Thai Environmental Engineering Journal Vol. 31 No. 1 (2017) : 1-9
www.eeat.or.th

Characterization of Ultrafiltration Membrane Foulant Using Fluorescence Signature of Natural Organic Matter in Surface Water

การตรวจสอบคุณลักษณะของสารที่ก่อให้เกิดการอุดตันในการกรองอัลตราฟิลเตรชันเมมเบรน โดยใช้ค่าสัญญาณฟลูออเรสเซนส์ของสารอินทรีย์ในน้ำผิวดิน

ปณิธาน จูฑาพร[*] **และ ออแลนโด โคโรเนล****
Panitan Jutaporn[*] **and Orlando Coronell****
*Department of Environmental Engineering, Faculty of Engineering,
Khon Kaen University, Khon Kaen 40002
**Department of Environmental Sciences and Engineering, Gillings School of Global Public Health,
The University of North Carolina at Chapel Hill
[*]E-mail : panitju@kku.ac.th

Abstract

This study evaluates the role of natural organic matter (NOM) fractions from surface water in Polyvinylidene fluoride (PVDF) ultrafiltration (UF) membrane fouling using fluorescence excitation-emission matrices (EEMs). The hollow fiber filtration experiments were performed using four surface water sources as raw and pretreated with magnetic ion exchange (MIEX) resin. Fouling potentials were quantified and the NOM in raw, and treated feed water, permeate, and backwash waters were characterized in terms of NOM concentration and composition. Results showed that: (i) microbial protein-like NOM is a more important contributor to fouling than terrestrial humic-like NOM; (ii) UF membrane fouling potentials of surface water sources before and after MIEX pretreatment were strongly correlated to the fluorescence of microbial NOM at excitation-emission coordinates of 275 nm/340 nm. Overall, the high predictive power of fluorescence EEM to fouling potential suggests its potential use as a tool for the evaluation of fouling potential of surface water.

Keywords : membrane; ultrafiltration; fouling; natural organic matter; fluorescence

บทคัดย่อ

งานวิจัยฉบับนี้ศึกษาการประเมินบทบาทของสารอินทรีย์ชนิดต่างๆ ในน้ำที่ส่งผลกับการอุดตันของโพลีไวนิลลิดีนฟลูออไรด์ (PVDF) อัลตราฟิลเตรชัน (UF) เมมเบรนโดยใช้ค่าสัญญาณฟลูออเรสเซนส์แบบ Excitation-Emission Matrix (EEM) การทดลองนั้นประกอบไปด้วยการกรองน้ำโดยใช้เมมเบรนแบบท่อกลวง (hollow fiber) ซึ่งใช้น้ำผิวดินจากสี่แหล่งทั้งในแบบน้ำดิบและผ่านการบำบัดด้วยเรซินแลกเปลี่ยนประจุที่มีคุณสมบัติแม่เหล็ก (MIEX resin) ค่าความอุดตันที่เกิดขึ้นในการกรองนั้นได้ถูกประเมินเป็นตัวเลข และสารอินทรีย์ในน้ำก่อนและหลังการกรอง และในน้ำล้างย้อนเมมเบรน ได้ถูกนำมาวิเคราะห์ในเชิงปริมาณและลักษณะองค์ประกอบของสารอินทรีย์ ผลการทดลองนั้นแสดงให้เห็นว่า (i) สารอินทรีย์กลุ่มที่มีแหล่งกำเนิดมาจากจุลินทรีย์ ซึ่งมีคุณสมบัติเหมือนโปรตีน มีบทบาททำให้เกิดการอุดตันของเมมเบรนมากกว่าสารอินทรีย์กลุ่มที่มีแหล่งกำเนิดมาจากพืช และมีคุณสมบัติเหมือนกรดฮิวมิก; (ii) ค่าความอุดตันที่เกิดขึ้นในการกรองน้ำผิวดินทั้งก่อนและหลังการบำบัดด้วย MIEX resin แปรผันอย่างมีนัยสำคัญตามค่าสัญญาณฟลูออเรสเซนส์ของสารอินทรีย์กลุ่มที่มีแหล่งกำเนิดมาจากจุลินทรีย์ ที่ตำแหน่งพิกัด 275 nm/340 nm โดยรวมแล้วค่าสัญญาณฟลูออเรสเซนส์สามารถนำมาประยุกต์ใช้เพื่อจำแนกชนิดของสารอินทรีย์ที่ก่อให้เกิดการอุดตันของเมมเบรนที่เกิดจากการกรองน้ำผิวดินในเบื้องต้นได้

