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Fluorescent natural organic matter fractions responsible for ultrafiltration membrane fouling: Identification by adsorption pretreatment coupled with parallel factor analysis of excitation–emission matrices

Senlin Shao, Heng Liang*, Fangshu Qu, Huarong Yu, Kai Li, Guibai Li

State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology, 73 Huanghe Road, Nangang District, Harbin 150090, PR China

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ABSTRACT

A novel approach using adsorption pretreatment coupled with parallel factor analysis of excitation–emission matrices (PARAFAC-EEMs) was proposed to rapidly identify the role of fluorescent natural organic matter (NOM) fractions in ultrafiltration (UF) membrane fouling for given feed water and membrane. Two anion exchange resins, three polymeric resins and a powdered activated carbon (PAC) with diverse adsorption characteristics were adopted in the adsorption of raw water. The matrix of fluorescent NOM was substantially changed by the adsorption pretreatment, which rapidly enabled a diversity of fluorescent NOM with the components of an identical origin. PARAFAC-EEMs were employed to characterize the variation of fluorescent NOM during the adsorption, which in turn allowed to correlate the fluorescent NOM components with the membrane fouling in the following UF test. The results showed that, for the Songhua River water and PVDF UF membrane (Litree, China), three statistically significant fluorescent components (arbitrarily labeled C1, C2, and C3) were obtained through PARAFAC analysis, in which two humic-like (C1 and C2) and one protein-like (C3) components were identified. Total and irreversible fouling were highly correlated with the maximum fluorescence intensity (F_{max}) of C3, while poorly correlated with the F_{max} of C1 and C2, suggesting that C3 can act as an indicator for the UF membrane fouling. Moreover, C1, C2 and C3 have a considerable synergistic contribution to the irreversible fouling of the UF membrane with the analysis of multiple linear regression. These results are expected to provide important implications for monitoring and controlling UF membrane fouling.

1. Introduction

Fluorescent natural organic matter (NOM) refers to the fraction of NOM that exhibits fluorescence in both ultraviolet and visible range. Not all the NOM in water show fluorescence, but fluorescent NOM is a crucial issue in ultrafiltration (UF) membrane fouling. Some of the fluorescent NOM, e.g. proteins and humic substances, have been regarded as culprits of UF membrane fouling [1–3]. And the fluorescent NOM can be rapidly, sensitively and online detected by fluorescence spectroscopy technique [3,4]. Therefore, understanding the role of fluorescent NOM fractions in membrane fouling is essential for monitoring and controlling the membrane fouling of UF.

However, adequate understanding of the impact of fluorescent NOM on the UF membrane fouling is still lacking. Even among the published studies, discrepancies remain in terms of the contributions of fluorescent NOM fractions to the membrane fouling. Sutzkover-Gutman et al. [1] suggested that the accumulation of humic substances on the surface and/or in the pores of the UF membranes caused severe membrane fouling. In sharp contrast to these results, Peldszus et al. [2] found that it was proteins rather than humic substances that contributed to the reversible and irreversible fouling of UF membrane. Meanwhile, Peiris et al. [3] reported that both humic- and protein-like substances contributed to the hydraulically irreversible fouling. These inconsistencies can be associated with the complexity of fouling phenomenon, the heterogeneity of NOM, and the diversity of UF membrane used in the studies. Consequently, for specific membrane and given feed water, an approach which could rapidly identify the role of

* Corresponding author. Tel./fax: +86 451 86283001.
E-mail addresses: shaosenlin@gmail.com (S. Shao), hitliangheng@163.com (H. Liang), qufangshu@163.com (F. Qu), huarongyu@gmail.com (H. Yu), likai02007@126.com (K. Li), hitsteven@gmail.com (G. Li).

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fluorescent NOM fractions in the UF membrane fouling is necessary.

The fluorescent NOM can be sensitively and rapidly detected by fluorescence excitation–emission matrix (EEM) [5]. Parallel factor analysis (PARAFAC) can decompose complex EEMs into independent fluorescent components which represent groups of similar fluorophores [6–8]. Previous researchers have utilized parallel factor analysis of excitation–emission matrices (PARAFAC-EEMs) to characterize the fluorescent NOM [6,7,9], assess disinfection byproduct formation [10], and evaluate process performance [11,12]. It has been shown that PARAFAC-EEMs have direct implications for online fluorescence monitoring of water treatment plants [8]. Consequently, this practice is supposed to be able to track the problematic fluorescent NOM constituents in the UF process and provide additional information for monitoring and controlling the UF membrane fouling.

