



Chemically induced alterations in the characteristics of fouling-causing bio-macromolecules – Implications for the chemical cleaning of fouled membranes



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ABSTRACT

Chemical cleaning is an essential process for the permeability recovery of fouled membranes, which is highly related to the interactions between chemicals and bio-macromolecules in fouling layers. In this study, three bio-macromolecules (i.e., effluent biopolymers (i.e., 0.45 μm –100 kDa) from a full-scale municipal wastewater treatment plant, bovine serum albumin (BSA) and dextran) were exposed to different chemicals (i.e., NaClO, H₂O₂, NaOH, and HCl) with varied concentrations to understand the changes in their properties and functional groups. The results showed that exposure to oxidants and alkali decreased the consistency index of all bio-macromolecules. With an increased oxidant dose, the molecular sizes of effluent biopolymers and dextran continuously reduced because of the oxidative cleavage of the long molecule chains. However, the molecular size of BSA sharply increased after being treated with oxidants and alkali, likely due to the cross-linkage of protein molecules. Three-dimensional fluorescence excitation-emission matrix (3D-EEM) spectra showed that the aromatic protein-like and humic substances in the effluent biopolymers were destructed readily during the treatments of oxidants and alkali. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses further confirmed that exposures to NaClO, H₂O₂ and NaOH led to the destruction of protein structures (i.e., amide I, II and III), the increase of carbonyl and carboxyl groups, and the decrease of fatty acids/lipids, all of which could make the bio-macromolecules more hydrophilic. Most importantly, the bio-macromolecules exposed to chemicals had better filterability, and their permeability through membranes also significantly increased, which could be explained well by the above analysis. The chemical cleaning mechanisms of fouled membranes are understood in depth in this study, and all of the results shed light on the implementation of on-line chemical enhanced backwashing in membrane processes.

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1. Introduction

Membrane technologies, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse-osmosis (RO) and forward-osmosis (FO), have been increasingly applied for drinking water (Hallé et al., 2009; Huang et al., 2009) and wastewater treatment (Huang and Lee, 2015). The use of membranes can significantly improve the quality of the treated water (Zheng et al., 2010; Tadkaew et al., 2011) and recover nutrients (Qiu et al., 2015)/

energy (Scherson and Criddle, 2014; Li et al., 2015) from the wastewater; however, membrane fouling is still a vital limitation to membrane technologies (Meng et al., 2009). Even though vast efforts have been made to control membrane fouling, such as pre-treatment of feed water (Gamage and Chellam, 2014), development of anti-fouling strategies (Adout et al., 2010; Kim et al., 2013) and optimization of operating parameters (Huang et al., 2011b), this issue has not yet been well resolved until now.

Among the strategies used for fouling control, chemical cleaning is an essential process for the permeability recovery of severely fouled membranes (Porcelli and Judd, 2010; Wang et al., 2014a). Five types of chemical cleaning reagents are normally employed (Liu et al., 2001): bases (e.g., NaOH), acids (e.g., HCl), disinfectants

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or oxidants (e.g., NaClO, H₂O₂), chelates and surfactants. Permeability recovery is achieved by means of chemical reactions between the cleaning reagents and the deposited foulants, e.g., the bases and acids can alter membrane foulant characteristics through solubilization and/or hydrolysis, while the oxidants can destruct the foulants via the oxidation of chemical functional groups (Liu et al., 2001; Porcelli and Judd, 2010). Nevertheless, the implementation of chemical cleaning in membrane-based facilities is usually based on rules of thumb; the factors affecting cleaning efficiency, such as chemical species, reagent concentrations and the reaction time of chemicals with foulants, have not been well defined. One of the key challenges to the resolution of this issue is the poor mechanistic understanding of the chemical cleaning processes. For instance, how do chemical cleaning reagents change the deposition or adsorption propensities of foulants on membranes? What types of structural and functional groups of the foulants are more susceptible to chemical reagents?

Bio-macromolecules are believed to be one primary compound leading to membrane fouling in membrane facilities used for wastewater treatment and effluent reuse (Meng et al., 2011). They are composed of proteins, polysaccharides and humic substances and mainly produced by microorganisms. Previously, considerable efforts have suggested that the fraction of bio-macromolecules with a molecular size above approximately 100 kDa, referred to as biopolymers, is the predominant foulant in membrane bioreactors (MBRs) (Rosenberger et al., 2006; Meng et al., 2011), UF filtration systems (Laabs et al., 2006; Zheng et al., 2010), and drinking water treatment processes (Hallé et al., 2009). Moreover, the cross-linked structure of biopolymers, particularly the polysaccharide fractions, grants the biopolymers with strong gelling properties (Seviour et al., 2010; Bar-Zeev et al., 2015), which is significantly attributed to the formation of gel layers on membrane surfaces (Rosenberger et al., 2006; Wang and Waite, 2009a; Xiao et al., 2013; Hong et al., 2014). Lei et al. (2016). and Xiao et al. (2013). further revealed the formation mechanism and evolution process of gel layers with mathematical models. In addition to the large-size nature and sticky character, the hydrophilic/hydrophobic interactions between gelling biopolymers and membranes could be another important contributor to membrane fouling (Liang et al., 2007; Xiao et al., 2014). Yamamura et al. (2014). and Shen et al. (2010), for example, showed that the hydrophilic fractions were likely responsible for the high fouling potential of biopolymers, which could be mainly related to their larger size. In contrast, the hydrophobic fractions were thought to cause higher pore blocking and gel layer resistance due to their smaller size and higher abundance of carboxylic complexing groups (Xiao et al., 2014; Zheng et al., 2014). Overall, these previous studies suggest that the chemical cleaning of fouled membranes should be aimed at two aspects: i) the changes in the physicochemical properties (i.e., gelling properties and size natures) of the biopolymers and ii) more crucially, the chemically induced alterations in the functional or structural makeup of biopolymers (i.e., carboxylic groups (Wang and Waite, 2009a; Xiao et al., 2014)), which could be one major mechanism for the detachment of biopolymers from the membranes (Mo et al., 2010; Zeng et al., 2014).

