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Study on characteristics and removal of NOM by pre-coated filtration

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ABSTRACT

Natural organic compounds are a mixture of various chemical structures with different properties that are responsible for color and taste of water, and contribute to the formation of disinfection by-products. Currently, there is a great focus on the use of membranes in technologies related to water treatment due to their high treatment efficiency but the pretreatment is necessary to prevent fouling. In recent years, a number of studies have been conducted in order to minimize fouling. And since the feed quality can have a significant impact on fouling,in this study we have evaluated the components of NOM by characterizing the feed water and water treated by pre-coated absorbent, using spectrophotometric analysis.

Keywords: HAOPs; Membrane fouling; Natural organic matter; PARAFAC; Pre-coat filtration

1. Introduction

The seasonal variability and the increase of natural organic matter (NOM) concentration impose challenges on the drinking water industry and water treatment facilities in terms of process control. Proper characterization of the NOM in raw water can be an important tool for the selection of water treatment processes, or monitoring of the performance of different treatment steps and assessing the quality of water in the distribution system [1]. NOM contributes to the color and taste of the water and NOM compounds exert both the disinfectant and coagulant demands, and serve as the precursors of chlorinated disinfection by-products (DBPs) [2].

NOM is a heterogeneous mixture of organic compounds that includes humic substances, carbohydrates, amino acids, and numerous other classes of organic compounds. The most common methods of NOM characterization are analytic techniques like ultraviolet absorbance at 254 nm (UVA_{254nm}), specific UVA_{254nm}(SUVA) and DOM (dissolved organic matter), all of which provide the initial information regarding its quantity. Organic matter in water can also be characterized based on its nominal molecular weight usually determined by high performance size exclusion chromatography (HPSEC). Lately, other analytical techniques have also gained attention due to their ability to characterize NOM without fractionation and with minimal sample preparation. For instance, the fluorescence excitation-emission matrix (F-EEM) spectroscopy has been increasingly more used for NOM characterization in drinking water. Even more detailed information about NOM can be obtained by using F-EEM spectra and parallel factor analysis (PARAFAC), a statistical method used to decompose multi-dimensional data [1].

Since the structural characterization of aquatic NOM is still under evaluation, various removal processes such as coagulation, active carbon adsorption, oxidation, ion exchange and pressure-driven membrane separation processes are utilized. Several researchers have been investigating the efficiencies of those processes [3–21].

Microfiltration (MF) and ultrafiltration (UF) are being increasingly more used as the alternatives to the conventional filtration and clarification to remove turbidity, microorganisms and NOM from drinking water [3,22,23]. The major challenge limiting their performance is fouling which causes the decline of flux and affects the permeate quality. However, the mechanism of pores blocking in membranes is difficult to analyze because of NOM's variety [1,21]. Over the past several years, researchers have been involved in

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studies on different techniques for NOM qualitative and quantitative measurement [24–32].

The heated aluminum oxide particles (HAOPs) is an absorbent adopted to pretreat surface waters upstream of low-pressure membranes. Depositing HAOPs on a membrane or porous support structure (woven or stainless steel mesh) forms a thin pre-coated layer. Adsorption on that layer combined with the filtration in granular media was described as a hybrid process [9–10,15–17,22,23,33].

This paper describes further research following the one reported in the prior papers dealing with the benefits of passing the feed through a pre-deposited layer of HAOPs prior to membrane filtration that the research group from University of Washington has published. In this study, we have evaluated the components of NOM by characterizing both the feed water and the HAOPs-treated water using the spectrophotometric analysis (UV, EEM/PARAFAC, FT-IR). The main purpose of this paper is to evaluate the reproducibility of treatment performance and to assess the efficiency of NOM removal. In order to facilitate that, the fluorescence excitation-emission matrices and parallel factor (PARAFAC) analysis have been utilized.

