

Biologically active ion exchange (BIE) for NOM removal and membrane fouling prevention

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ABSTRACT

The natural organic matter (NOM) removal efficiency and regeneration behavior of ion-exchange filters with promoted biological activity (BIE) was compared to operation where biological activity was suppressed (i.e. abiotic conditions). The impact of BIE pre-treatment on fouling in subsequent ultrafiltration was also investigated. Biological operation enhanced NOM removal by approximately 50% due to an additional degradation of smaller humic substances, building blocks and low molecular weight acids. Promotion of biological activity significantly increased the time to breakthrough of the filters and, therefore, is expected to lower the regeneration frequency as well as the amount of regenerate of which to dispose. Pre-treatment using BIE filters resulted in a significant decrease in total and irreversible fouling during subsequent ultrafiltration. The decrease was attributed to the effective removal of medium and low molecular weight NOM fractions. The results indicate that BIE filtration is a robust, affordable and easy-to-operate pre-treatment approach to minimize fouling in ultrafiltration systems and enhance the quality of the produced permeate.

Key words | biological ion exchange, irreversible fouling, membrane fouling, NOM removal, ultrafiltration

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INTRODUCTION

Organic colloids (e.g. biopolymers, humic substances) and dissolved organic matter are ubiquitous in drinking water sources. The removal of natural organic matter (NOM) is a crucial step during drinking water treatment, since NOM can cause color, taste and odor problems, form disinfection by-products, mobilize heavy metals and other pollutants by complexation and may lead to microbial regrowth in distribution systems (Grøn *et al.* 1996; Nikolaou *et al.* 2004; Tan *et al.* 2005; Matilainen *et al.* 2010; Penru *et al.* 2013). Furthermore, certain fractions of NOM have been identified as the main foulants during drinking water treatment of natural waters by membrane filtration (Amy 2008). Fouling increases the required chemical cleaning frequency and the operational costs of membrane systems while reducing membrane operational lifespan (Howe & Clark 2002; Sutzkover-Gutman *et al.* 2010).

Treatment by macro-porous anion exchange is a promising option to effectively remove NOM from drinking water sources, decrease membrane fouling and increase filtration performance (Cornelissen *et al.* 2008; Apell & Boyer 2010). Anion-exchange resins remove NOM by exchanging negatively charged counter ions from its surface with polar, negatively charged dissolved organic matter ions from the solution (Cornelissen *et al.* 2008). Ion-exchange resins can also provide a favorable environment for microbial growth due to their macro-porous structure containing a high surface area (Flemming 1987). Biological activity was reported to provide several advantages in deep bed filters. In filters containing biological activated carbon (BAC), microbial biodegradation of adsorbed organic substrates serves to decrease the frequency of filter backwashing and, by

biodegradation of adsorbed NOM, efficiently biologically regenerate the exhausted activated carbon surface. As a result, an increase of the removal efficiency and prolongation of service life can be achieved (Takeuchi *et al.* 1997; Simpson 2008). While the performance of BAC systems has been extensively studied, knowledge of the biological operation of IEX filters is limited. Our previous studies indicated that NOM removal can be improved and the time to breakthrough can be significantly extended when biological activity in packed bed ion-exchange systems is promoted (Wray *et al.* 2015).

The objective of the present study was to assess the performance of ion-exchange filters, with and without biological activity, in terms of NOM removal as well as a pre-treatment step prior to ultrafiltration (UF) to reduce membrane fouling. The impact of the presence of a biofilm on the regeneration efficiency of the ion-exchange resins was also investigated.

MATERIAL AND METHODS

Raw water

Jericho Pond water (Vancouver, Canada) pre-filtered through 1 μm glass fiber filters (Cat # 1827-125, Whatman, UK), diluted with tap-water to a dissolved organic carbon (DOC) concentration of 5 mg/L, was used as a model raw-water. A summary of raw water quality is given in Table 1.

Size exclusion chromatography with organic carbon detection (LC-OCD) indicated a broad molecular weight distribution of the organic constituents in the raw water, containing typical NOM fractions (biopolymers, humic substances, building blocks, low molecular weight acids and neutrals) present in surface waters (see Figure 1(b)) (Huber *et al.* 2011).

