy]; PES, Polyether Sulfone; PP, Polypropylene; PVDF, Polyvinylidene Difluoride, PVP, Polyvinyl Pyrrolidone; RO, Reverse Osmosis; SEM, Scanning Electron Microscopy; SDS, Sodium Dodecyl Sulfate; TGA, Thermogravimetric Analysis; ToF–SIMS, Time of Flight – Selected Ion Monitoring Spectroscopy; UF, Ultrafiltration; XPS, X-Ray Photoelectron Spectroscopy; XRD, X-Ray Diffraction

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1. Introduction

In low pressure membrane research, performance deterioration is a ubiquitous topic. In the 1980's and 1990's, research focused on understanding fouling and designing cleaning procedures to combat fouling. Since 1980, thousands of journal publications have been published which focus on membrane fouling, and hundreds on membrane cleaning. Recently, the study of the long-term changes in membranes during use, dubbed 'ageing' has grown as well. Of these, roughly 50 journal articles address ageing of low-pressure membranes for water treatment. This literature analysis was first performed using the ScienceDirect database by Regula et al. but updated using identical search terms [1].

Most low pressure membrane ageing research relates to water treatment, which are widespread and high-volume applications. In drinking water treatment, membrane systems are easily automated, and reliably produce a high quality effluent, despite variable raw water characteristics. For wastewater treatment, membranes are generally incorporated into membrane bioreactors (MBRs) to minimize plant footprint and provide high effluent quality. These advantages have enabled membranes to be one of the fastest-growing water treatment technologies.

Fouling in low pressure membranes is caused by the accumulation of feed solution constituents at or in the membrane, usually causing an increase in resistance to permeate flow. Fouling control methods include both physical or hydraulic cleaning, and chemical cleaning techniques. It is common to use multiple cleaning methods in any particular application. For example, hydraulic cleaning is often carried out using air scouring, cross-flow, and backwashing. Cleaning with various chemical reagents is common in routine operation (i.e. chemically-enhanced backwash), as well as periodically, when more extensive cleaning is required (recovery or clean-in-place) [2]. Chemical cleaning agents include oxidants, acids, bases, surfactants, and chelating agents, each targeting particular foulants. Sodium hypochlorite, an oxidant and disinfectant, is the most common cleaning agent used in water treatment applications [3], so it is featured in this review.

Despite the importance of fouling control for maintenance of long-term membrane performance, cleaning agents can have unintended impacts on the membrane materials [4]. The combination of long-term exposure to cleaning agents, accumulation of irreversible foulants, and other rigours of membrane use combine to result in membrane ageing. In this review, membrane ageing is defined as the change observed in membrane properties over long-term use (i.e. irreversible changes). These properties can be expressed either as membrane physical and chemical characteristics (e.g. chemical composition, pore size), or as performance factors (e.g. fouling rate, membrane resistance). Though membrane characteristics cause changes in performance, the relationship between the two types of parameters is not thoroughly understood.

The present discussion focuses on low pressure polymeric membranes. These types of membranes are prone to organic reactions with cleaning agents and components of the feed water and, therefore, are susceptible to ageing. Although ceramic or inorganic membranes are also applied in water treatment, their very low reactivity and high resilience mean that ageing effects can be easily reversed, without compromising the membranes' chemical or physical properties [5]. Also, polymeric membrane account for 80–90% of the global treatment capacity [1].

To date, three major studies have focused on membrane ageing [1,2,6]. In addition to these, approximately 50 journal publications have reported on ageing of specific types of membranes in specific applications. Most publications consider performance factors or membrane characteristics without emphasizing the link between these. Also, no work to date has considered a retrospective overview of all performance factors and characteristics. The present review focuses on three objectives to begin to bridge this knowledge gap.

The first objective is to identify changes in membrane performance factors as membranes age, and determine the characteristics that cause these changes. Because the mechanism leading to the ageing process itself is not considered as part of this objective, multiple types of membrane chemistries are considered in parallel. However, only ageing resulting from exposure to sodium hypochlorite is considered, as this is the most common cleaning agent. The second objective is to understand changes in chemical and physical characteristics as a result of membrane ageing. To do this, data from analytical methods used in ageing experiments are interpreted. Because changes are often chemical-specific, membranes with polyvinyledene difluoride (PVDF)-based chemistry are considered. PVDF-based membranes are among the most commonly used in water treatment applications [1], but the approach developed in the present discussion can be used to investigate ageing of other membrane chemistries. The third objective is to use the compiled knowledge to identify research directions that are necessary to understand and strategically minimize membrane ageing.