2. Materials and methods

2.1. Raw water

Water was collected near the shoreline of Lake Union (LU, located at Portage Bay in Seattle, WA, sampling point location: latitude 47.648823°, longitude–122.310967°). The lake connects Lake Washington with Puget Sound through the Ship Canal. The saltwater intrusion into the freshwater areas through the canal, especially during warmer summer months, is of environmental concerns since it can create aquatic areas without oxygen. Typical values of water quality reported by King County were: ammonia nitrogen 0.014 mg·dm^{-3}, dissolved oxygen 10.60 mg·dm^{-3}, total nitrogen 0. 372 mg·dm^{-3}, total phosphorus 0.0185 mg·dm^{-3}, chlorophyll–a 2.1 µg·dm^{-3}, and conductivity 120.0 µm hos·cm^{-1}.

During the reported study the following parameters have been recorded: pH 6.7 on average, UV$_{254nm}$ 0.055534 cm^{-1}, DOC 2.0 mg·dm^{-3}, SUVA$_{254}$ 2.8 m^{-1}·(mg·dm^{3})$^{-1}$, and turbidity 0.57 NTU.

2.2. Experimental procedures

HAOPs were prepared by first neutralizing a solution of aluminum sulfate (10 g·dm^{-3} as Al) to pH 7.0 with NaOH to precipitate $Al(OH)_3$. The suspension was heated in a closed container at 110°C for 24 h and then cooled and stored at room temperature until use. Control experiments indicated that a layer of particles up to several hundred µm thick causes negligible fouling when deposited on a porous support [9,15]. This novel contact method of the discussed absorber and natural water has been covered in previous papers [9,15]. Briefly, the method integrates granular media filtration and packed bed adsorption by passing the water through a layer of pre-deposited HAOPs on a filter media (membrane or support structure such as mesh). In a typical filtration experiment with pre-deposition of HAOPs, a stock solution of HAOPs was circulated axially through the mesh tube while maintaining a water flux of 225 LMH across the wall. The flux carried the HAOPs to the wall, where they were captured and deposited in a thin layer [23].

In the presented report HAOPs were pre-deposited at a dose of 7.5 g cm^{-2} as aluminum on the mesh and the duration of the deposition process was less than 3 min. HAOPs were pre-coated on a coarse structures made of stainless steel mesh which was a 200 × 1400 twilled Dutch weave with nominal 10-µm openings (Howard Wire Cloth Co., Hayward, CA).

Before each filtration cycle the HAOPs deposition was conducted and then the LU filtration was performed in dead-end mode at a constant flux of 150 L·m^{-2} h^{-1} (LMH). During the filtration the HAOPs unit became gradually clogged as the particles were adsorbed. When the TMP built up to a point where either the TMP had reached its acceptable limits (e.g., 75–138 kPa), or 24 h of filtration had passed the backwash was initiated (comprising the combination of pulses of pressurized air and water introduced to the system). After that, a new cycle of filtration was started preceded by the deposition of fresh HAOPs. The multi-cycle experiments demonstrated that the increases in the TMP that occurred during each cycle were nearly eliminated by the backwash.

The permeate collected from the upstream unit (HAOPs-treated water) was exposed to the downstream (UF) unit. The UF unit captured and removed contaminants not removed during the preceding treatment processes and it was set to be cleaned once the TMP increased more than ~138 kPa/d. The downstream unit (UF) was working with a constant flux of 150 L·m^{-2} h^{-1} (LMH) and wasn't backwashed at all during the whole experiment. The TMP increase on the UF unit was 1.1 kPa.

3. Analytical methods

3.1. UV_{254nm}, TOC

UV_{254nm} was measured using a dual-beam spectrophotometer (Perkin-Elmer Lambda-18) with a 1-cm quartz cell, which operated between 200 and 400 nm at 1-nm resolution. Dissolved organic carbon (DOC) was measured in filtered samples through a filter with a 0.45 µm pore size by Shimadzu TOC-VCSH analyzer. Specific UV absorbance (SUVA) is often used as a surrogate measurement for DOC aromaticity, since there is a strong correlation between UV_{254nm} and DOC concentration.

3.2. Fluorescence excitation-emission matrix (EEM) spectroscopy

Absorbance spectra and the fluorescence excitation-emission matrix (EEM) was acquired by the fluorescence spectrometer LS-55, Perkin-Elmer Co., USA. The EEM scanning involved the excitation wavelength of 200–450 nm and acquired the emission spectra of 250–800 nm. The EEM data was then processed in order to remove Rayleigh and water-Raman scattering.