Table 1 | Raw water quality during operation of biotic and abiotic ion-exchange columns

	pH [–]	EC [$\mu\text{S}/\text{cm}$]	DOC [mg/L]	TOC [mg/L]	UVA [m^{-1}]	SAC ₄₃₆ ^a [m^{-1}]	turbidity [NTU]
Median	6.97	58	4.88	5.26	10.70	0.46	0.22
10th perc.	6.85	53	4.67	4.79	10.10	0.40	0.19
90th perc.	7.09	61	5.13	5.68	12.40	0.56	0.24
<i>n</i>	23	23	23	5	23	23	6

^aSpecific light absorption at 436 nm.

IEX column tests

Six laboratory-scale columns (bed height = 0.1 m; diameter = 0.01 m) containing a strongly basic anion-exchange resin (Purolite[®] A860–Dow Chemicals, USA) designed for NOM removal were operated continuously for two months. Filtration velocity was set to 0.2 m/h (≈ 2 BV/h; ≈ 0.0175 L/h). Biological activity was suppressed by dosing sodium azide (0.01% w/v) in the raw water in three of the columns (i.e. abiotic systems), while the other three columns were operated without inhibition (i.e. biotic systems).

Regeneration

Columns were regenerated in-situ monthly. Three regeneration strategies were considered: (1) brine (100 g NaCl/L), (2) caustic + brine (20 g NaOH/L + 100 g NaCl/L), (3) pre-disinfection + caustic + brine (0.1% peracetic acid before 20 g NaOH/L + 100 g NaCl/L). Each regeneration strategy was applied to one of the biotic and one of the abiotic columns. The procedure was carried out according to instructions from the resin manufacturer (Purolite 2014). Briefly, the columns were first backwashed with 8 BV of previously generated filtrate at a flow equivalent to 45 BV/h to remove coarse particles from the filter bed. To assess the impact of disinfection on regeneration efficiency, the resin of one of the biotic and one of the abiotic columns was then soaked in peracetic acid solution for 2.25 h (the resins in the other columns were soaked in Milli-Q water). Regeneration was then performed by soaking the resins in either brine or caustic + brine solutions for 4 h. After 2 h of the 4 h, the regeneration solutions were replaced by fresh ones. Before returning to operation, the columns were rinsed with 28 BV of Milli-Q water at a flow equivalent to 2 BV/h.

