Fate and fouling characteristics of fluorescent dissolved organic matter in ultrafiltration of terrestrial humic substances

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HIGHLIGHTS

- EEM-PARAFAC is applied to track the fate of different HS constitutes in UF.
- Removal was greater for protein/tannin-like (C1) vs. humic-like components.
- Fouling behaviors of humic-like components (C2–C4) depend on their molecular sizes.
- C2 and C4 are associated with irreversible and reversible fouling, respectively.
- Large sized C4 is suggested a surrogate for predicting UF membrane fouling.

GRAPHICAL ABSTRACT
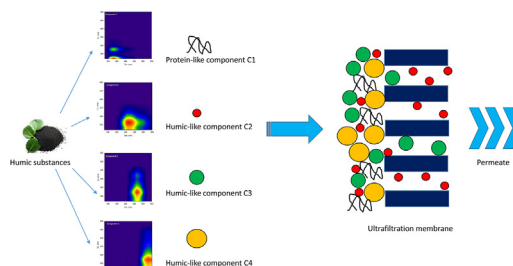
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ABSTRACT

Ultrafiltration (UF) membrane fouling caused by terrestrial input of dissolved organic matter (DOM), especially during high flood periods, is poorly understood. In this study, we examined the fouling characteristics of three different terrestrial humic substances (HS) on regenerated cellulose (RC) UF membranes with the pore sizes of 30 k–3 kDa via conventional bulk HS measurements as well as an advanced fluorescence spectroscopy. The fluorescence excitation-emission matrix coupled with parallel factor analysis (EEM-PARAFAC) identified one protein-like (C1) and three humic-like fluorescent components (C2–C4) from soil and leaf-derived HS. The fate of the different fluorescent components was individually tracked for the UF processes. The higher removal rates were found generally on the order of high molecular weight (HMW) C1 to smaller sized humic-like components (C4 > C3 > C2) regardless of the HS sources, implying the importance of HS molecular sizes on the UF operation. Among the humic-like components, C2 was the most associated with irreversible fouling, while other two humic-like components contributed more to reversible fouling. For soil-derived HS, C4 can be suggested as a good surrogate for membrane fouling, as evidenced by the highest correlation between the removal rates and the total fouling indices among the tested HS variables including conventional bulk parameters. Our study demonstrated a promising application of EEM-PARAFAC for probing membrane fouling of terrestrial DOM, which provided additional insight into the fate of different fluorescent components on the UF processes.

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1. Introduction

Recent advances in membrane technology over the last two decades pose membrane filtration a highly attractive and effective process for treating water/wastewater. From an economic point of view, ultrafiltration (UF) can be suggested as an attractive option for industrial, agricultural uses, and/or as a pretreatment method prior to nanofiltration and reverse osmosis (Van Der Bruggen et al., 2003; Villacorte et al., 2015; Dolar et al., 2016). Nevertheless, membrane fouling is considered a major obstacle for successful implementation of UF processes, which deteriorates membrane lifespan and increases the frequency of backwashing (Amy, 2008), resulting in the reduction of permeability and increase of energy consumption (Zularisam et al., 2006). Although many factors are responsible for membrane fouling, organic constituents contained in surface water and/or wastewater have been suggested as a critical element for membrane fouling (Al-Amoudi, 2010). Heterogeneous properties of organic matters make it more difficult to resolve membrane fouling problems.

Terrestrial humic substances (HS), one dominant group of dissolved organic matter (DOM) ubiquitous in freshwater systems, have been neglected concerning the effectiveness of UF operation despite their resistant nature and the relatively large molecular sizes (Zularisam et al., 2006; Sutzkover-Gutman et al., 2010). Potential detrimental effects of terrestrial HS on UF processes can be more pronounced in surface water during a high flood period when diverse soil-/leaf-derived organic substances are washed out from upstream catchments into water supplies (mostly, rivers and lakes) (Dong et al., 2014; Quang et al., 2015; Yang et al., 2015b). To date, ultraviolet absorbance (UV) and dissolved organic carbon (DOC) have been widely adopted to quantitatively track the factors responsible for the membrane rejection of HS and its fouling potential (Amy, 2008; Sutzkover-Gutman et al., 2010). The efficiency of membrane filtration is affected by several variables such as DOM composition, membrane properties (e.g., pore sizes, hydrophobicity, surface charge, and roughness), and hydrodynamic conditions (Sutzkover-Gutman et al., 2010). Depending on bulk DOM parameters, conflicting results have been reported on the relationships between UF membrane pore sizes and removal rates. For example, Domany et al. (2002) reported a higher UV removal rate of a commercial HS (85–90%) versus natural well water (62–72%) independent of UF membrane pore sizes, while a lower removal rate of DOC was consistently observed for relatively large pore sized UF membranes in other studies (Lowe and Hossain, 2008). Such inconsistent trends imply the complication in the linkages between membrane fouling and DOM characteristics and/or the heterogeneous composition of DOM.