Parallel factor analysis (PARAFAC) was used to decompose the EEM spectra into a set of independent components. The decomposition process was performed with MATLAB®

N-way_toolbox following the procedures described by Andersson et al. [34]. The EEM spectra arranged in a three-way arraywere decomposed into a set of independent components. The decomposition process was fitted using PLS Toolbox for MATLAB 7.8.0. Based on the experimental knowledge, the non-negativity and unimodality constraints were applied to the sample and the excitation modes, respectively. The crucial issue in the application of the PARAFAC method is the estimation of the number of components. Several methods can be used to solve this problem (split-half analysis or core-consistency, among others). In the present paper, one of the three components of PARAFAC model was fitted to the analyzed data. Then, the validation of the appropriate number of independent fluorophores had been done by analyzing the residuals and the core consistency value.

3.3. FT-IR (Fourier transform infrared)

FT-IR spectra were recorded on Bruker Biospin Corporation FT-IR spectrometer. The spectra of the analyzed samples were measured in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The KBr pellet technique (1.0 mg of the dry sample was pressed with 200 µg KBr to form a pellet) had been used to determine the composition of sample.

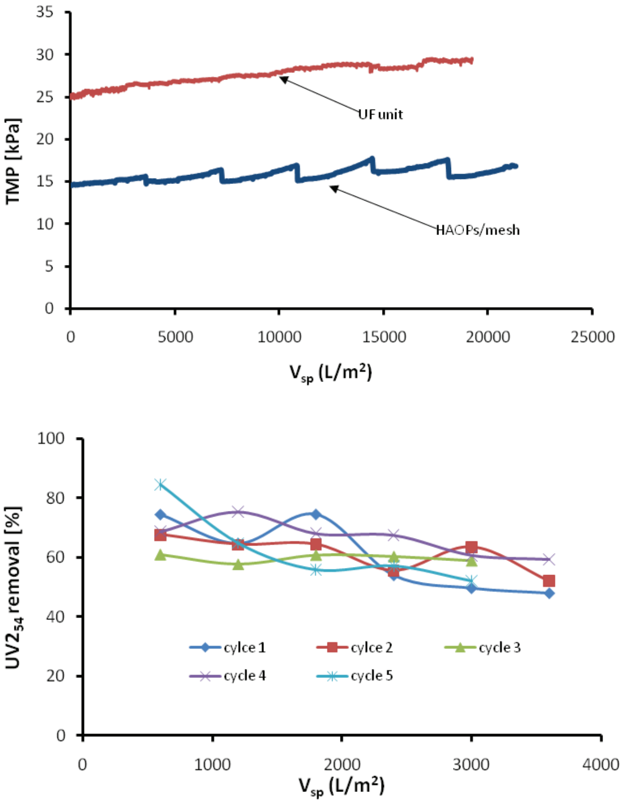

Fig. 1. (a) Pressure loss across the system components (HAOPs/mesh and downstream UF unit) and (b) UV_{254nm} removal during 5 d of sequential, 24-h filtration cycles. Flux was 150 LMH to the units.

4. Results and discussion

Figs. 1a and 1b present the pressure increase profile and the average fractional NOM removal (presented in normalized UV_{254nm}) in each filtration cycle. In both plots, the abscissa indicates the specific volume (Vsp) of permeate produced per unit of membrane area, for the flux of 150 LMH (L m^{-2}·h^{-1})used in these experiments.

During the first five days of the test the HAOPs unit was hydraulically cleaned every day. The TMP across the HAOPs unit was 14.6 kPa initially, and the initial rate of TMP increase was less than 1.6 kPa/d on average. The TMP increase accelerated after five days. Given the slow TMP build up, a slight hydraulically irreversible fouling was evident, and therefore on the sixth day the filtration run lasted only 18 h followed by the chemical cleaning (Fig. 1a).