คำสำคัญ : เมมเบรน; อัลตราฟิลเตรชัน; การอุดตัน; สารอินทรีย์; ฟลูออเรสเซนส์

Introduction

The application of ultrafiltration (UF) membranes in drinking water treatment has accelerated over the past decade. UF membranes can effectively remove microbial and particulate contaminants with relatively low energy consumption [1]. Compared to conventional media filtration, membrane filtration has the advantages of having a smaller foot-print, being a physical barrier with a specific pore size or molecular weight cut-off, and providing constant permeate water quality. However, a major limiting factor that constrains the implementation of UF membranes in water treatment systems is membrane fouling [1]. Fouling occurs when organic or inorganic particles and/or microorganisms deposit on the membrane surface or into the membrane pores which leads to flux decline over time. One of the most important foulants on UF membranes, when used to treat surface water is natural organic matter (NOM) [2].

Magnetic ion exchange (MIEX) resin is a strong base anion-exchange resin with magnetic properties that is developed specifically to remove NOM from water.In recent years, MIEX has been proven effective in removing DOC from a broad range of source waters [3], thus it is reasonable to expect that MIEX can potentially minimize NOM fouling in membrane filtration. NOM in water comprises a wide range of organic compounds, including aromatic and aliphatic molecules with a variety of functional groups. Despite NOM being identified as major foulants of UF membranes, it is not possible to estimate the fouling potential of a specific water based on commonly measured water quality parameters, such as dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA_{254}). Thus, a more advance technique is needed to characterize NOM fractions that significantly contribute to fouling.

A technique that has proven successful in organic matter characterization is fluorescence excitation-emission matrix (EEM) spectroscopy [4]. EEM provides information regarding the type, structure, and abundance of functional groups of NOM [5]. Fluorescence NOM are generally classified into two distinct groups: terrestrially derived (humic-like material) and microbially derived (protein-like material) [6]. EEM spectroscopy has been used to track DOM in both drinking water and wastewater treatment plants [7, 8]. EEM analysis also revealed that microbial DOM is more important to UF fouling than terrestrial DOM [9], and that protein-like substances were the major cause of low pressure membrane fouling in secondary effluent [10]. Therefore, the ability of EEM to monitor microbial protein-like DOM suggests that EEM analysis can potentially be used to identify the relative abundance of foulants in UF membrane systems.

The objective of this study is to investigate the relationship between the fluorescence signature of different NOM fractions and the associated UF fouling potential in surface water with and without MIEX pretreatment, which suggests whether EEM spectroscopy can be used as a qualitative or (semi)quantitative predictor of fouling potential of surface water.

Materials and Methods

Surface water samples were either collected directly from nearby water treatment plants or transported to the laboratories via overnight shipping refrigerated with cold-packs. Immediately upon receipt, all water samples were filtered with Whatman (Piscataway, NJ) GF/C 1.2-μm glass fiber filters to remove suspended solids, stored at 4°C in the dark, and allowed to reach room temperature (20±2 °C) prior to each experiment. The water quality parameters of interest for the four "Raw" waters are presented in Table 1. "Raw" refers to the state of the waters after 1.2-μm filtration as described above.