Given the significance of chemical cleaning mechanisms and the lack of related information, the intention of this study is to reveal the chemically induced changes in effluent biopolymers (0.45 μ m–100 kDa) from a full-scale municipal wastewater treatment plant (WWTP) and two model foulants (bovine serum albumin (BSA, 66 kDa) and dextran (500 kDa)) upon exposure to different chemicals (i.e., NaClO, H₂O₂, NaOH, and HCl) with varied concentrations. During chemical exposure assays, physicochemical properties (i.e., the consistency index, zeta potential and molecular size) and functional groups of the treated bio-macromolecules were

characterized by multiple techniques such as Zetasizer, rheometer, fluorescence spectrometer, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Finally, the filterability of bio-macromolecules upon exposure to chemicals was studied by a series of stirred dead-end filtration tests.

2. Materials and methods

2.1. Bio-macromolecules and chemical cleaning reagent solutions

In this work, the wastewater effluent was taken from a full-scale municipal WWTP (A²/O process, Li-Jiao plant, Guangzhou, China) and then the fraction of 0.45 μ m–100 kDa in the effluent was extracted and concentrated as the effluent biopolymer stock solutions by a tangential flow filtration (TFF) system (Cogent™ M, Millipore Corporation, USA). The TFF technique has been widely used in the sampling of water and wastewater because of considerable advantages, such as the ability to concentrate larger sample volumes and lower membrane clogging through parallel fluid flows tangent to the filter surfaces (Cai et al., 2015; Ellis et al., 2015). In this pretreatment, Pellico® 2 microfiltration (HVMP, 0.45 μ m, hydrophilic polyvinylidene fluoride (PVDF)) and ultrafiltration (Bio-max-100, 100 kDa, modified polyethersulfone (PES)) mini filters were employed. The total organic carbon (TOC) concentration of the concentrated effluent biopolymer solution was determined to be 98.5 mg/L by a TOC analyzer (TOC-VCPH, Shimadzu, Japan). The effluent biopolymer is a complex mixture, consisting mainly of large-molecular size proteins and polysaccharides. To provide more clear insights into the physicochemical property changes in these bio-macromolecules compounds exposed to chemicals, pure dextran (T-500 kDa, Sigma-Aldrich) and BSA (66 kDa, Sigma-Aldrich) were investigated as two typical model bio-macromolecules. They were received in the powder form and separately dissolved in deionized (DI) water to prepare stock solutions (10 g/L) without further purification. Four types of chemical cleaning reagents, including NaClO, H₂O₂, NaOH, and HCl, were used. More detailed information on these chemicals is provided in Table S1. The NaClO solution with 10.0% effective chlorine was diluted in DI water to obtain a set of NaClO solutions (2–140 ppm (mL/L)). A 30.0% H₂O₂ solution was used to prepare a series of H₂O₂ solutions between 0.2 and 20.0%. A series of pH solutions ranging from 0.7 to 13.3 was prepared using 1 M HCl and 1 M NaOH solutions. All of the solutions mentioned above were freshly prepared to avoid concerns of deterioration prior to the chemical exposure assays.

2.2. Chemicals exposure assays

The bio-macromolecule solutions (i.e., dextran, BSA, and effluent biopolymers) were added into different chemical cleaning reagent solutions at a volume ratio of 1:1 in a 60 mL glass bottle and then gently stirred at 25 °C for approximately 2 h. The concentrations of dextran, BSA, and effluent biopolymers in the mixed solutions were 5 g-dextran/L, 5 g-BSA/L, and 49.25 mg-TOC/L, respectively. Such high bio-macromolecule concentrations used in the chemical exposure assay allow these mixed solutions to reach lower limits of the rheometer measurement, while having a similar condition as the zone near the membrane surfaces (e.g., concentration polarization area). Afterwards, 20 mL of the mixtures were taken out for rheological analyses, and the rest was used for the measurements of the zeta potential and molecular size. Before these analyses, the pH of all mixtures was determined. As a blank, the same volume ratio (1:1) of bio-macromolecule solutions to DI water was mixed for the same analyses as described above. To avoid the effects of additives on the compositions and properties of the

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