The adsorption of NOM onto HAOPs has been characterized by UV_{254nm} (usually considered to be a surrogate of organic matter) in order to determine the process efficiency. The reduction in UV_{254nm} between the feed and the permeate (HAOPs-treated water) indicated an improvement corresponding to the reduction in fouling (Fig. 1b). The UV_{254nm} removal at the beginning of the filtration was more than 72% on average and at the end of the filtration cycle it was about 57% (Fig. 1b). The DOC removal efficiency was a bit lower than UV_{254nm}, and the average removal was 47%. The UV_{254nm} and SUVA results both suggest that HAOPs pretreatment removed the majority of the aromatic components. Consistently with the previous research, HAOPs were more efficient at removing UV_{254nm} than DOC [9,10,15–17,22,23,33]. Additionally, Cai’s research showed, that the bare membrane removed only 40% of the UV_{254nm} absorbing compounds and even less DOC [10].

While alum is considered to be one of the best inorganic coagulants, and it can remove high molecular weight UV absorbing compounds, its efficiency in DOC removal depends on a dose of coagulant. At the same time, a pre-deposited HAOPs layer removes more NOM than alum at an equivalent dose [22].

On the other hand, powdered activated carbon (PAC) is the one of the most commonly utilized adsorbent in pretreatment processes (combination of PAC adsorption with UF). Cai’s research [10] showed that PAC and HAOPs remove some foulants while adsorbing different fraction of NOM [10]. However, PAC can have different affinity towards NOM macromolecules depending on the type of applied activated carbon [35].

After passing through the HAOPs and the mesh, water was fed to a commercially available (PES) hollow fiber ultrafiltration (UF) membrane module containing fibers with nominal 8-nm pores. In the presented test the TMP increase on the UF membrane was less than 4.5 kPa during five days of continuous run without any backwashing (Fig. 1a). The efficiency of HAOPs treatment followed by a conventional membrane filtration step was a subject of investigation by researchers from University of Washington [9,10,15–17,22,23,33]. Given the earlier results the precoated HAOPs is able to significantly mitigate fouling due to their high affinity to humic-like substances. The presented results are in good agreement with those reported earlier [23]. The flux on the downstream ultrafiltration unit decreased slowly compared to that of the membrane without any pretreatment. And HAOPs pretreatment prior to ultrafiltration resulted in a significant decrease of fouling.

The complex nature of NOM results in conflicting reports on identification of compound affecting the fouling phenomenon (foulant) and therefore the results presented provide an additional insight into NOM composition. And since the NOM structure and its character changes seasonally, this work explored the interactions of NOM with HAOPs in order to better understand their influence on the filtration process itself.

5. Characterization of NOM

According to previous research the large-(LMW) and intermediate- molecular weight (IMW) fractions in raw water were substantially removed during HAOPs treatment [10]. The LMW substances in NOM are typically attributed to polysaccharides. According to some researchers, a non-humic fraction such as polysaccharides or proteins were major foulants [5,13,14,18,36], while others identified humic-like substances [4,24] to be the crucial fouling factor. Although employing the UV_{254nm} to detect the polysaccharides is difficult due to its relatively low UV absorbance, the excitation-emission matrix (EEM) analysis is known to be capable of capturing spectra that are related to most of NOM foulants [27].

In this work, the EEM approach with PARAFAC analysis combined with FT-IR analysis were pursued to explore the HAOPs pretreatment effectiveness in NOM removal. The results from experiments are presented in Figs. 2 and 3. According to Chen et al. [25], by utilizing a fluorescence spectroscopy to characterize dissolved organic matter (DOM) five principal fluorophore groups can usually be found. Region I associated with protein-like I (ex: 200–250 nm; em: 280–330 nm), Region II, with aromatic protein II (ex: 200–250 nm; em: 330–380 nm), Region III, with fulvic acid–like (ex: 200–250 nm; em: 380–550 nm), Region IV, with soluble microbial by product–like (ex: 250–400 nm; em: 280–380 nm); and Region V, with humic acid–like (ex: 250–400 nm; em: 380–550 nm) [7,25]. The EEM approach is suitable for identifying crucial flux-declining fractions such as humic-like and protein-like substances. The humic-like substances can be retrieved from both allochtonous and autochthonous sources. The protein-like components such as tryptophan-like substances are usually used as an indicator of microbial activity in natural water. They mainly consists of dissolved amino-acids which are often bound to humic and fulvic substances. Mostofa et al. [29] reported that there is a linear relationship between DOC concentration and protein-like fluorescence intensity what indicated an autochthonous input.