For membrane fouling tests, source waters were used either in their raw state or pretreated using magnetic ion exchange (MIEX resin, Ixom Watercare Inc.). MIEX was stored in 5% NaCl solution then was rinsed three times with lab grade water before use. To measure resin volume, MIEX was allowed to settle in a glass graduated cylinder for 30 min then its concentration was reported as milliliter of resin per liter of water. The optimum dose of MIEX was determined using a six-paddle stirrer (Phipps and Bird Inc., Richmond, VA, USA) as and the mixing protocol was conducted as described previously [3]. MIEX dose of 2 mL/L was used for all water samples as increasing MIEX concentration beyond this point did not result in appreciably DOC removal. This concentration agrees well with an optimum dose reported in a previous study [9]. MIEX-treated water was then decanted after settling and filtered through a 1.2-μm glass fiber filter prior to membrane fouling tests to remove any remaining MIEX beads. Thus, in this study, fouling occurred only from dissolved (<1.2 μm in size) fractions of organic matter.

Table 1 Raw water quality

Sample Name	Source	pH	UVA_{254} (cm^{-1})	DOC (mg/L)	SUVA (L/mg.m)
University Lake (UL), Carrboro, NC	Lake	6.9	0.146	5.6	2.7
Palm Beach (PB), West Palm Beach, FL	Lake	7.0	0.239	14	1.7
Muscle Shoals (MS), Muscle Shoals, AL	River	7.5	0.042	2.3	1.9
White River (WR), Indianapolis, IN	River	7.6	0.077	3.8	2.0

Polyvinylidene fluoride (PVDF) hollow fiber membrane filtration experiment was performed under a constant vacuum pressure of 40 kPa as depicted in Figure 1. The membrane was obtained from GE Water & Process Technologies (Oakville, Ontario, Canada) and has a nominal pore size of 0.04 μm with an outside diameter of 1.95 mm. The module consisted of four fibers with the length of 16 cm providing 39.2 cm^2 total surface area. For each filtration experiment performed, the fouling potential of the water sample was quantified using the unified membrane fouling index (UMFI, m^2/m^3) [11] as defined by

$$\frac{J_0}{J_t} = 1 + UMFI \cdot V_S , \qquad (1)$$

where J_0 (m/s) and J_t (m/s) correspond to the water fluxes at time zero and time *t*, respectively, and V_S (L/m^2) corresponds to the cumulative volume of water filtered at time *t* per unit area of membrane.

At the end of the 5-hour filtration cycle, membrane was backwashed at 100 kPa using lab grade water. Membrane feed, permeate, and backwashed waters were characterized for their NOM concentration and composition. DOC was determined using a TOC-V organic carbon analyzer (Shimadzu, Atlanta, GA). UVA_{254} was measured using a U-2000 spectrophotometer (Hitachi Instruments Inc., Danbury, CT). SUVA values were calculated as SUVA = 100 (UVA_{254}/DOC). Fluorescence EEMs were measured using a Fluorolog-321 spectrofluorometer (Horiba JobinYvon, Edison, NJ, USA) over the range of excitation wavelengths of 240-450 nm, and emission wavelengths of 320-550 nm. EEMs were corrected for instrument-specific excitation and emission effects using manufacturer-generated emission correction factors and user-generated excitation correction factors. To account for the inner filter effects, a matrix of correction factors was created from absorbance spectra of samples [12] measured with a diode array UV-Vis spectrophotometer (Hewlett Packard, Palo Alto, CA, USA). The relative abundance of different types of NOM in solution was characterized via the emission intensities of the common reoccurring fluorophores in the three peak regions A, C, and T. Peak A (terrestrial fulvic-like), peak C (terrestrial humic-like), and peak T (microbial protein-like) are identified by their emission intensities at excitation/emission pairs of 250/450, 350/450, and 275/340 (nm/nm), respectively [4] (Figure 3a). NOM in each type of water and pretreatment tested analyzed at least in duplicate. Fluorescence intensities are reported in Raman units (RU) by normalization of the intensities to the area under the water-Raman peak at an excitation of 350 nm [13].

