CrossMark

Ultrafiltration performance of EfOM and NOM under different MWCO membranes: Comparison with fluorescence spectroscopy and gel filtration chromatography

GuoJin *, LiuHong, LiuJianhong, WangLiying

School of Environment and Energy Engineering, Beijing University of Technology, 100124, Beijing, China

HIGHLIGHTS

• Polysaccharides, proteins and colloids in EfOM could be easily removed by UF.
• HS in NOM were more easily removed with the decreasing of membrane's MWCO.
• HS were the main potential foulants during UF membrane processing of surface water.
• Polysaccharides, proteins, colloids and HS in EfOM were the potential foulants.

ABSTRACT

Ultrafiltration performance of wastewater effluent organic matter (EfOM) and background natural organic matter (NOM) under different molecular weight cutoff (MWCO) membranes was investigated. Permeates of EfOM and NOM from ultrafiltration were systematically compared by using fluorescence spectroscopy and gel filtration chromatography. The results revealed that anthropogenic polysaccharide- and protein-like substances including polysaccharides, proteins, and colloids in EfOM were mainly removed by ultrafiltration with the 100 kDa membrane, which accounts for a large proportion of the total DOC in EfOM. With the decreasing of the membrane's MWCO, the humic substances in NOM were more easily removed compared with that in EfOM. The polysaccharides associated with the colloidal fraction, as well as the humic substances were speculated as the main potential foulants for UF membranes processing wastewater EfOM. As for NOM, humic substances were regarded as the main potential foulants. The fouling mechanism (cake filtrations or pore blocking) of EfOM or NOM in the ultrafiltration process was related with the MWCO of the membrane and the molecular size of the main foulants.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Wastewater effluent organic matter (EfOM) is composed of soluble microbial products (SMP), background natural organic matter (NOM) originating from drinking water, and disinfection by-products (DBPs) generated during the disinfection processes of water and wastewater treatment, along with natural and synthetic trace chemicals (SOC) [1]. SMP are generated during biological treatment by bacteria as a result of substrate metabolism and biomass decay [2], which are a factor that causes membrane fouling [3] as well as a precursor to produce nitrogenous DBPs [4]. NOM is a complex mixture of organic compounds present in all fresh water, particularly surface waters, which consists of a range of different compounds, from largely aliphatic to highly colored aromatics [5]. The amount and characteristics of NOM depend on

climate, geology and topography [6,7]. Traditional drinking water treatment plants remove some NOM from the source water and the remaining recalcitrant material is conveyed into wastewater. As a result, bulk organic matter in wastewater effluent-derived surface water consists of both allochthonous NOM and anthropogenic EfOM characteristics [8].

Several investigations differentiated the EfOM from NOM with various characterization methods [8–10]. These characterization methods included total or dissolved organic carbon analyzing (TOC or DOC), ultraviolet spectrum (UV_{254}, SUVA), fluorescence spectroscopy and gel permeation chromatography, as well as fractionating bulk organic matter to dissolved organic subcomponents with varying compositions and functional properties. Fluorescence spectroscopy is a simple and sensitive technique to obtain the structural information of aqueous dissolved organic materials (DOM) at relatively low concentrations (<20 mg/L TOC) [11–13]. 3D fluorescence excitation–emission matrix (EEM) was widely used in the study of structural information of multi-component

* Corresponding author.
  E-mail address: guojin1979@gmail.com (J. Guo).

humic solutes, which related to the position, shift, and intensity of fluorescence peaks [11,12,14–17]. High performance gel permeation chromatography (HPGPC) was also used to characterize DOM based on differential permeation of molecules. HPGPC-UVA [18], HPGPC-on-line specific Ex/Em fluorescence [19], HPGPC-on-line 3D EEM fluorescence [20] as well as HPGPC-online TOC detection systems [21] had been developed to analyze the chemical qualitative and structural features in addition to molecular size. Besides that, based on the XAD resin fractionation methods put forward in 1981 [22,23], XAD fractionation methods were adopted by many researchers to characterize the subcomponents of DOM [24–28].

Recently, with the wide application of ultrafiltration technology in water and wastewater field, operational problems that are related with NOM or EfOM during ultrafiltration treatment are attracting more and more attention. NOM or EfOM was considered as the major foulants that will cause organic fouling during surface water purification and wastewater reclamation [29–32]. Compared with NOM, EfOM was relatively slightly studied. Although the characteristics of EfOM and NOM overlap extensively, diverse ultrafiltration performance was expected owing to their dissimilar origin and characteristics. Especially, there might exist different fouling potentials relating with surface water purification or wastewater reclamation, as the major foulants in EfOM and NOM were quite different. However, the difference between NOM and EfOM during ultrafiltration progress was rarely paid attention. In this study, the ultrafiltration performance of EfOM and NOM under different molecular weight cutoff (MWCO) membranes is investigated. To characterize and compare the major foulants, permeates of EfOM and NOM from ultrafiltration are systematically compared by using fluorescence spectroscopy and GPC. Then, the difference with respect to removal efficiency and fouling potential in UF process between NOM and EfOM is further analyzed.