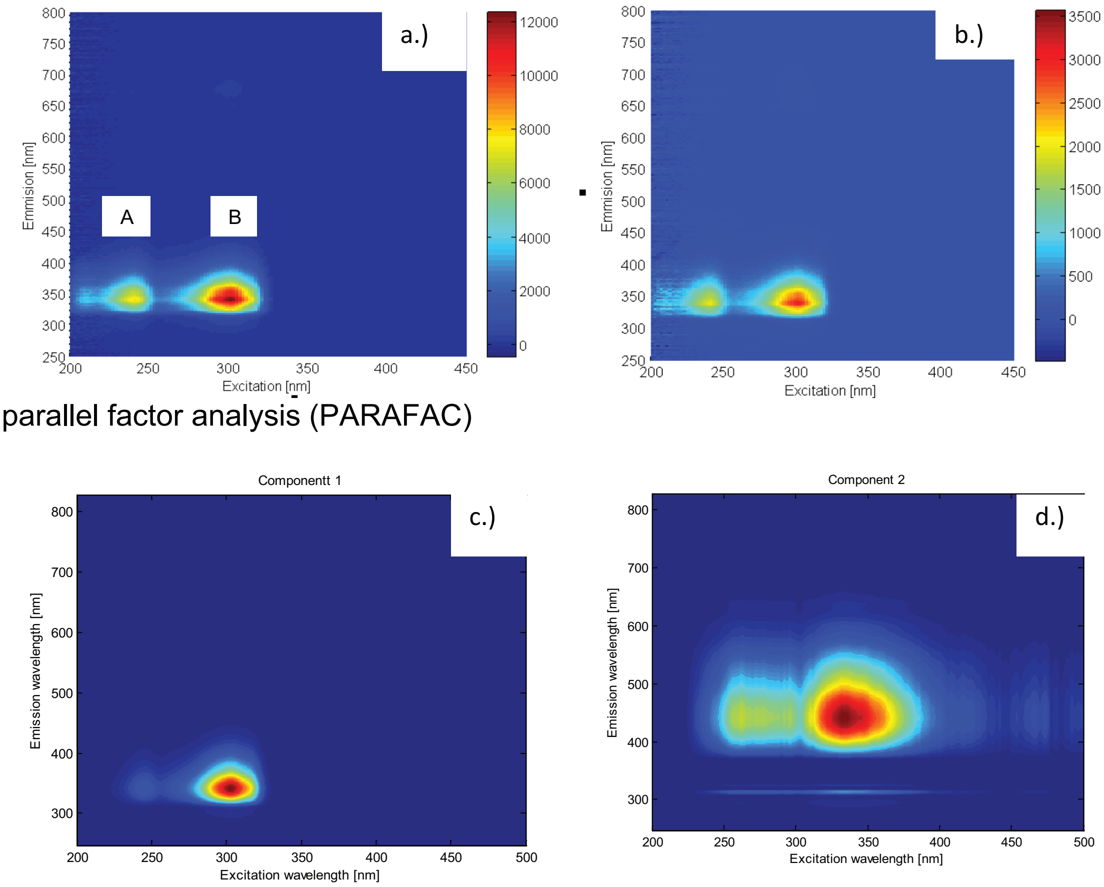

Fig. 2. EEM fluorescence spectra of (a) raw and (b) HAOPs-treated water, and the spectra of (c) aromatic proteins and (d) fulvic-like substances in the raw water, as inferred from mathematical decomposition of the overall spectrum using PARAFAC analysis.