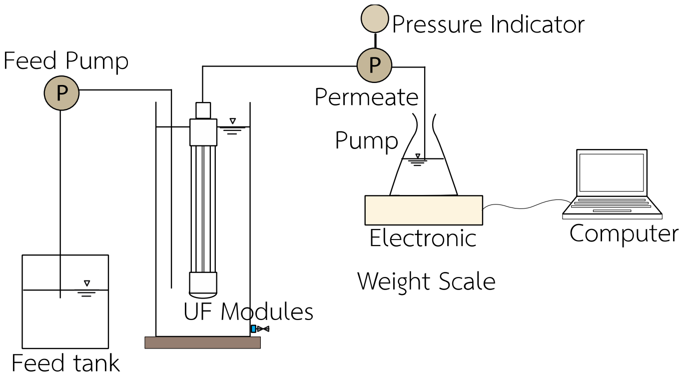

Figure 1 UF membrane filtration system used for filtration experiments [9]

Results and Discussion

Increasing MIEX dose from 1 to 2 mL/L resulted in 12-17% increase in DOC removal, while increasing MIEX dose further from 2 to 3 mL/L only resulted in 0.2-11% increase in DOC removal in these four surface water sources. This result suggests that 2 mL/L was an optimum dose of MIEX for these waters, thus this concentration was applied as pretreatment to all membrane filtration experiments.

Pretreated water with 2 mL/L MIEX resin resulted in fouling reduction as indicated by a lower flux decline over time (Figure 2a, using MS water). The experimental results for J_0 / J_t and V_S were fitted to Equation 1 to obtain UMFI values as a slope (Figure 2b for illustrative example using MS water). Similar results (not shown) were obtained for all water and the fouling potentials as quantified by UMFI are presented in Figure 2c. The results show that UMFI reduction by MIEX varied with water sources. Specifically, the percentage UMFI reduction was 11% for PB, 16% for UL, 26% for WR, and 58% for MS water, showing a promising potential of MIEX as a pretreatment to reduce membrane fouling. Consistent with observations in previous study [14], fouling potential was only weakly correlated to DOC content (p=0.003, R^2 = 0.27) and UVA$_{254}$ (p<0.001, R^2 = 0.40) in membrane raw and MIEX-pretreated feed waters (figure not shown). Thus, DOC and UVA$_{254}$ measurements are not a good indication of membrane fouling potential.