Adsorption process is an approved way to lower the amount of organic matter in water treatment. Different adsorbents preferentially adsorb different organic matter. Anion exchange resins, powdered activated carbon (PAC) and polymeric resins are three common types of commercially available adsorbents. Anion exchange resins have a strong affinity for high charge density and aromatic NOM [13–15], and preferentially remove intermediate molecular weight NOM [16–18]. PAC preferentially adsorbs hydrophobic, intermediate and low molecular weight organic compounds in water [19,20]. Polymeric resins differ from the ionic exchange resins in their lack of ionic functional groups and are widely used for separation and purification [21,22]. It can be tailor-made by controlling the polymerization conditions, thereby, certain groups of organic chemicals are selectively absorbed [21]. Similarly, the tailor-made polymeric resins may potentially adsorb certain groups of NOM. Notably, adsorption pretreatment can change the concentration of NOM constituents without introducing new organic components. Accordingly, adsorption with alternative adsorbents may have the potential to modify the fluorescent NOM matrix in feed water, and further, lend insight into the fouling potential of fluorescent NOM components.

Bench-scale studies are generally utilized for membrane fouling evaluation. Flat-sheet membrane in a constant-pressure operating mode over a single filter run was typically adopted by researchers [23–25]. But this system may not effectively simulate full-scale commercial membrane filtration systems, which often used hollow-fiber membrane. Moreover, the initial adsorption fouling of new membrane would not reveal longer-term fouling trends. Howe et al. [26] demonstrated that there were big differences between hollow-fiber and flat-sheet membrane performance, and the multi-cycle fouling test with hollow-fiber membranes was a robust system for membrane fouling assessment. Fouling index is increasingly used to quantify the membrane fouling [16,18,19,27–29]. It can bridge different experimental scales' fouling results, and can be potentially used for fouling prediction [27,28,30]. Therefore, the fouling index of the multi-cycle fouling test with hollow-fiber membranes is an effective tool for the long-term membrane fouling assessment.

The objective of this study was to investigate a new approach to rapidly investigate the role of different fluorescent NOM fractions in the UF membrane fouling for a given membrane and raw water. The fluorescent NOM matrix of water collected from the Songhua River (Northeast China) was modified with six types of adsorbents. The PARAFAC-EEMs method was used to characterize the fluorescent NOM of raw and adsorbents treated water. The multi-cycle fouling test on a bench-scale, hollow-fiber UF system was adopted for membrane fouling assessment. Total fouling index (TFI) and hydraulically irreversible fouling index (HIFI) were used to quantify total and irreversible fouling potentials. Then, the relationships between the fluorescent components and the membrane fouling described by TFI and HIFI were examined by statistical analysis. The results were expected to give practical suggestions for selecting fouling control strategy and monitoring membrane fouling with fluorescence spectroscopy in the UF treatment process.

2. Materials and methods

2.1. Materials

Five samples of raw water were collected during March, 2013 from a same sampling site of the Songhua River. They were all filtered through 0.45 μm cellulose ester membrane (Taoyuan, China) prior to the experiment and analysis. The water qualities of the five samples collected are as follows: dissolved organic carbon (DOC) concentration: 4.42–5.72 mg/L, ultraviolet absorbance (UV_{254}): 0.095–0.129 cm^{-1}, Ca^{2+}: 24.5–24.8 mg/L, Mg^{2+}: 6.5–6.7 mg/L, and pH: 6.9–7.2. A typical EEM of the raw water was

Table 1
Properties of the adsorbents (manufactures' data).

Polymeric resins					
Resin	Matrix	Polarity	Surface area (m^2/g)	Average pore diameter (nm)	Particle diameter (mm)
ADS5	Polystyrene DVB	Non	520–600	25.0–30.0	0.3–1.25
AB8	Polystyrene DVB	Weak	450–500	12.0–16.0	0.3–1.20
ADS17	Acrylic acid DVB	Middle	90–120	25.0–30.0	0.3–1.25
Anion exchange resins (chloride form)					
Resin	Matrix	Functional group	Total volume capacity (eq/L)		Moisture retention (%)
D301R	Polystyrene DVB	$-N(CH_3)_2$	≥ 1.4		50–60
D201	Polystyrene DVB	$-N^+(CH_3)_3$	≥ 1.1		50–65
Powered activated carbon (PAC)					
Average particle size (μm)	BET surface area (m^2/g)		Average pore size (nm)	Pore volume (cm^3/g)	
32.1 ± 0.7	1219 ± 13		2.2 ± 0.1	0.372 ± 0.021	