Fig. 2 shows fluorescence EEM characterization of NOM in analyzed water before and after the HAOPs treatment. EEM revealed two prominent peaks based on peak-picking method: one peak being associated with protein-like and the other one with fulvic-like matter. Tryptophan-like fluorescence occurs at 242 nm excitation, 340 nm emission and fulvic-like at 302 nm excitation, 340 nm emission. The tryptophan-like fluorescence intensity (peak A) could be attributed to the amount of microbially-derived, hydrophilic and low-molecular weight fraction of organic matter. The humic-like fluorescence (peak B) was found to be blue-shifted (a shift of emission to a lower wavelength). This could be caused by increased microbial activity as a substrate for bacterial growth or salinity. Del Castillo et al. [26] suggested that high salinity leads to changes in chromophoric DOM. The idea was followed by Milbrandt et al. [30] who reported a linear relationship between salinity and fluorescent DOM.

Parallel factor analysis (PARAFAC) was used to deconstruct the EEM spectra into underlying fluorescent components. The two components identified by the analysis were humic-like substances (fulvic-like) and tryptophan-like ones. Such result suggests that NOM clearly had a higher content of hydrophilic material than humic-like material. The fluorescence intensities in both peak regions were substantially decreased, especially within the areas of the highest initial fluorescence intensity. The maximum fluorescence intensity was decreased by 70% when the water passed through the HAOPs layer, indicating that significant amounts of both aromatic protein-like substances and fulvic-like substances were removed by the HAOPs.

The NOM removal is also accompanied by the changes in its structural and chemical properties, therefore both the raw and the HAOPs-treated water was analyzed using FT-IR method. According to You et al. [37], FT-IR method can be used to explore non-fluorescent substances. As indicated in Fig. 3, major absorption bands were found in the regions of 3200–3500 cm^{-1} (corresponding to H-bonded OH groups of alcohols, phenols and organic acids), 1500–1700 cm^{-1} (which are attributed to amides and amines, that are indicative of the presence of proteins and aminosugars), 1385 cm^{-1} (corresponding to C–O stretching and OH deformation of COOH) and 2200–2500 cm^{-1} (COOH and O–H groups in humic-like substances). These results confirmed that the spectra show the predominance of groups (OH, COOH, COO). The fulvic acid has usually more pronounced adsorption in region of 1720 cm^{-1} and 1250 cm^{-1} due to its larger carboxyl group concentration. Since FT-IR spectra cannot be compared directly, all bands' baseline correction was conducted (scattering removed) followed by the normalization to the total area, then the peak height ratios of the spectra were used to interpret the structural change between raw and HAOPs-treated water. The decrease in the intensity of the bands at 2300–2400 cm^{-1} suggests that these bands were removed by the HAOPs treatment by 84%. These peaks are attributed to humic-like substances. The band intensities belonging to carbohydrates and methyl groups decreased by 31% and 48%, respectively. The analyzed NOM appears to contain more carboxyl fraction and less alkyl groups suggesting that the fulvic acid is the dominant fraction of the humic acid-like substances. Application of the FT-IR technique revealed that HAOPs treatment removed aromatic proteins less substantially overall, but more selectively for aromatic over aliphatic groups.

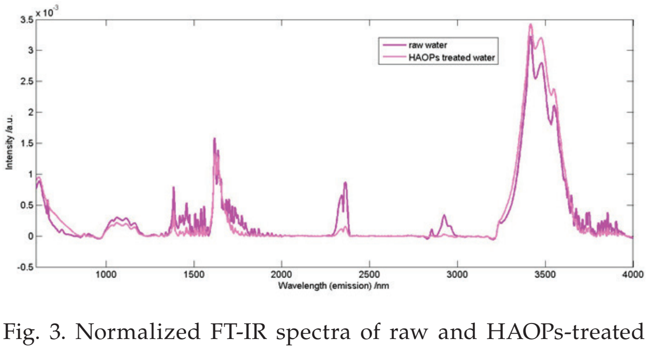

Fig. 3. Normalized FT-IR spectra of raw and HAOPs-treated water.

The EEM analysis indicated that humic acid-like substances and tryptophan-like substances are present in the raw water, and that both groups of molecules are removed to a significant extent by HAOPs pretreatment. Consistent with the EEM data, the FT-IR showed that the compounds removed by HAOPs were rich in carbohydrates. The results of the differential excitation-emission matrices (ΔEEM) model indicated that HAOPs reveals the highest efficiency in removing a humic-like fluorophore.