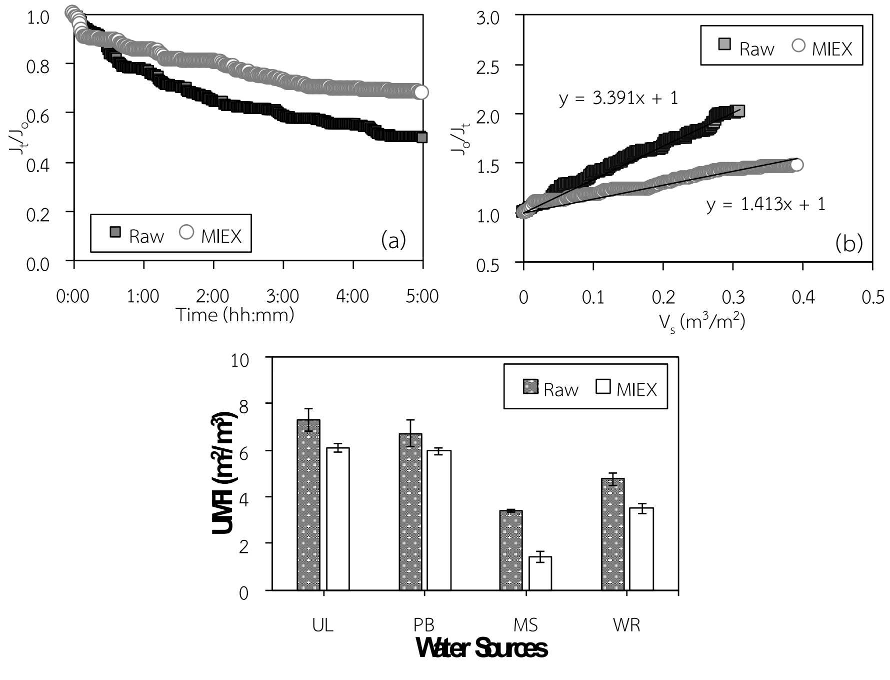

Figure 2 (a) flux decline in MS water; (b) regression of UMFI using MS water; and (c) fouling potential as quantified by UMFI in raw and pretreated UL, PB, MS, and WR waters

Given that fouling potential did not correlate well with DOC or UVA_{254} in the feed water. Towards this end, EEM spectroscopy was used to characterize more detail of the relative abundance of terrestrial and microbial DOM in membrane feed (raw and pretreated) and backwashed waters. Figure 3 presents representative contour plots of EEMs generated from the analyses of MS water. For MS raw water, the terrestrial fractions of NOM (peaks A and C) had higher fluorescence intensity than the microbial fractions (peak T), indicating greater abundance of terrestrial NOM over microbial NOM in surface water. MS water pretreated with MIEX 2 mL/L (Figure 3b), when compared to Figure 3a, has remarkably less intensity of fluorescence at peaks A and C, but peak T appeared to be have greater intensity compare to peaks A and C. This result qualitatively suggests that MIEX had preferential removal of peaks A and C over peak T, thus MIEX changes NOM composition of its treated water toward greater abundance of microbial NOM relative to terrestrial NOM.

Backwash water containing DOM from the foulant layer of membranes fouled by MS raw (Figure 3c) showed relatively greater fluorescence intensity at peak T and compared to peaks A and C, suggesting that peak T is a more important foulant. Foulant layer of membranes fouled by MIEX-treated MS water (Figure 3d) showed dominantly abundance of peak T together with the absence of peak A and C. This finding confirms the previous observation that MIEX prefer to remove peaks A and C over peak T in the feed water, thus successfully reduce the abundance of peaks A and C in the foulant layer. The preferential removal of terrestrial humic-like NOM by MIEX is consistence with the previous finding [15] reporting that MIEX had a greater preference for NOM present in high SUVA waters, i.e., hydrophobic NOM.