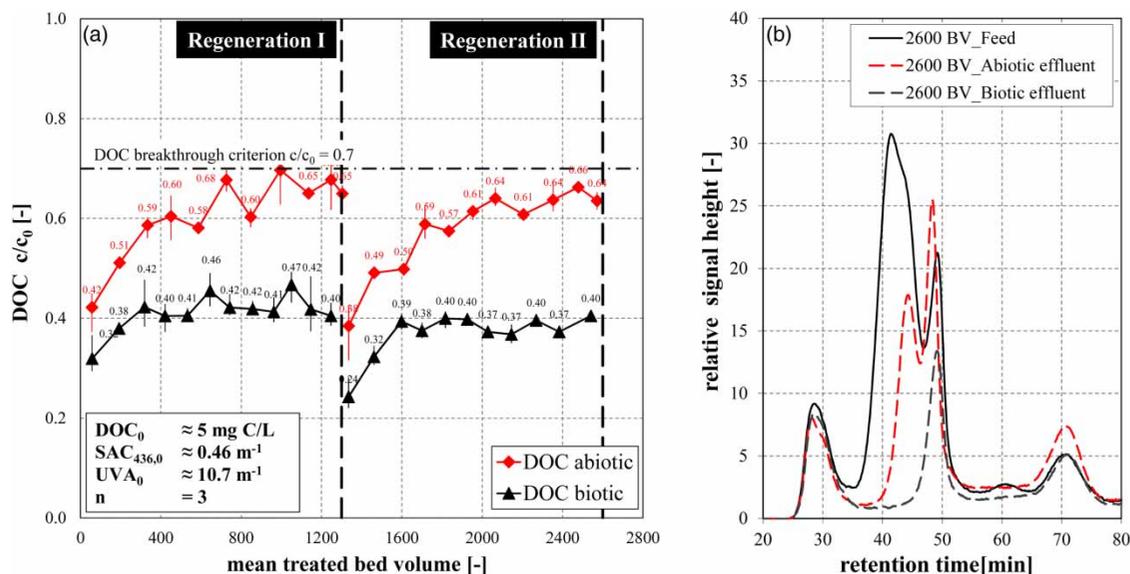


Figure 1 | (a) Normalized DOC in the effluent of biotic and abiotic ion-exchange columns ($n = 3$; $T = 20 \pm 1^\circ\text{C}$; error bars represent maximum and minimum values); (b) LC-OCD chromatograms of raw water (feed) and effluent of abiotic and biotic IEX columns after 2,600 treated BV (biopolymers [MW > 10,000 Da; retention time $t_R = 25\text{--}35$ min], humic material [MW $\approx 500\text{--}1,000$ Da; $t_R = 35\text{--}45$ min], building blocks [MW $\approx 300\text{--}500$ Da; shoulder of humic peak at $t_R = 45$ min] and low molecular weight acids [MW < 350 Da; $t_R = 47\text{--}55$ min] and neutrals [MW < 350 Da; $t_R > 55$ min] as defined by Huber et al. (2011).

Ultrafiltration tests

Ultrafiltration experiments were conducted using a bench-scale system containing GE Zeeweed 1000 fibers made of PVDF with a pore size of $0.02\ \mu\text{m}$ (GE Water and Process Technologies, Canada) operated in dead end mode, outside-in flow, in a pressurized casing. Each membrane module had a total filtration area of approximately $0.0035\ \text{m}^2$. The flux was kept constant at $50\ \text{L m}^{-2}\ \text{h}^{-1}$. All experiments were carried out in duplicate and at room temperature ($20 \pm 1^\circ\text{C}$). Fouling was monitored by recording the trans membrane pressure at intervals of 30 seconds. Before a filtration test, virgin membrane modules were soaked for 1 h in a solution containing hypochlorite at 500 ppm (as free chlorine) to remove shipping preservatives. Clean water (Milli-Q) filtration tests were then performed to quantify the intrinsic resistance for each membrane module. Following each filtration test, the membrane modules were backwashed for 10 minutes with previously generated permeate at a flux of $60\ \text{L m}^{-2}\ \text{h}^{-1}$. After backwash, clean water filtration tests were again performed to quantify the extent of hydraulically irreversible resistance. The total, reversible and irreversible fouling resistances were calculated according to Crittenden et al. (2005).

Analytical methods

The organic composition of raw water, IEX filtrate from the biotic and abiotic columns and UF permeate was characterized using total organic carbon (TOC) analysis (Phoenix 8000 TOC analyser, Dohrmann, USA) as well as specific light absorption at 254 nm (UVA_{254}) and 436 nm (SAC_{436}) (UV300 UV-vis spectrometer, Spectronic Unicam, USA). Size distribution of the dissolved organic water constituents was determined by size exclusion chromatography (liquid chromatography–organic carbon detection (LC-OCD), DOC Labor Dr. Huber (DE), column HW-50S) as described by Huber et al. (2011). Prior to analyses, samples were pre-filtered using $0.45\ \mu\text{m}$ cellulose nitrate membrane filters (Cat. # 09-719-555, Fisher Scientific, CA). Any samples that could not be analysed immediately were stored at 4°C . All analyses were carried out at least in duplicate.

Adenosine triphosphate (ATP) content of the raw water and filtrate of the biotic and abiotic columns as well as of the resins was quantified as an indicator of biological activity using LuminUltra Biofilm test kits (LuminUltra, CA).

The exchange capacity of the virgin and regenerated resins was determined by replacing the counter ions (Cl^-) of a defined mass of resin by washing it with concentrated

sodium nitrate solution (26 g/L). Afterwards the Cl^- concentration in the solution was determined by titration (Mohr Method) and the capacity was calculated.

RESULTS AND DISCUSSION

DOC removal

Both the biotic and abiotic columns could effectively remove a large portion of the DOC present in the raw water (Figure 1(a)). However, substantially greater DOC removal was achieved for the biotic columns. The greater removal, which was observed to occur immediately following startup, was attributed to the biodegradation of some of the NOM components and suggests that a microbial community established itself rapidly in the biotic columns. These results are consistent with the ATP measurements as discussed in the section below on biological activity (Figure 2(a)). During the 2 month study period ($\approx 2,600$ BV), the biotic columns achieved an average DOC removal of 60–62% while abiotic columns only achieved 39–42% removal.

As expected based on studies by others (Cornelissen *et al.* 2008), ion exchange could effectively remove the larger humic material fraction of the NOM (Figure 1(b)).