6. Summary and conclusions

Presented results confirmed that the content of organic matter can be significantly decreased during the HAOPs pretreatment to the amount suitable for drinking water. Pre-coated HAOPs remove NOM effectively from natural waters, and they demonstrate high affinity to humic-like substances, especially those of high content of carboxylic and alcoholic functional groups.

HAOPs pretreatment is effective in controlling the membrane fouling and, at the same time, in decreasing the need for hydraulic cleaning of ultrafiltration membrane.

Applied spectroscopic methods proved to be useful for characterization of various NOM subcomponents. However, further study on the NOM composition particularly to cover the chemical analysis of the different NOM fractions should provide more insight into the foulants influencing the filtration process.

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References

[1] S.A. Baghoth, Characterizing natural organic matter in drinking water treatment processes and trains, dissertation, UNESCO-IHE Institute for Water Education, The Netherlands, 2012.

[2] A. Waniek, M. Bodzek, K. Konieczny, Trihalomethane removal from water using membrane processes, Polish J. Environ. Stud., 11(2) (2002) 171–178.

[3] M. Kabsch-Korbutowicz, A. Biłyk, M. Mołczan, The effect of feed water pretreatment on ultrafiltration membrane performance, Polish J. Environ. Studies, 15(5) (2006) 719–725.

[4] C. Combe, E. Molis, P. Lucas, R. Riley, M.M. Clark, The effect of CA membrane properties on adsorptive fouling by humic acid, J. Membr. Sci., 154 (1999) 73–87.

[5] C.F. Lin, T.Y. Lin, O.J. Hao, Effects of humic substance characteristics on UF performance, Water Res., 34(4) (2000) 1097–1106.

[6] N. Hilal, O. Oluwaseun Ogunbiyi, N.J. Miles, R. Nigmatullin, Methods employed for control of fouling in MF and UF membranes: A comprehensive review. Separ. Sci. Technol., 40(10) (2005) 1957–2005.

[7] L. Fan, T. Nguyen, F.A. Roddick, J.L. Harris, Low-pressure membrane filtration of secondary effluent in water reuse: Pretreatment for fouling reduction, Journal of Membrane Science 320 (2008) 135–142.

[8] L. Fan, J.L. Harris, F.A. Roddick, N.A. Booker, Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes, Water Res. 35 (2001) 4455–4463.

[9] Z. Cai, J. Kim, M.M. Benjamin, NOM removal by adsorption and membrane filtration using heated aluminum oxide particles. Environ. Sci. Technol., 42 (2008) 619–623.

[10] Z. Cai, Investigation of microgranular adsorptive filtration systems, Ph.D. Dissertation, University of Washington, 2012.

[11] M. Kabsch-Korbutowicz, A. Biłyk, M. Mołczan, The effect of feed water pretreatment on ultrafiltration membrane performance, Polish J. Environ. Stud., 15(5) (2006) 719–725.

[12] M. Kabsch-Korbutowicz, A. Urbanowska, Water treatment in integrated process using ceramic membranes, Polish J. Environ. Stud., 19(4) (2010) 731–737.

[13] S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res. 41 (2007a) 1713–1722.

[14] S. Meylan, F. Hammes,J. Traber, E. Salhi, U. von Gunten, W. Pronk, Permeability of low molecular weight organics through nanofiltration membranes, Water Res., 41(17) (2007b) 3968–3976.

[15] J. Kim, W. Shi, Y. Yuan, M.M. Benjamin, A serial filtration investigation of membrane fouling by natural organic matter, J. Membr. Sci. 294 (2007) 115–126.

[16] J. Kim, Z. Cai, M.M. Benjamin, Effects of adsorbents on membrane fouling by natural organic matter, J. Membr. Sci. 310 (2008) 356–364.

[17] J. Kim, Z. Cai, M.M. Benjamin, NOM fouling mechanisms in a hybrid adsorption/membrane system. J. Membr. Sci. 349, (2010) 35–43.