Fluorescence excitation emission matrix (EEM) spectroscopy has been popular as an efficient tool for probing the chemical composition of DOM, due to its easy, fast, and reliable data acquisition (Henderson et al., 2009; Fellman et al., 2010). Recent development of EEM-parallel factor analysis (PARAFAC) provided a semi-quantitative insight into the dynamic behaviors of different DOM constituents by statistically decomposing a EEM dataset into several independent fluorescent groups (Stedmon and Bro, 2008; Yang et al., 2015a). EEM-PARAFAC is very useful in tracing different sources/compositions of DOM. For example, Sanchez et al. (2014) reported using EEM-PARAFAC that humic-like substances were preferentially removed from a bulk DOM by aluminum-based coagulation processes. Meanwhile, it was reported that protein-like fluorescent components were more effectively eliminated by membrane filtration than humic-like components (Shutova et al., 2014).

Despite such a promising potential use for drinking water treatment processes, only a few applications of EEM-PARAFAC for

membrane filtration were reported. Furthermore, the previous studies mostly focused on algal-derived DOM (Yu et al., 2014) or natural water (Shao et al., 2014; Shutova et al., 2014), not fully reflecting a large variation of DOM composition and various DOM sources in water supplies. Considering a substantial contribution of terrestrial HS to surface water during high-flow periods, it would be very interesting to explore its fouling characteristics on UF membrane processes by using EEM-PARAFAC. The objectives of this study were (1) to examine the variations in the flux of terrestrial HS solutions with UF processes using different pore sized membranes, (2) to individually track the fate of different fluorescent components on the UF filtration, and (3) to compare the removal and the fouling characteristics between bulk HS parameters and different fluorescent components. Again, the heterogeneous composition of HS and the dynamic behaviors of different fluorescent groups in bulk HS were explored here by using EEM-PARAFAC to provide new insights into the roles of HS chemical composition on UF membrane fouling. This work is expected to be beneficial for further developing continuous on-line monitoring systems for membrane filtration processes.

2. Materials and methods

2.1. Preparation of feed HS solutions

Three different HS were selected as representative terrestrial HS for this study, which include a commercial humic acid (AHA, Sigma-Aldrich), Elliott soil humic acid (ESHA, International Humic Substance Society), and a leaf litter HS (LLHS). AHA was further purified, following Costa and de Pinho (2005). The preparation of LLHS is described in detail elsewhere (Phong and Hur, 2015). In brief, fallen leaves were collected from several locations around the Han River basin in Korea. They were air-dried, shredded, and mixed with distilled deionized water (DDW) for 24 h. LLHS was isolated from the water-soluble organic matter by passing the acidified extract (pH = ~2.0) through pre-cleaned DAX-8 resin. It was further purified by passing through a cation-exchange resin (Dowex 50WX8-100 Sigma), and freeze-dried.

All HS solutions (around 30 mg C/L) were prepared by mixing the powder form of HS with distilled deionized water (DDW), followed by the additions of $NaHCO_3$ (1 mM) and NaCl (20 mM), and $CaCl_2$ (1 mM). The pH was adjusted to 7.0 by adding 1 N HCl or NaOH. The high DOC was selected to induce accelerated membrane fouling. All HS solutions were filtered to remove any insoluble particles by cellulose acetate filters with a nominal pore size of 0.45 μm.

2.2. Experimental setup for membrane filtration

Flat-sheet regenerated cellulose (RC) membranes (Millipore, USA) with the molecular weight cut off (MWCO) of 30, 10, 5, and 3 kDa were used, which were denoted as RC30, RC10, RC5, and RC3, respectively. RC membranes, generally considered hydrophilic (Lee et al., 2006; Zhou et al., 2014), have been widely used for producing potable water (Lowe and Hossain, 2008; Liu et al., 2010). The membranes were stored in DDW for 48 h before the use, and subsequent backwashing was conducted with DDW until DOC in the permeate was <0.2 mg C/L. Pure water permeability of the clean membranes were 65, 110, 470, and 3120 L/m^2/h/MPa for RC3, RC5, RC10, and RC30, respectively.

Dead-end filtration runs were performed using an Amicon 8400 UF unit (Millipore Corp., USA) under N_2 gas, adopting the method of Jermann et al. (2007). A series of filtration runs was carried out using the UF unit pressurized to 0.2, 0.2, 0.1, and 0.05 MPa for RC3, RC5, RC10, and RC30, respectively. Permeate mass was continuously