The presence or absence of biological activity did not affect the removal of this fraction. However, when biological activity was promoted, smaller humic substances as well as building blocks, which are essentially the breakdown products of humic substances and HS-like material of lower molecular weight (Huber *et al.* 2011), and some of the lower molecular weight acids were also removed. These results are consistent with studies by others, which reported that building blocks and low molecular weight acids could be biodegraded (Simpson 2008). Neither the biotic nor abiotic system could effectively remove the biopolymer fraction of the NOM. This NOM fraction mainly consists of macromolecular NOM (e.g. polysaccharides, proteins) originating from microbial excretion (e.g. extracellular polymeric substances) having a molecular weight of 10 kDa up to several 100 kDa (Huber *et al.* 2011). Fabris *et al.* (2007) and Huang *et al.* (2012) also reported poor removal of biopolymers when using ion exchange. It is likely that the low or non-ionic character (Huber *et al.* 2011) and the large size of this fraction limited diffusion into the porous structure of the resins (Cornelissen *et al.* 2008).

The abiotic effluent had higher peaks for low molecular weight acids and neutrals compared with the feed water. This likely resulted from a breakthrough of these fractions caused by a replacement by molecules (e.g. humic

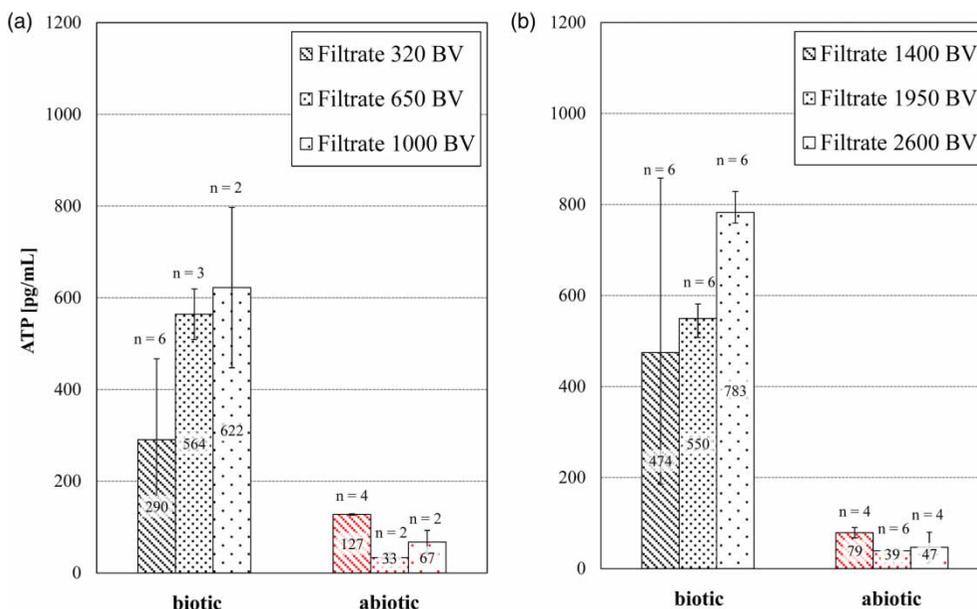


Figure 2 | ATP concentration in the effluent of biotic and abiotic ion-exchange columns (a) during the first filtration cycle, (b) during the second filtration cycle (after regeneration) in dependence of the treated bed volumes ($T = 20 \pm 1$ °C; error bars represent maximum and minimum values).

substances) having higher affinity to the resins' adsorption sites, which leads to an intermediate increase of the effluent concentration to values higher than that of the raw water.

DOC removal following regeneration was similar to that at the start of the study for both the abiotic and biotic systems, indicating that the growth of a microbial community in the biotic column had no adverse impact on regeneration efficiency. These results are also consistent with those discussed in the section below on regeneration efficiency.