[18] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res. 41(8) (2007) 1713 – 1722.

[19] K. Konieczny, M. Bodzek, M. Rajca, Coagulation – MF system for water treatment using ceramic membranes, Desalination, 198 (2006) 100.

[20] K. Konieczny, M. Bodzek, A. Kopeć, A. Szczepanek, Coagulation – submerged membrane system for NOM removal from water, Polish J. Environ. Stud., 16(4) (2007) 563–569.

[21] M. Bodzek, K. Konieczny, M. Rajca, Hybrid membrane processes for the removal of contaminations from natural water, Monographs of Environmental Engineering Committee of Polish Academy of Science, 32 (2005) 143.

[22] B. Malczewska, B.J. Liu, M.M. Benjamin, Virtual elimination of MF and UF fouling by adsorptive pre-coat filtration, J. Membr. Sci., 479 (2015) 159–164.

[23] B. Malczewska, M.M. Benjamin, Efficacy of hybrid adsorption/membrane pretreatment for low pressure membrane, Water Res., 99 (2016) 263–271.

[24] W. Yuan, A.L. Zydney, Humic acid fouling during microfiltration, J. Membr. Sci., 157 (1999) 1–12.

[25] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter. Environ. Sci. Technol. 37(24) (2003) 5701–5710.

[26] C.E. Del Castillo, F. Gilbes, P.G. Coble, F.E. Mqller-Karger, On the dispersal of riverine colored dissolved organic matter over the West Florida Shelf, Limnol. Oceanogr. 45 (2000) 1425–1432.

[27] M.M.D. Sierra, M. Giovanela, E. Parlanti, E.J. Soriano-Sierra, Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques, Chemosphere, 58 (2005) 715–733.

[28] K.M. Mostofa, T. Yoshioka, E. Konohira, E. Tanoue E., Dynamics and characteristics of fluorescent dissolved organic matter in the groundwater, river and lake water, Water, Air, Soil Pollut., 184(1) (2007) 157–176.

[29] K.M. Mostofa, Y. Honda, H. Sakugawa, Dynamics and optical nature of fluorescent dissolved organic matter in river waters in Hiroshima prefecture, Japan. Geochem. J. 39 (2005) 257–271.

[30] E.C. Milbrandt, P.G. Coble, R.N. Conmy, A.J. Martignette, J.J. Siwickea, Evidence for the production of marine fluorescence dissolved organic matter in coastal environments and a possible mechanism for formation and dispersion, Limnol. Oceanogr., 55(5) (2010) 2037–2051.

[31] D. Markechová, M. Tomková, J. Sádecká, Fluorescence excitation-emission matrix spectroscopy and parallel factor analysis in drinking water treatment: a review, Pol. J. Environ. Stud., 22(5) (2013) 1289–1295.

[32] H. Xu, J. Zhong, G. Yu, J. Wu, H. Jiang, L. Yang, Further insights into metal-DOM interaction: Consideration of both fluorescent and non-fluorescent substances. PLoS ONE, 9(11) (2014) e112272.

[33] J. Liu, Effect of operational parameters on microgranular adsorptive, Ph.D. Dissertation, University of Washington. 2016.

[34] C.A. Andersson, R. Bro, The N-way Toolbox for MATLAB, Chemomet. Intel. Lab. Syst., 52 (1) (2015) 1-4.http://www.models.life.ku.dk/source/nwaytoolbox/.

[35] J. Haberkampa, A.S. Ruhla, M. Ernstb, M.M. Jekela, Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration, Water Res., 41(17) (2007) 3794–3802.

[36] T. Carroll, S. King, S.R. Gray, B.A. Bolto, N.A. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment, Water Res., 34(11) (2000) 2861–2868.

[37] C. You, S.R. Miranda, B. Gider, P.S. Ghosh, I. Kim, E.B. Krovi, S.A., Bunz, U.H.F., V.M. Rotello, Detection and identification of proteins using nanoparticle—fluorescent polymer ‘Chemical nose’ sensors. Nature Nanotechnol., 2 (2007) 318–323.