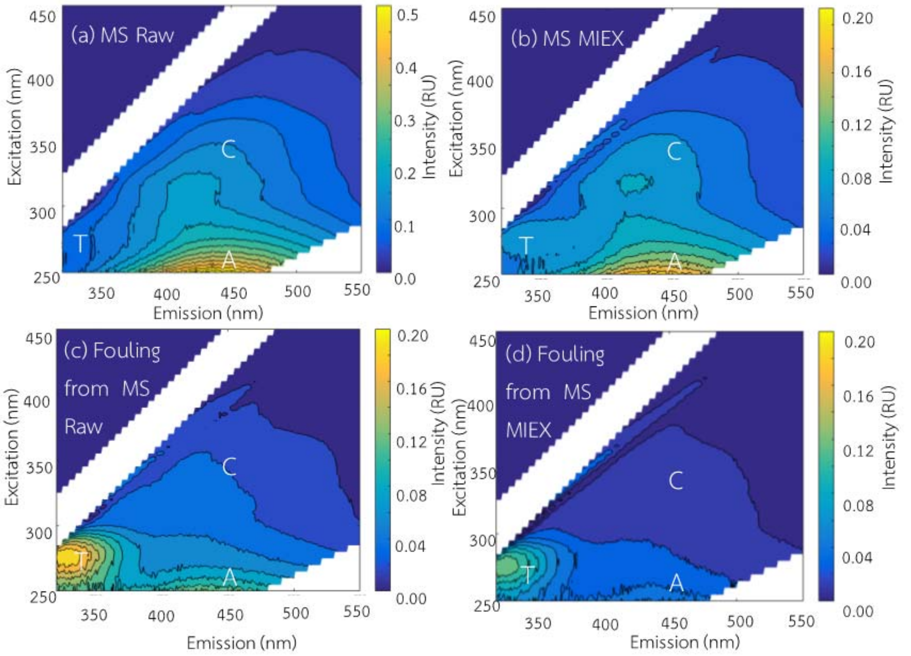

Figure 3 Representative contour plots of EEMs generated from (a) MS raw water; (b) 2 mL/L MIEX-treated MS water; (c) backwashed water of membrane fouled with MS raw water; and (d) backwashed water of membrane fouled with 2 mL/L MIEX-treated MS water

For a more quantitative analysis, fluorescence intensity at peak A, C, and T of the four water sources in feed water and foulant layer were presented in Figure 4a and 4b, respectively. Protein content of water sample was calculated as fluorescence intensity at peak T over the total intensity at peaks A, C and T combined. Protein content was in the range of 7.35-29.4% for the raw and MIEX-treated feed waters (Figure 4a) and in the rage of 38.9-72.6% for the foulant layers (Figure 4b). Paired t-test was conducted and the result indicated that protein content of the foulant layers is significantly ($p<0.0001$) greater than that of the feed waters. This result statistically confirms the visual observation form Figure 3 that microbial NOM (peak T) was the main foulant in UF of surface water. This finding is consistent with previous study [10] reporting that low-pressure membrane foulant layer was comprised predominantly of protein-like materials in the filtration of secondary treated effluent.

Moreover, a quantitative correlation between fouling potential and fluorescence intensity of microbial NOM (peak T) in feed waters was evaluated. Results in Figure 5 demonstrate that fouling potentials of raw and MIEX-pretreated UL, PB, MS and WR feed waters were strongly correlated to fluorescence intensity at peak T of feed waters (p=0.002, R^2= 0.75). The correlation between UMFI and peak T is remarkably stronger compared with that between UMFI and DOC or UVA_{254}, which indicates the validity of fluorescence intensity at peak T as a quick indicator for UF membrane fouling potential.

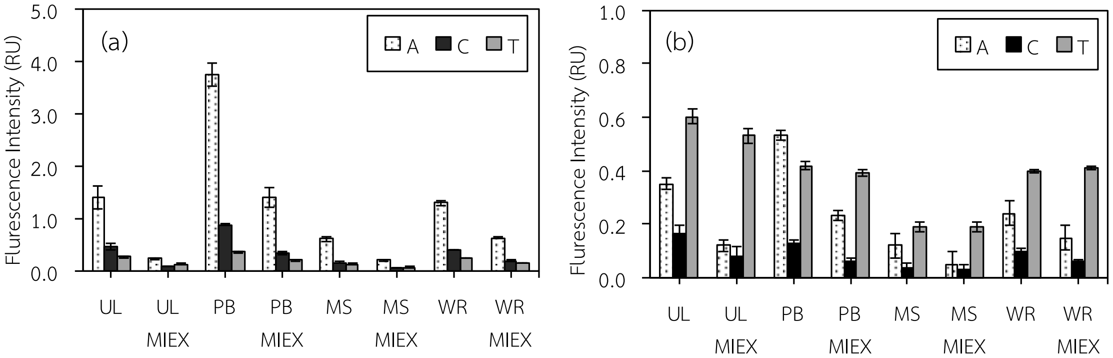

Figure 4 (a) fluorescence intensity at peak A, C, and T of raw and MIEX-treated feed waters; and (b) fluorescence intensity of foulant layers