Biological activity

ATP was used as an indicator for biological activity. ATP concentration in the effluent of the columns confirmed the establishment of biofilm in the biotic system (Figure 2(a)). The effluent of the abiotic columns contained consistently low ATP concentrations (mean value = 65 pg/mL), whereas in the effluent of the biotic columns, the ATP concentrations steadily increased over time. Biological ion-exchange filters offer synergistic effects that are likely responsible for the substantial removal of NOM observed in biotic columns: (1) due to the macro-porous structure of the ion-exchange resin, favourable conditions and a high surface area are available for microbial growth (Flemming 1987); (2) the chemical retention of NOM by ion-exchange resins provides a longer contact time between microorganisms and the organic compounds, which may promote biodegradation, as reported also for BAC systems (Simpson 2008). Upon regeneration, the mass of microorganisms (measured as ATP) in the biotic effluent decreased (Figure 2(b)). However, the microbial population was not entirely removed and re-establishment of the biofilm occurred quickly during subsequent operation. The results suggest that long-term effective NOM removal may be possible with no/infrequent regeneration, depending on the targeted DOC removal in the BIEX effluent.

Regeneration efficiency

Regeneration of all columns was conducted monthly with different regeneration strategies. Following regeneration, the capacity of the resins was determined (Figure 3). A loss in capacity of 5–10%, compared with the virgin resin, was observed for all columns. This can be related to the

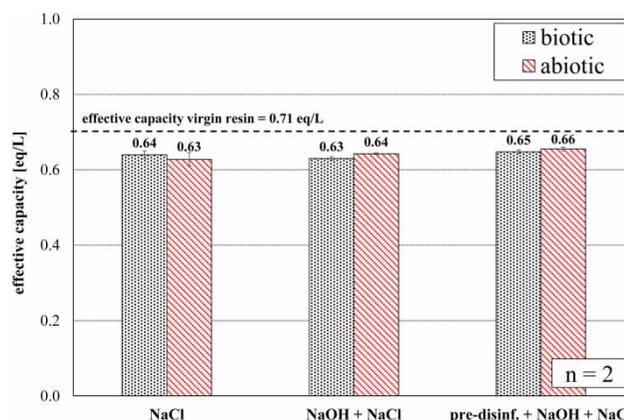


Figure 3 | Effective capacity of biotic and abiotic anion-exchange resins after regeneration at 2,600 treated BV with different regenerate solutions ($n = 2$; error bars represent maximum and minimum values).

poor access of the regeneration solution to deeply embedded resin pores and is consistent with results from previous studies (Bolto et al. 2004). No differences in regeneration efficiency were observed between the biotic and the abiotic columns, indicating that the biofilm had no negative impact on regeneration. Furthermore, no differences of recovered capacities with different regeneration strategies were observed. Pre-disinfection of the resin prior to regeneration to increase the release of the biofilm from the resin surface was not required for effective regeneration.

The composition of the regenerate solution was characterized (results not shown). A carbon mass balance (comparing DOC removal during operation and DOC release of the abiotic and biotic columns during regeneration) confirmed the mineralization of 15–20% of the DOC in the biotic columns.

Fouling behavior

The effect of the change in NOM composition due to BIEX pre-treatment on the fouling behavior and reversibility in a UF membrane was investigated. Development of the total fouling resistance over filtration time during ultrafiltration of the raw water and the effluent of the BIEX columns is illustrated in Figure 4(a).

When filtering water treated with BIEX through the UF, total fouling (i.e. increase in fouling resistance) was significantly lower than when filtering raw water. The rate of increase in total fouling resistance was $7.4 \times 10^9 \text{ m}^{-1} \text{ min}^{-1}$ and $15.5 \times 10^9 \text{ m}^{-1} \text{ min}^{-1}$ for the BIEX effluent and the