2. Materials and methods

2.1. Isolation of NOM and EfOM

Raw water collected from River Songhua (located in the north-east part of China) was passed through a 0.45 micron filter and a cation exchange resin sequentially to remove the suspended particles, and divalent and trivalent cations in water. Then the filtered, cation-exchanged sample was flowed into the RO system. The concentrated NOM was stored in the dark at 4 °C before use. Effluent sample was collected from XiaoHongMen WWTPs that incorporated the activated sludge treatment process. Water samples for this study were collected at a secondary settling tank and filtered immediately through a 0.45 micron cellulose filter. Then the collected EfOM was stored in the dark at 4 °C. DOC concentration of EfOM was around 12 mg/L. Before the ultrafiltration experiment, the concentrated NOM was diluted to around 8 mg/L (the typical DOC of its source water).

2.2. Ultrafiltration experiment

All ultrafiltration experiments were performed under room temperature (22 ± 1 °C). A 50 mL ultrafiltration stirred cell (8050 stirred cell, Millipore, USA) with a series of membranes (Ultracel PL 1 kDa, 3 kDa, 5 kDa, 10 kDa, 30 kDa, 100 kDa, Millipore, USA) was used. Before ultrafiltration, the membranes were floated with skin side down in a beaker of Milli-Q water (with resistance of 18.2 MΩ·cm) for at least 1 h with three water changes before use. The operating pressure of the stirred cell was controlled at 0.1 MPa with N_2. Preparatory experiment proved that the remaining residues on the membrane could be removed by passing 50 mL of Milli-Q water through the membrane. During the ultrafiltration experiment, the first 10 mL and the last 10 mL of each filtrate of NOM or EfOM were discarded, then the residual 30 mL permeates were analyzed with a DOC analyzer, GPC and EEM.

2.3. DOC

A total organic carbon analyzer (Multi N/C 3000, analytik-jena, Germany) was used to determine the DOC. The non-purgeable organic carbon (NPOC) testing method was selected, which involved purging an acidified sample with carbon-free air prior to measurement. Then the total carbon in the sample was combusted into carbon dioxide and monitored by an NDIR detector. The total carbon standard substance, using the potassium hydrogen phthalate, was stored at 4 °C for no longer than 1 month.

2.4. Gel filtration chromatography

The permeate samples of EfOM and NOM from a series of ultrafiltration membranes were analyzed with high performance liquid chromatography–gel filtration chromatography (HPGFC) with an ultraviolet (UV) detector. HPGFC comprised a high pressure liquid chromatography pump (Waters 1525), a dual λ absorbance detector (Waters 2487), a manual sampler equipped with a 20 μL sample loop, and a Waters Protein-pak 125 column. Sodium polystyrene sulfonates (PSS, Fluka) with molecular weights of 210, 1400, 3400, 13,000, and 32,000 Da were used as the standards. The mobile phase was Milli-Q water buffered with phosphate (0.0024 M NaH_2PO_4 + 0.0016 M Na_2HPO_4) to pH 6.8 and 0.025 M Na_2SO_4 was added to reach a total ionic strength of 0.1 M. The sample volume was 20 μL and the flow rate was controlled at 0.7 mL min^{-1}. The sample that flowed out of the protein-pak column was detected by UV absorption at 254 nm and 280 nm (indicative of the aromaticity of compounds).

2.5. EEM

All EEM spectra were measured by a 1-cm cuvette using luminescence spectrometry (F-7000, Hitachi). EEM spectra were collected with subsequent scanning emission spectra from 300 to 550 nm at 1.0 nm increments by varying the excitation wavelength from 200 to 400 nm at 5 nm increments. Excitation and emission slits were maintained at 5 nm and the scanning speed was set at 1200 nm/min for all the measurements. The X-axis represents the emission spectra from 300 to 550 nm, whereas the Y-axis is the excitation wavelength from 200 to 400 nm. The spectrum of Milli-Q water was recorded as the blank. The result is a three-dimension spectrum in which fluorescence intensity is represented as a function of excitation and emission wavelengths.
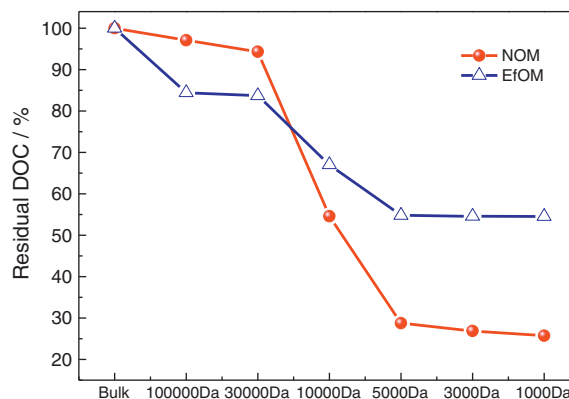

Fig. 1. Residual DOC of NOM and EfOM after ultrafiltration with series of the MWCO membrane.