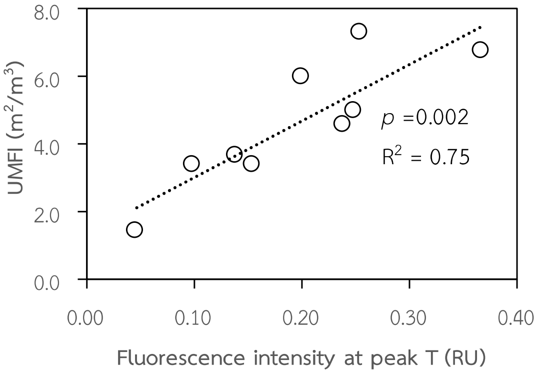

Figure 5 Relationship between fouling potential (UMFI) and fluorescence intensity of microbial DOM (peak T) in raw and MIEX-treated feed waters

Conclusions

MIEX was found to be effective in membrane fouling reduction in surface water as in 11-58% UMFI reduction. Fluorescence EEMs analysis reveals that microbial protein-like NOM is a more important contributor to fouling than terrestrial humic-like NOM. Also, a significant correlation has been established between the UF membrane fouling potential of surface water sources before and after MIEX pretreatment and fluorescence intensity of microbial NOM at excitation-emission coordinates of 275 nm/ 340 nm (peak T). Thus, peak T can be used as a quick indicator for UF membrane fouling potential. Overall, the results demonstrated the potential use of fluorescence EEM as a tool for the evaluation of fouling potential in surface water filtration.

Reference

[1] H. Huang, K. Schwab, and J. G. Jacangelo. 2009. Pretreatment for Low Pressure Membranes in Water Treatment : A Review. Environ. Sci. Technol. 43: 3011-3019.

[2] K. J. Howe and M. M. Clark. 2002. Fouling of microfiltration and ultrafiltration membranes by natural waters. Environ. Sci. Technol. 36(16): 3571-3576.

[3] P. C. Singer and K. Bilyk. 2002. Enhanced coagulation using a magnetic ion exchange resin. Water Res. 36: 4009-22.

[4] P. G. Coble. 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Mar. Chem. 51(4): 325–346.

[5] J. Chen, E. J. LeBoeuf, S. Dai, and B. Gu. 2003. Fluorescence spectroscopic studies of natural organic matter fractions. Chemosphere. 50: 639-647.

[6] D. M. McKnight, E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46(1): 38-48.

[7] S. A. Baghoth, S. K. Sharma, and G. L. Amy. 2011. Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. Water Res. 45(2): 797-809.

[8] K. R. Murphy, A. Hambly, S. Singh, R. K. Henderson, A. Baker, R. Stuetz, and S. J. Khan. 2011. Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model. Environ. Sci. Technol. 45: 2909-2916.

[9] P. Jutaporn, P. C. Singer, R. M. Cory, and O. Coronell. 2016. Minimization of short-term low-pressure membrane fouling using a magnetic ion exchange (MIEX®) resin. Water Res. 98: 225-234.

[10] L. Fan, T. Nguyen, F. A. Roddick, and J. L. Harris. 2008. Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction. J. Membrane Sci. 320: 135-142.

[11] H. Huang, T. A. Young, and J. G. Jacangelo. 2008. Unified Membrane Fouling Index for Low Pressure Membrane Filtration of Natural Waters: Principles and Methodology. Environ. Sci. Technol. 42: 714-720.

[12] T. Ohno. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environ. Sci. Technol. 36(4): 742-746.

[13] D. N. Kothawala, K. R. Murphy, C. A. Stedmon, G. A. Weyhenmeyer, and L. J. Tranvik. 2013. Inner filter correction of dissolved organic matter fluorescence. Limnol. Oceanogr. Methods. 11: 616-630.

[14] J. yu Tian, M. Ernst, F. Cui, and M. Jekel. 2013. Correlations of relevant membrane foulants with UF membrane fouling in different waters, Water Res. 47: 1218-1228.

[15] T. H. Boyer and P. C. Singer. 2006. A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions, Water Res. 40(15): 2865-2876.