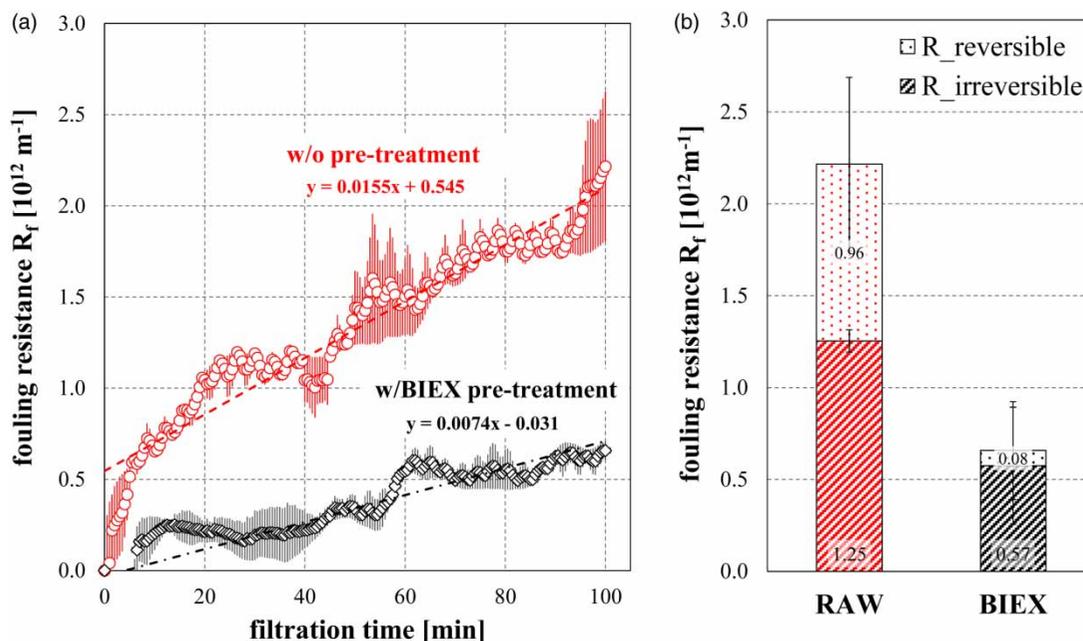


Figure 4 | Effect of BIEX pre-treatment on (a) fouling resistance development over filtration time and (b) fouling reversibility in subsequent ultrafiltration (pore size = $0.02 \mu\text{m}$; $T = 20 \pm 1^\circ\text{C}$; $n = 2$; error bars represent maximum and minimum values).

raw water, respectively. The mean total fouling resistance decreased by 70% from $2.21 \pm 0.41 \times 10^{12} \text{ m}^{-1}$ to $0.66 \pm 0.05 \times 10^{12} \text{ m}^{-1}$ (after 100 min of filtration). Because the turbidity of the raw water ($0.22 \pm 0.03 \text{ NTU}$) and of the BIEX effluent ($0.18 \pm 0.08 \text{ NTU}$) was low and not significantly different, fouling by particulate matter is assumed to be negligible. Therefore, the reduction of fouling was attributed to the removal of specific NOM fractions from the water by biological ion exchange.

Both the hydraulically reversible ($\approx 91\%$) and hydraulically irreversible ($\approx 54\%$) fouling resistance were substantially lower when filtering effluent from the BIEX column compared to the raw water. This was attributed to the removal of humic substances during BIEX treatment (see Figure 1(b)). Humic substances are known to have a high potential to accumulate at membrane surfaces and potentially irreversibly foul polymeric membranes by adsorption onto and into the membrane matrix and as a result a narrowing or complete blocking of membrane pores (Sutzkover-Gutman *et al.* 2010).

Although medium and small molecular weight fractions (humics, building blocks, low molecular weight acids) are preferentially removed by BIEX, high molecular weight fractions (biopolymers) are poorly retained. These substances can potentially block membrane pores (Howe & Clark

2002) and, due to hydrophobic interactions, proteins especially can adhere to the membrane surface contributing to the residual portion of hydraulically irreversible fouling (Haberkamp *et al.* 2008).

CONCLUSIONS

The promotion of biological activity in IEX systems (i.e. by applying a low filtration velocity and infrequent regeneration) can significantly enhance NOM removal and increase the time to breakthrough compared with conventional ion-exchange operation. Lower operational cost, effort of maintenance and regeneration frequency can be expected, while the biofilm had no negative impact on regeneration. Hence, the volume of regenerate of which to dispose can be eliminated or be substantially decreased. The presented results indicate that BIEX filtration is a robust, affordable and easy-to-operate treatment technology to reduce NOM concentration during drinking water production.

Application of BIEX as a pre-treatment step for membrane filtration is a promising option to reduce NOM fouling, especially when the NOM fraction is dominated by

medium molecular weight fractions (e.g. humic substances). With BIEEX pre-treatment, both the total as well as the hydraulically irreversible fouling were substantially lowered. This decreases the energy demand and chemical cleaning requirements, while increasing the membrane operation lifespan. Furthermore, BIEEX and UF can act synergistically in terms of contaminant removal, increasing final water quality. BIEEX can remove predominantly smaller and medium-sized NOM (i.e. humic substances and low molecular weight acids), while UF serves as an absolute barrier for bacteria, including bacteria released from the biomass in the filter as well as for larger NOM (i.e. biopolymers).

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